

ELECTRO-PLATING: BASICS

The following section would like to explain the physical and chemical basis for electroplating to the extent as it is useful for understanding the following chapters.

The Metal Potential

A Metal in Aqueous Solution

If a metal is dipped in an aqueous solution (a salt solution, a diluted acid, or only water), some of the metal goes into the solution as positive ions, where the metal is negatively charged by the electrons remaining left (Fig. 127).

The system consisting of metal and solution strives for minimally free enthalpy $H = U - T \cdot S$ (U = internal energy, T = temperature, S = entropy). The change in the internal energy affects both the lattice energy of the metal atoms required when leaving the solid state and the energy released during the hydration of the dissolved ion.

Both, the greater degree of freedom (= increase in the entropy) of a metal ion in solution previously bound in the solid state, and the stronger localisation (= decrease in the entropy) of the previously freely mobile water molecules bound to the metal ion during hydration, contribute to the entropy change.

The two phase transitions, the dissolution of the metal atoms and their replacement in the solid state, remain in equilibrium. The potential difference between the dissolved phase and the solid state in the equilibrium state is called metal potential.

Physical Description: The Nernst Equation

The Nernst equation can be described as the function of the metal potential E of certain environmental conditions:

$$E = E_0 + \frac{RT}{z_e F} \ln(C_{M+})$$

Where E_0 is the standard electrode potential (see next section), T is the temperature, R is the molar gas constant, F is the Faraday constant, z_e is the degree of ionisation of the dissolved metal atoms, and C_{M+} is the concentration in solution.

The metal potential increases accordingly with the temperature (by more powerful thermally activated diffusion of the hydrated metal ions, they can go more away from the electro-chemical double layer in solution), as well as - for the same reason - with the concentration of dissolved metal ions. The increase in the metal potential is weaker in metals with a higher ionisation stage since, from the electro-chemical point of view, a double-charged metal ion builds up the electro-chemical boundary layer to the same extent as two single-charged ions.

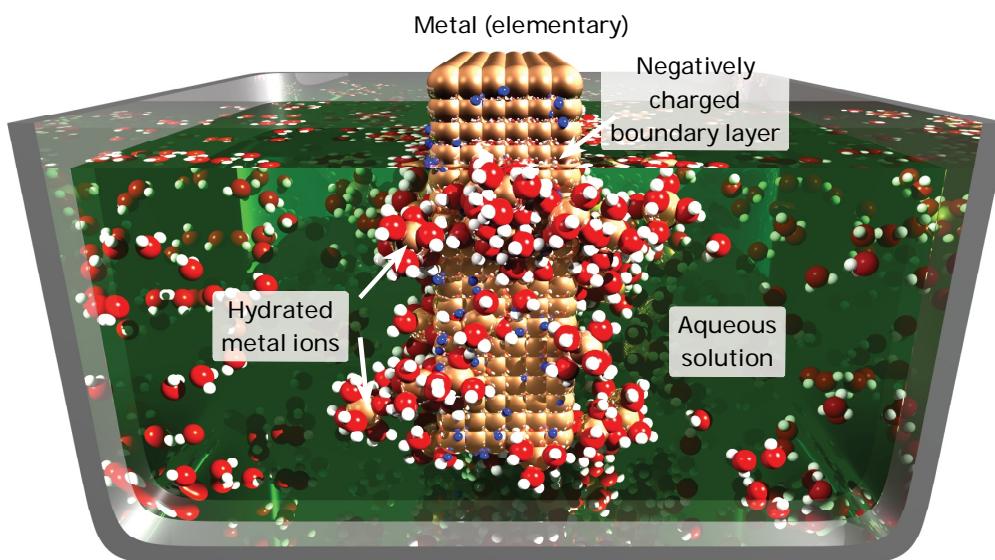


Fig. 127: Formation of an electro-chemical double layer on the surface of a metal dipped in an aqueous solution: Atoms from the metal go as positive ions hydrated in solution, the negatively charged electrons (blue) remain in the metal or on its surface.

The Electropotential Series

Theory

The metal potential between the negatively charged electrode and the electrolyte enriched with positive metal ions is not measurable itself, however the potential between two different electrode potentials is.

In order to be able to compare the relative size of the metal potentials of different metals, a measurement with a counter-electrode is carried out under standard conditions (25°C, 101.3 kPa, one-molar solution of the metal under investigation). A platinum electrode bathed by H₂ serves as a counter-electrode, on the catalytically active surface of which the H₂ gas dissociates into atomic hydrogen, which forms an atomic layer (normal hydrogen electrode) on the Pt electrode.

Normal Potentials and Their Importance

If such a measurement is carried out under standard conditions for certain elements by (Fig. 128), its standard potentials are listed in Table 7.

The higher the standard potential of a metal the more noble the metal: Metals with a positive standard potential are, by definition, noble metals, which are not attacked by acids (except oxidising acids). Base metals with negative standard potential dissolve in acids under H₂ formation.

The Electropotential Series of Neutral Elements

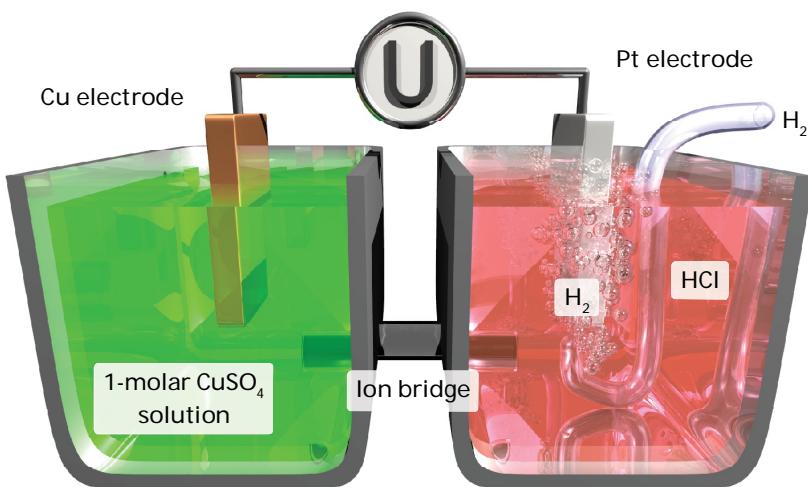


Fig. 128: Diagram of the determination of the standard potential of a metal (in this example, copper, left basin) relative to a standard hydrogen electrode (right), which is a platinum electrode in diluted hydrochloric acid bathed with hydrogen.

The following table lists the standard potential of several elements or electrode reactions. The more negative the standard potential, the less noble the metal.

Element	Electrode reaction	Normal potential (V)	Element	Electrode reaction	Normal potential (V)
Lithium	Li → Li ⁺ + e ⁻	-3.02	Tin (IV)	Sn → Sn ⁴⁺ + 4e ⁻	+0.05
Potassium	K → K ⁺ + e ⁻	-2.92	Antimony	Sb → Sb ³⁺ + 3e ⁻	+0.20
Barium	Ba → Ba ²⁺ + 2e ⁻	-2.92	Arsenic	As → As ³⁺ + 3e ⁻	+0.30
Strontium	Sr → Sr ²⁺ + 2e ⁻	-2.89	Copper	Cu → Cu ²⁺ + 2e ⁻	+0.345
Calcium	Ca → Ca ²⁺ + 2e ⁻	-2.84	Copper	Cu → Cu ⁺ + e ⁻	+0.52
Sodium	Na → Na ⁺ + e ⁻	-2.75	Iodine	2I ⁻ → I ₂ + 2e ⁻	+0.536
Magnesium	Mg → Mg ²⁺ + 2e ⁻	-2.38	Silver	Ag → Ag ⁺ + e ⁻	+0.80
Aluminium	Al → Al ³⁺ + 3e ⁻	-1.66	Palladium	Pd → Pd ²⁺ + 2e ⁻	+0.83
Manganese	Mn → Mn ²⁺ + 2e ⁻	-1.05	Mercury	Hg → Hg ²⁺ + 2e ⁻	+0.85

Zinc	$Zn \rightarrow Zn^{2+} + 2e^-$	-0.76	Platinum	$Pt \rightarrow Pt^{2+} + 2e^-$	+1.20
Chromium	$Cr \rightarrow Cr^{3+} + 3e^-$	-0.71	Chlorine	$2 Cl^- \rightarrow Cl_2 + 2e^-$	+1.358
Iron (II)	$Fe \rightarrow Fe^{2+} + 2e^-$	-0.44	Gold	$Au \rightarrow Au^{3+} + 3e^-$	+1.42
Nickel	$Ni \rightarrow Ni^{2+} + 2e^-$	-0.24	Gold	$Au \rightarrow Au^+ + e^-$	+1.7
Lead	$Pb \rightarrow Pb^{2+} + 2e^-$	-0.125	Fluorine	$2 F^- \rightarrow F_2 + 2 e^-$	+2.85
Hydrogen	$H \rightarrow H^+ + e^-$	0.000			

Table 7: The standard potential of several elements or electrode reactions. Because measurement is done in the reference to a hydrogen electrode, its standard potential is 0 V.

Charge Exchange

Dip Deposition: A Metal in the Salt Solution of a Noble Metal

If a less noble metal such as iron (see diagram below) is dipped into an aqueous solution of a metal salt (e.g. copper as a $CuSO_4$ solution), atoms are first dissociated from the iron as ions in solution (Fig. 127). For each dissolved Fe^{2+} ion, two electrons in iron remain, which bond with a Cu^{2+} ion from the solution to

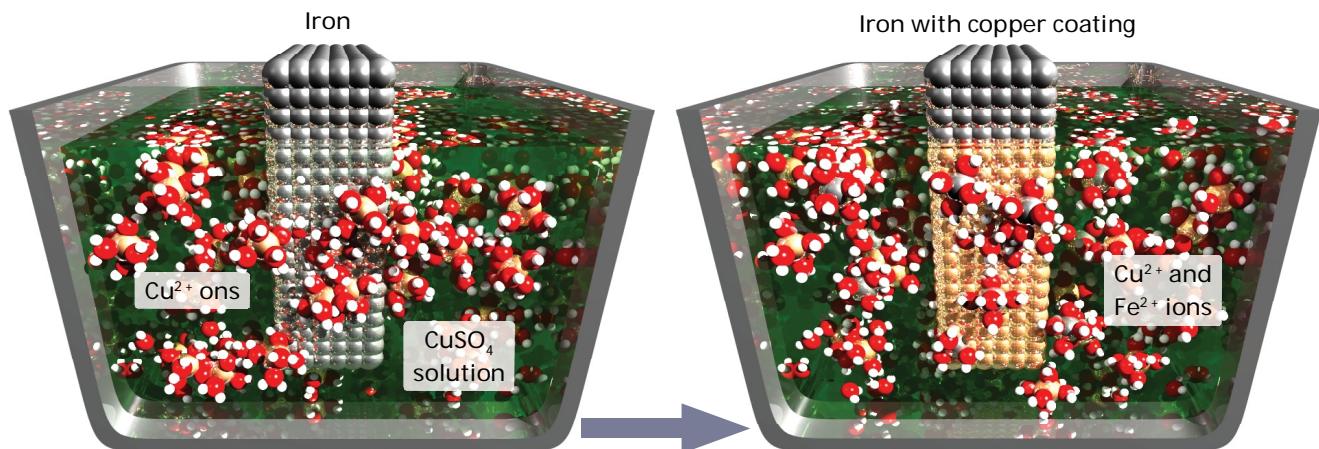


Fig. 129: The charge exchange between two metals (the less noble metal in a solution of the nobler metal) with different standard potentials is carried out until the nobler metal has formed a coating on the less noble metal which prevents further dissolution of the less noble metal.

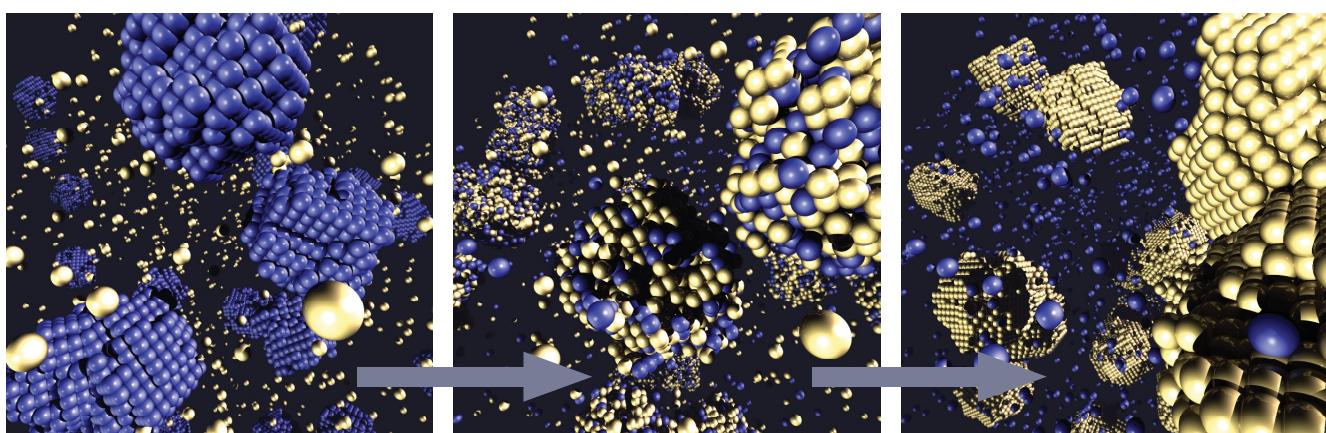


Fig. 130: In the case of a metal powder (shown as blue) in the solution of a nobler metal (represented in gold colours), this replaces the less noble metal through charge exchange.

elemental copper. This copper deposits as a thin film on the iron, preventing the further transfer of iron ions in solution and ultimately stopping the process of charge exchange between iron and copper.

This currentless mechanism of the charge exchange is applied on an industrial scale such as in the copper-plating of iron, or the silver-plating of copper or brass in a silver nitrate solution.

Cementation: A Metal Powder in the Salt Solution of a Noble Metal

If the principle of dip deposition is not applied to a metal rod, but to a powder of a metal in a salt solution of a nobler metal, the conversion may be complete : If the size of the metal particles of the powder is comparable to the thickness of the dissolved layer or the thickness of the coating of the nobler metal, the less noble metal particles dissolve completely, and until then serve as substrate for the growth of a particle of the nobler metal.

In this way, for example, elementary copper can be obtained from a copper solution, or elementary gold from a cyanide gold solution with zinc dust (schematically shown in Fig. 130).

The Galvanic Cell

Two Metals in An Acid

If, as shown in Fig. 131, two different metals (one less noble than the other, iron and copper in this example) are dipped in an acid (in this example sulphuric acid), this is referred to as a galvanic element. From the time of dipping in the acid, the following electro-chemical reactions take place:

From the electrode with the less noble metal, iron in this example, iron ions are converted into solution via $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$. The two electrons migrate through the electrical connection of both electrodes to the nobler copper electrode, where they form neutral hydrogen via $2 \text{H}_3\text{O}^+ + 2\text{e}^- \rightarrow 2 \text{H}_2\text{O} + \text{H}_2$, which rises in gas form. The reaction does not come to a standstill until either the iron electrode or the acid is consumed.

As long as the reaction takes place, the voltage measurable between the two electrodes is the difference between the standard potentials of both metals (approximately 0.8 V in this example), which is the basic principle of a battery.

An undesirable effect of the principle of galvanic cells is electro-chemical corrosion: If components made of, for example, iron and aluminium, or iron and copper are electrically conductive, the less noble metal begins to corrode as soon as the components are wetted by (e.g. rain) water.

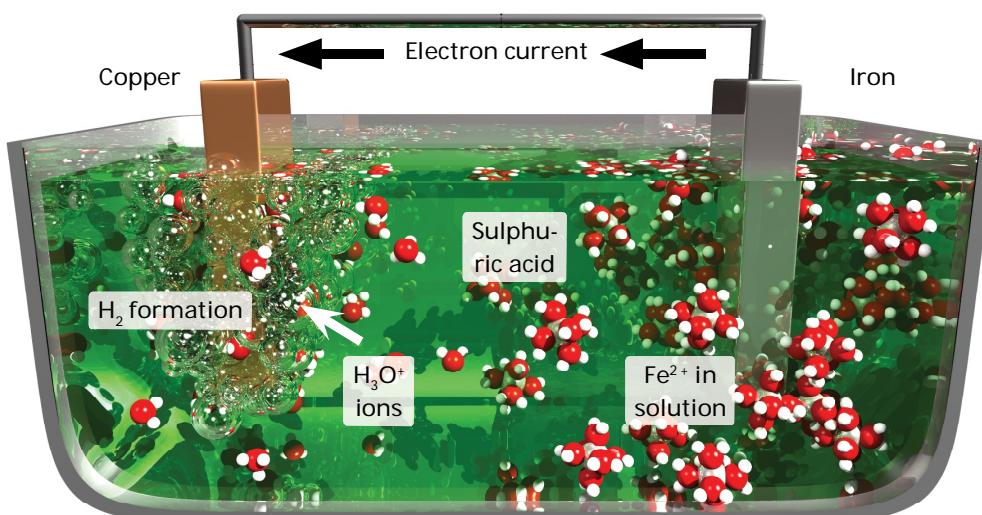


Fig. 131: A galvanic cell consisting of two connected electrodes of different metals in an acidic solution.

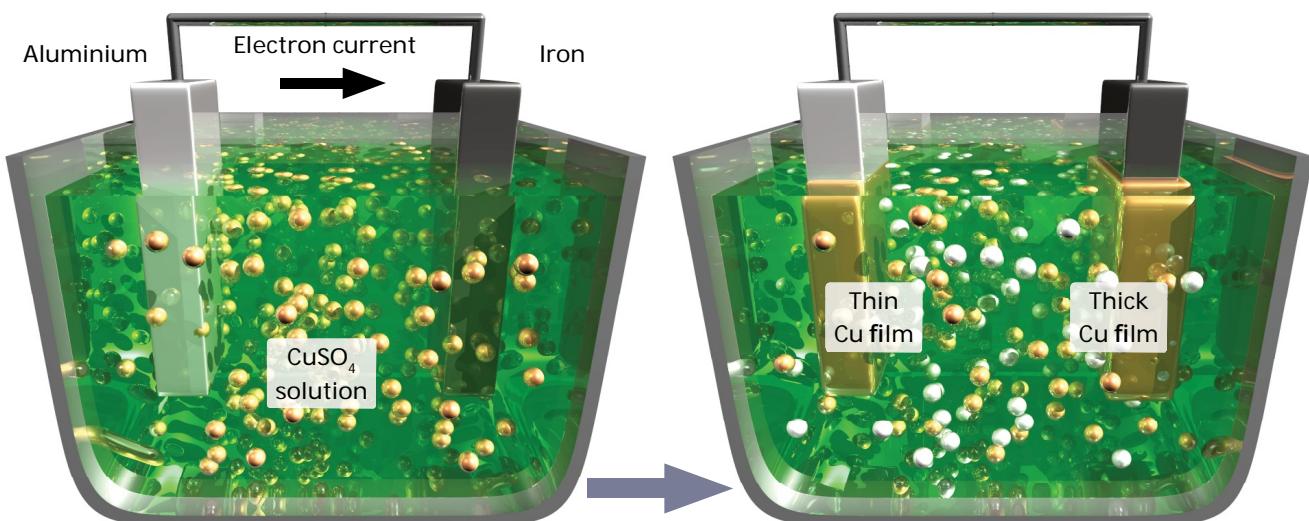


Fig. 132: Diagram of the copper-plating of iron with the help of aluminium in a CuSO_4 solution. Left: Immediately after the dipping of the metals in the solution; right: The process stops when the aluminium is copper-plated over the entire surface.

Two Metals in the Salt Solution of a Third Metal

If two electrically conductive, differently noble metals (e.g. iron and aluminium in Fig. 132) are dipped in the aqueous solution of a salt of a nobler metal (e.g. copper), iron as well as aluminium begin to dissolve in solution. In accordance with the principle of the charge exchange, elemental copper deposits on both metals.

The aluminium, which is less noble than iron, is thus faster to dissolve, which would lead to a more rapid charge of the aluminium. This potential difference causes an electron flow from the Al to the Fe electrode. Once there, the electrons can neutralise Cu^{2+} ions so that the copper film grows even further on the iron when the iron is already copper-plated over the whole surface.

This process ends when the aluminium is coated over the entire surface by copper. In this state, no further Al ions can dissolve, correspondingly no further e⁻ can flow to the iron and neutralise Cu ions. For a technical application of the copper-plating of metals, the less noble metal is thus provided with a much larger surface.

Electrolysis

Definitions: Electrodes, Electrolyte and Electrolysis

The previously treated electro-chemical processes between metals and solutions, such as the formation of a metal potential, the charge exchange or the processes in a galvanic element, take place without an external voltage or current source.

If the metals dipped in solution are connected to a voltage source, they act as electrodes (negative cathode or positive anode). The liquid (an aqueous salt solution, a diluted acid or base), which functions as an ion current conductor between the electrodes, is called electrolyte. The resulting electro-chemical processes and those which are treated in the following sections on the surfaces of the electrodes are designated as electrolysis.

Example 1: Electrolysis of Hydrochloric Acid with Insoluble Anode

Diluted hydrochloric acid as a strong acid is almost completely dissociated in the form of oxonium (H_3O^+) ions and chloride (Cl^-) ions. If an electrode pair, for example, platinum or graphite, which is connected via a voltage source, is dipped in such a solution and a direct voltage is applied to the latter, two reactions take place (Fig. 133):

The negatively charged chlorine ions release their electrons on the positive anode and are converted to neutral chlorine gas via $2 \text{Cl}^- \rightarrow 2\text{e}^- + \text{Cl}_2$. On the negatively charged cathode, the oxonium ions are converted via $2 \text{H}_3\text{O}^+ + 2\text{e}^- \rightarrow 2 \text{H}_2\text{O} + \text{H}_2$ to water and hydrogen gas. The process only ends when the hydrochloric acid is consumed.

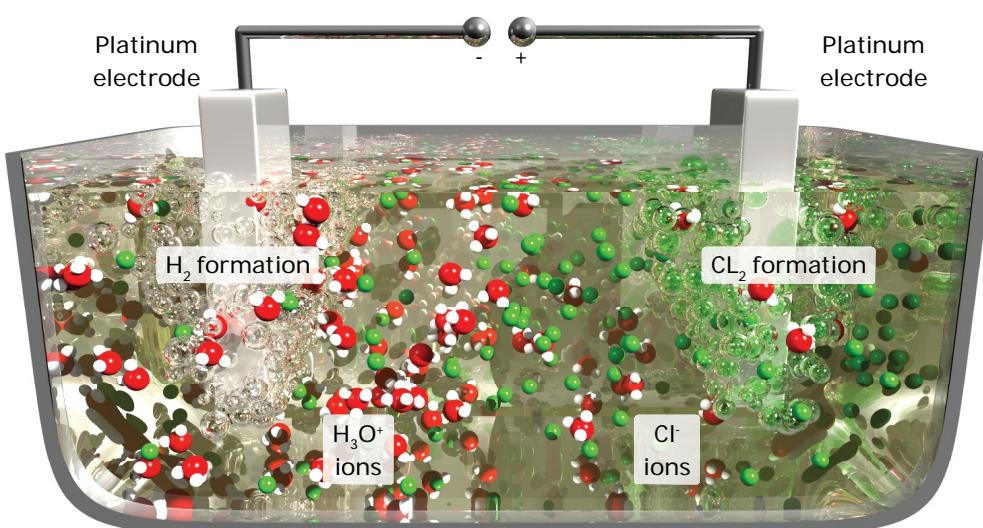


Fig. 133: Diagram of the electrolysis of hydrochloric acid: After applying a DC voltage to the electrodes in an electrolyte of diluted hydrochloric acid, the H_3O^+ ions migrate to the cathode, where they are neutralised to H_2 , the Cl^- ions to the anode where they form chlorine (Cl_2).

Example 2: The Daniell Element

The Daniell element, which is to be listed here as a historical example of a galvanic element, consists of two electrolytes connected via an ion bridge: One with a solution of zinc sulphate, into which a zinc electrode is dipped and one with a solution of copper sulphate, into which a copper electrode is dipped. The task of the ion bridge is to prevent the intermixing of both electrolytes, but to allow directed ion migration (drift) in the electric field between the electrodes. A DC voltage is applied to the electrodes which initiates two electro-chemical processes:

Zinc ions go into solution from the zinc anode, while elementary copper deposits on the copper cathode. For charge balancing, SO_4^{2-} ions migrate via the ion bridge from the copper to the zinc electrolytes.

Ion Transport in the Electrolytes

Convection is a macroscopic movement of the entire electrolyte, which moves all atoms, ions, and molecules contained therein equally, regardless of their size and charge state.

In addition to the forced convection due to, for example, stirring or pumps, convection can also occur without external forces due to gas formation on the electrodes or density differences in the electrolyte under the influence of gravitation. Such differences in density can be due to local chemical transformations or temperature differences.

Diffusion is a result of the non-directional thermal movement of particles (atoms, molecules, ions) in the electrolyte, where concentration gradients are smoothed. While the velocity of such particles at room

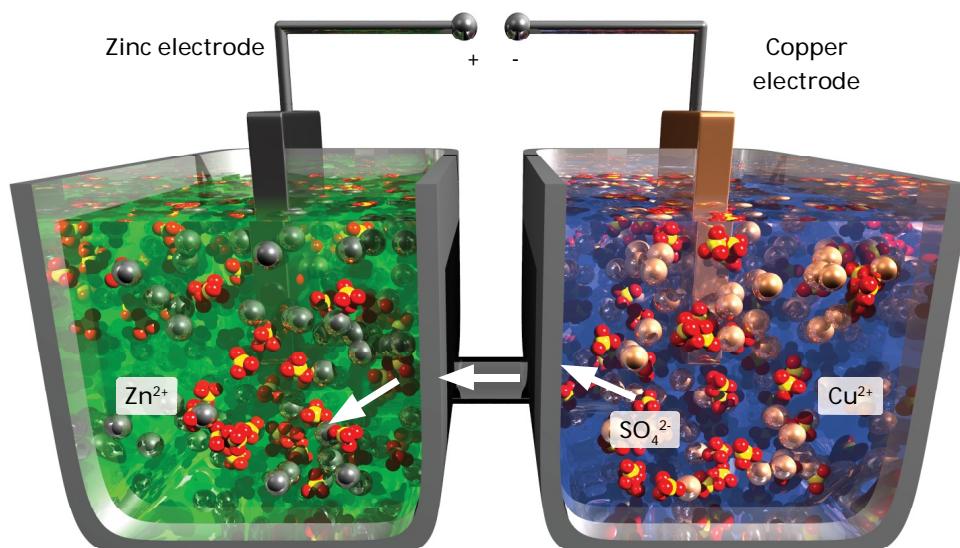


Fig. 134: Diagram of a Daniell element: After applying a DC voltage, Zn goes in solution on the Zn electrode, Cu deposits on the copper electrode, and SO_4^{2-} -ions migrate via a ion bridge from the electrolyte of the Cu cell to the electrolyte of the Zn cell for charge equalisation.

temperature is typically several 100 m/s, the "net" distance travelled by several mm or cm per hour is due to constant changes in direction due to collisions with other particles in the electrolyte (typically 10^{11} collisions/second).

Drift, on the other hand, is a movement which is superimposed on the diffusion but is directed by external forces, such as they experience ions of the electrolyte in the electric field of the electrodes. The speed of migration of the ions depends on, among other things, their mobility in the electrolyte, on the temperature, the charge state of the ions, and the electric field strength in the electrolyte, and is, under typical conditions, several cm per hour.

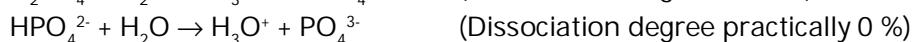
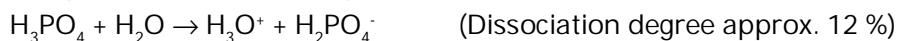
Dissociation in the electrolyte

If an acid is mixed in water, some of the acid dissociates to form oxonium ions and the anions of the acid (e.g. $\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$). Bases dissociate partially to hydroxide ions and the cations of the base (e.g. $\text{KOH} \rightarrow \text{K}^+ + \text{OH}^-$). The dissolving of salts based on their dissociation in anions and cations (e.g. $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$). In the electro-chemical consideration of acidic, base or electrolytes consisting of dissolved salts, it is therefore important to know which part of the solute is actually dissociated.

The degree of dissociation as the ratio of dissociated acid, base or salt molecules or ions to their initial concentration depends on the substance itself, as well as the temperature and concentration of the substance in the aqueous solution. Example numerical values for room temperature and a 0.1 normal solution are shown in the following table:

Substance response (0.1 N solution)	Degree of ionisation	Substance response (0.1 N solution)	Degree of ionisation
$\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$	91 %	$\text{KOH} \rightarrow \text{K}^+ + \text{OH}^-$	86 %
$\text{HNO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{NO}_3^-$	89 %	$\text{Ba}(\text{OH})_2 \rightarrow \text{Ba}^+ + 2\text{OH}^-$	78 %
$\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$	69 %	$\text{NH}_4\text{OH} \rightarrow \text{NH}_4^+ + \text{OH}^-$	11 %
$\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-$	21 %	$\text{CuSO}_4 \rightarrow \text{Cu}^{2+} + 2(\text{SO}_4)^{2-}$	39 %

For multi-protonic acids, such as phosphoric acid or boric acid, the situation is more complex: These substances can yield one or more protons, correspondingly dissociated in different charge states. For a 0.1 N phosphoric acid, the following numerical values can be given for the concentrations of possible dissociation products at room temperature:



The higher the electrical charge of an ion, the more unlikely is the release of a further H^+ so that phosphoric acid at room temperature contains only a comparatively small concentration of free phosphate ions.

Temperature Dependencies

The temperature determines nearly all chemical and physical processes occurring in the electrolysis: The degree of dissociation of the substances dissolved in the electrolyte, the diffusion of the particles in the electrolyte, as well as chemical reactions in the electrolyte and on the surface of the electrodes.

Overvoltage

Theoretically, iron would have to dissolve in neutral water because, according to the electropotential series, the dissolution of iron ($\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$) under hydrogen formation from the oxonium ions ($2\text{H}_3\text{O}^+ + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{H}_2\text{O}$) should take place without an external voltage source.

Also theoretically, the necessary voltage should be the sum of both electrode potentials during electrolysis, which is, however, in practice too low a value.

Reasons for this discrepancy are physical and chemical reactions in the electrolyte and on the electrode surface which require energy in addition to the actual redox reactions such as:

- The electrical resistivity of the ion migration
- The diffusion of the ions through the boundary layer on the electrode

- The stripping of the hydration shell of the ions
- Possible chemical reactions on the electrode surface
- The accumulation of the ions to the electrode
- The change in the position of the accumulated atoms on the electrode up to the integration into an energetically favourable lattice site.
- For gaseous reaction products such as H₂, Cl₂ or O₂ their formation from the atoms

The difference between the voltage required for the electrolysis and the theoretical potential difference derived from the electropotential series is called overvoltage.

PROCESSES ON THE ELECTRODES

The electro-plating is an electro-chemical process of which, with the exception of the electroless deposition, takes place at the electrode formed by the substrate to be coated. On the surface and in the layer directly above, the complex transport processes and chemical reactions take place before the metal atoms are finally incorporated at a certain site in the growing film.

Ion Transport between Electrolyte and Electrode

Anode and Cathode

All the transport mechanisms described below between the electrolyte and the electrodes also apply to the transport path away from the electrode as well as to it. Therefore, the transport of cations to the cathode is described as representative for both transport directions.

Convection

The diffusion movement due to the thermal movement of the ions and molecules in the electrolyte as well as the drift movement of ions in the electric field of the electrodes is too low to maintain electro-plating deposition at the required rate when the region in the immediate vicinity of the electrode is already depleted of suitable ions.

Therefore, a convection of the electrolyte is essential. Such a macroscopic circulation of all the particles of the electrolyte does not necessarily have to be dictated from the outside, but takes place by spatial temperature differences, and thus differences in the density of the electrolyte.

Convection alone, however, can not lead ions or molecules directly to the electrode, since a diffusion boundary layer always forms over solids in moving fluids, the thickness of which decreases with increasing convection speed.

Diffusion in the Boundary Layer

The ions or molecules directly on the electrode surface adhere to the electrode surface, which means

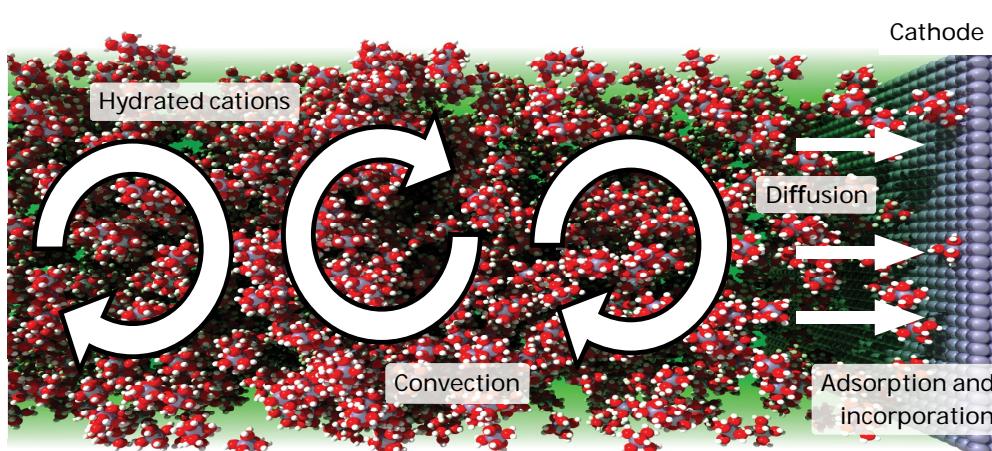


Fig. 135: Material transport from the electrolyte means i) transport by convection, ii) transport by diffusion, iii) hydration layer removal, and iv) adsorption onto the cathode.

they are bound to them physically by different interaction forces. The situation above the electrode can be visualized with a simple model: Stacked particle layers parallel to the electrode surface, each can move parallel to the previous layer with a particular difference in speed thus increasing with the distance to the electrode. From a certain distance, this diffusion layer passes into the convective region of the electrolyte. Within the diffusion layer, the concentration of the ions which are consumed at the electrode by growth (e.g. $\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$) or phase transformation (e.g. $2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2$) decrease in the direction of the electrode which acts as "sink" for these ions. This concentration gradient as the driving force is all the greater, the thinner the diffusion layer, that is, the stronger the convection velocity over it. Strong convection therefore also promotes diffusion through the diffusion barrier layer

Adhesion to The Electrode

Cations are always hydrated in aqueous solutions, i.e. they are surrounded by a hydrate shell from the water molecules due to the ion-dipole interaction. This shell must first be stripped before the cation can attach to the cathode.

A Closer Look at The Diffusion Boundary Layer

Within the diffusion boundary layer two areas can be defined: The inner Helmholtz layer designates the monolayer adsorbed to the electrode of the solvent molecules (e.g. H_2O) or other ions of the electrolyte. The outer Helmholtz layer consists of the hydrated ions of the electrolyte, which are attached to the inner Helmholtz layer.

To get from the electrolyte to the surface of the electrode (or go into solution from the electrode), the ions must penetrate the Helmholtz layer (transient reaction). Subsequently, the ions strip off their hydration shells and are incorporated in the lattice of the solid. The passage through the boundary layer as well as the stripping of the hydration shell requires an activation energy, which must be applied to the external voltage source by an increased voltage (*transient overvoltage*).

Layer Growth

Physical Basics

After the cations have reached the cathode and have stripped off their hydration shells, they are initially loosely bound as *adatoms* to the surface of the solid. They can diffuse thermally activated there until they are permanently incorporated into the crystal structure at an energetically favourable place.

Simulation ...

The following simulations illustrate the mechanism of attachment and incorporation of a cation into the solid state in a simplified manner: Each particle in a cubic lattice has 26 neighbour sites (6 over the sides,

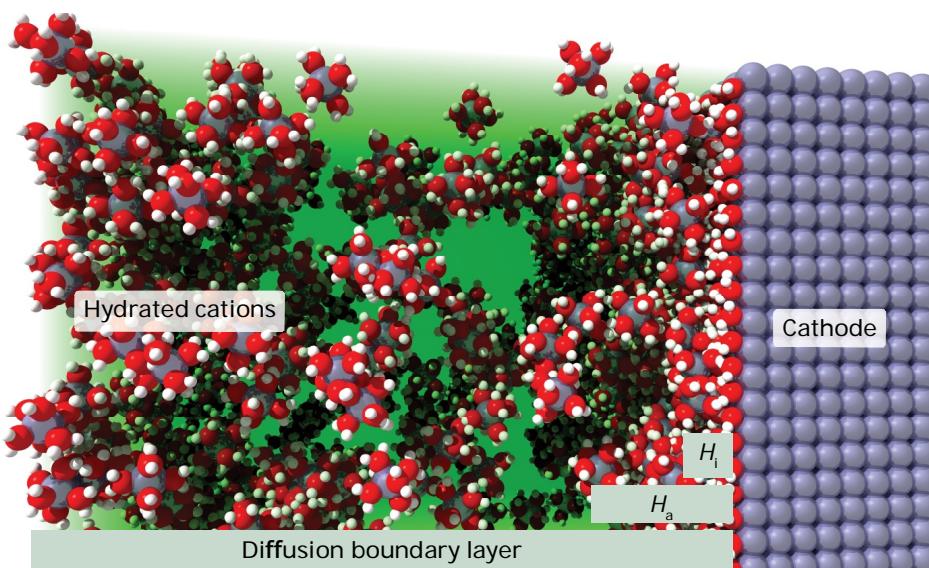


Fig. 136: A schematic diagram of the diffusion boundary layer with the outer (H_a) and inner (H_i) Helmholtz plane.

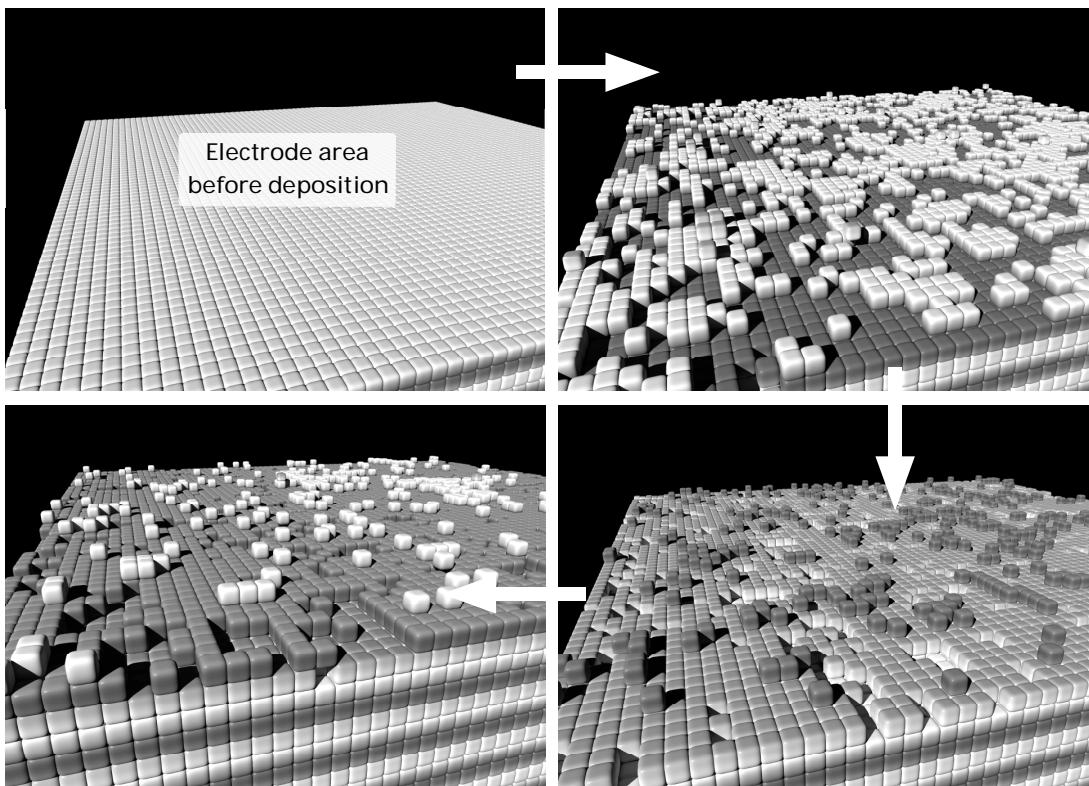


Fig. 137: In our simple model, deposition starts with i) the physical adsorption of ions on a random site of the solid, ii) thermally activated jumps to energetically more attractive crystal sites with more neighbours and iii) finally the incorporation into the growing crystal. The colouring of the different layers aims for a better visualisation.

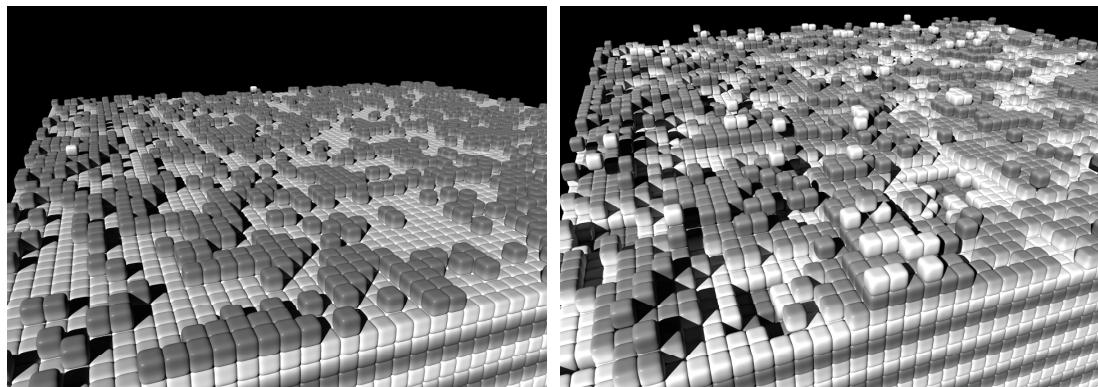
12 over the edges, and 8 over the corners of the central cell), each of which can be occupied or unoccupied. The more occupied neighbour sites a particle has (the neighbour sites contributing less to the edges and corners due to the greater distance), the greater its bonding energy at this location. The probability p for a thermally activated jump from a lattice location (energy E_1) to an adjacent location (E_2) is thus:

$$p = c \cdot \exp\left[-\frac{E_2 - E_1}{kT}\right]$$

where kT is the kinetic energy of the particle, and c is a constant. The series of images in Fig. 137, shows the growth of a layer simulated exclusively by this model, monolayer by monolayer, at different stages:

The more time the deposited particles have for the search for an energetically best possible lattice site (for example, a lower deposition rate and/or higher temperature), the smoother the layer (Fig. 138) grows. Not only the bonding energy to adjacent occupied lattice sites but also the local electric field contributes to the energy balance of a particle jump on the surface of the electrode: The smaller the radius of curvature of the surface, the greater the local electric field, and the more likely the incorporation of a particle at this site. Fig. 139 shows the result of a simulation that takes this aspect into consideration: Small, ran-

Fig. 138: A slower growth rate (left) lead to smoother layers, since the adsorbed atoms have more time (= more jumps between different sites) to find a crystal site with a maximum number of neighbours. The colouring of the different layers aims for a better visualisation.



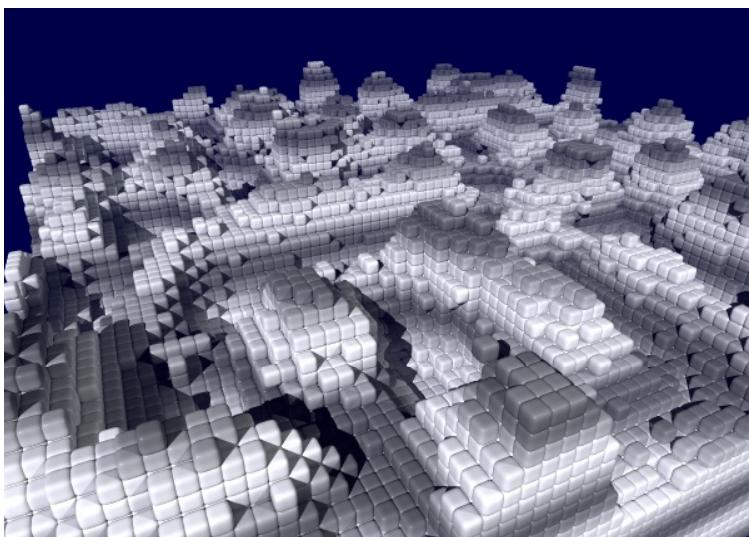


Fig. 139: Near spikes, the electric field is higher which promotes the adsorption and incorporation of cations, hereby promoting the growth of already existing crystallites. The colouring of the different layers aims for a better visualisation.

dom irregularities at the beginning of the deposition (nucleation) intensify with the further growth as new particles are preferentially incorporated there.

... and Practice

The reality of electro-plating deposition is much more complex than the assumptions of the simulations treated here:

Electrodes are usually not single crystals but amorphous or nano-crystalline solids, whereby the bonding conditions are locally different on their surface.

Also ignored were the transport mechanisms within the diffusion boundary layer, in particular the passage through the inner and outer Helmholtz layer.

The stripping of the hydration shell and chemical reactions also affect the energy balance of a particle between adsorption and incorporation into the crystal.

Electrodes

Electrodes of the First Kind

These are the "typical" metal electrodes treated in the preceding sections, from which the metal emerges in the form of dissolved ions and remains in the electrode in accordance with the oxidation number z of the metal ions according to $\text{Me} \rightarrow \text{Me}^{z+} + z e^-$.

The equilibrium potential can be determined using the Nernst equation. The metal is available in two phases: Elemental in the electrode and dissolved in electrolytes.

Electrodes of the Second Kind

With electrodes of the second kind, the dissolved ions do not (or only to a small extent) dissolve in solution, but form with (usually) anions from the electrolyte a poorly soluble compound which deposits almost completely. The metal of the electrode of the second type exists in three different phases: Metallic, ionised in solution and deposited as a salt.

The equilibrium potential can also be calculated here from the Nernst equation, whereby the concentration of the free ions from the solubility product of the precipitating compound in the electrolyte must be determined.

An example of an electrode of the second kind is a silver electrode in a solution of potassium chloride, producing poorly soluble AgCl .

The silver is elemental in equilibrium (as electrode), deposited AgCl and to a small extent dissolved in the electrolyte (free Ag^+ ions).

Electrodes of the Third Kind

If more than one substance of the electrolyte reacts with the electrode, a plurality of redox systems are present in parallel which, when both systems share the same anions, are coupled to one another via their solubility products. An example for electrodes of the third type is a silver electrode dipped in AgS and PbS .

Redox Electrodes

Redox electrodes do not go into solution, but only take part as electron donor or acceptor and if necessary, as a catalyst for the electro-chemical redox reactions. The platinum electrodes used in the electrolysis of diluted hydrochloric acid to form H_2 and Cl_2 are such redox electrodes. Redox electrodes are also



used as measuring probes, for example, for pH measurement, where the electrode must not dissolve so that it does not contaminate the medium to be measured, on the one hand, and on the other hand, for stable measurements, where no surface and shape change may occur.

Gas Electrodes

A gas electrode is a metal electrode bathed by a certain gas which is ideally adsorbed as a continuous monolayer on the metal surface. An example of a gas electrode is the standard hydrogen electrode as a reference electrode for determining the standard potential of a substance. This is a platinum electrode bathed by hydrogen, on the catalytically active surface of which H_2 is split to form hydrogen atoms, which are deposited on the platinum.

ELECTRO-CHEMICAL DEFINITIONS

This chapter defines the electro-chemical terms used in the following chapters in the treatment of the electro-plating deposition of certain metals.

Neutral, Ionised and Dissolved Substances

Electro-chemical Equivalent

The theoretical maximum amount of a substance (in grams) deposited on the electrode per ampere hour is defined by the formula $A_E = M/(z F)$, where M is the molar mass, F is the Faraday constant, and z is the oxidation number of the substance.

Typical values for metals are between 0.3 g/Ah for the light Al with the oxidation number +3, and 7.3 for the heavy gold with the oxidation number +1.

(Electrolytic) Dissociation

The dissociation of a compound into anions and cations in a solvent, e.g. saline in water according to $NaCl \rightarrow Na^+ + Cl^-$ or hydrochloric acid in water via $HCl + H_2O \rightarrow H_3O^+ + Cl^-$. The degree of dissociation of a substance indicates the proportion of this substance which is dissociated under the given conditions (concentration, pressure, temperature, ...).

Hydration

Adsorption of water molecules to dissolved ions via ion/dipole interactions, or to neutral molecules via hydrogen bonds or/and interactions between static (H_2O molecule) and induced dipoles. The associated hydration energy as well as the change in the entropy (due to a stronger localisation of the water molecules) has a decisive contribution to the free enthalpy of the solution of a substance and thus helps determine its solubility.

Ionisation Energy

The energy necessary to ionise an atom or molecule. Within a period of the periodic table, the first ionisation energy (removal of an electron from the neutral atom) increases due to the increasing atomic number (e.g. Li ... Ne: 5.4 ... 21.6 eV), in order to rapidly fall back again to the next period due to the now next higher shell occupied by the atomic nucleus. Already n-fold ionised substances have a significantly higher n ionisation energy (e.g. iron: 7.9 eV, 16.2 eV and 30.6 eV for the first, second and third ionisation).

Solubility

The maximum concentration c_{max} of a substance in another, where the mixture is at equilibrium in single phase. In the case of substances with an exothermic solution reaction (e.g. NaOH), the solubility decreases with increasing temperature; for substances with an endothermic solution reaction (e.g. KNO_3 or NH_4NO_3) the solubility increases with temperature. The size of c_{max} defines whether a substance is, for example, easily or poorly soluble.

Standard Potential

The normal or standard potential of a substance is the potential that exists between this substance and a hydrogen electrode when both are dipped in a 1 molar solution of the substance under standard state



(25°C, 101.3 kPa). The more positive the standard potential, the more "noble" the substance or the metal (e.g. lithium = -3.02 V, gold = +1.7 V).

Oxidation Number

The charge number of an atom in a bond assuming that the valence electrons of an atom or molecule are each attributed to the more electro-negative ligand. Atoms in the elementary state always have the oxidation number 0, for monatomic ions the oxidation number corresponds to the ion charge (e.g. Fe³⁺ has the oxidation number +3).

Electrolytes and Electrodes

Coverability

The ability of an electrolyte to deposit a close metal layer without holes. Particularly at low average current densities, local fluctuations in the current density can lead to areas on the surface of the workpiece, on which the current density is too low for a sufficient metal deposition.

Conductivity of the Electrolytes

Electrolytes are pure ionic conductors with a certain electrical conductivity. Theoretically, the conductivity can be derived from the mobilities of the (different) ions contained in the electrolyte, the concentration of which is determined by the concentration of the contents as well as their degree of dissociation dependent on temperature and concentration.

In practice, interactions between the ions as well as polarisation effects on the electrolyte/electrode interface also play a role, so that the system electrode/electrolyte behaves only in a more or less good approximation like an ohmic resistance.

pH Value

Pure water contains, via the autoprotolysis $\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^-$ at room temperature about 10^{-7} mol H_3O^+ and OH^- per litre, which accordingly

$$pH = -\log_{10}[\text{H}_3\text{O}^+]$$

corresponds to a neutral pH of 7. Because the autoprotolysis is thermally activated, the pH value of 100°C hot water is already approximately 6. Acids as proton donors increase in aqueous solutions via the dissociation of protons (e.g. hydrochloric acid: $\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$) the concentration of H_3O^+ ions, where the pH-value drops. Some examples of pH values:

Substance	HCl (20 %)	Gastric acid	Acetic acid	DI water	Soapsuds	KOH (1.4 %)	KOH (50 %)
pH value	-1	1-3	3	7	8-12	13	14.5

Table 8: The pH values of various fluids

Throwing Power

Due to the geometric shape of the electrodes and the inhomogeneous surface of the electrode (roughness, nanocrystallinity) which is on a microscopic scale, the current density varies across the surface of the electrodes, which has an effect on the electro-chemical reactions occurring on the electrode. A distinction is made here between ...

Brightness Throwing Power

Electrolytes, in which glossy layers can be deposited over a large range of the current density distribution, have a high brightness throwing power

Macro Scattering

Electrolytes with high macro scattering allow uniform layer growth over a certain range of the current density distribution varying by the geometric electrode shape.

Micro Scattering



Electrolytes with high micro scattering enable uniform layer growth over a certain range of the current density distribution varying due to the roughness of the electrode surface.

Yield

The ratio of the amount of metal actually deposited on the cathode to the theoretical value calculated according to the electro-chemical equivalent. Values < 100% are due to reactions parallel to metal deposition, which also consume electrons (e.g. H₂ formation from H₃O⁺ ions in the electrolytes). Values above 100% occur when the anode dissolves not only electrolytically, but also chemically, with released electrons being available for metal deposition.

Oversoltage

The difference between the voltage required for the electrolysis and the theoretical potential difference derived from the electrochemical voltage. The causes of oversoltage are energy-consuming processes in the electro-chemical reaction chain, such as diffusion, adsorption, stripping of the hydration shell, gas formation, etc.

Decomposition Voltage

The necessary potential difference between the cathode and the anode calculated theoretically for the electrolysis according to the Nernst equation, plus the oversoltage.

Deposited Metal Layer

Ductility

The ability of a material not to break during external mechanical (overload) loading but to deform.

A few ductile substances, such as glass at room temperature, are brittle and break easily, while soft metals such as gold with high ductility can be readily formed even at room temperature (e.g. such as gold leaf). The ductility of a substance depends greatly on its crystalline structure and thus the deposition conditions of the layer.

Shine and Brightness

Which surface properties of a substance lead to a brilliant impression is not yet fully understood, even if a very smooth, fine-crystalline structure plays an important role. In electro-plating deposition, this generally requires a high nucleation density while suppressing the growth of these nuclei to larger crystallites.

Hardness

The mechanical resistance where a material opposes the penetration of a foreign body. Hard layers do not easily scratch and wear less due to abrasion. There are various methods of hardness testing, such as the Rockwell hardness test (penetration of a test specimen into the substance), according to Brinell (determination of the area of the impression of a steel ball pressed onto the test specimen) or Mohs: The Mohs hardness is an empirical table of unified values between 1 (talc) and 10 (diamond) in which a substance is capable of scratching another substance which is below this substance on the scale (greater Mohs hardness). The hardness of a substance depends strongly on its (nano)crystalline structure and thus the deposition conditions of the layer.

Porosity

The ratio of the microscopic void volume (pores) of a substance to its total volume. In material engineering, porosity is classified according to micro-porous (pores < 2 nm), meso-porous (2 ... 50 nm) and macro-porous (> 50 nm). The attained porosity of a sealed metal layer strongly depends on the deposition conditions and can only theoretically reach a value of 1.

Our Photoresists: Application Areas and Compatibilities

Recommended Applications ¹		Resist Family	Photoresists	Resist Film Thickness ²	Recommended Developers ³	Recommended Removers ⁴
Positive	Improved adhesion for wet etching, no focus on steep resist sidewalls Spray coating Dip coating Steep resist sidewalls, high resolution and aspect ratio for e. g. dry etching or plating Elevated thermal softening point and high resolution for e. g. dry etching	AZ® 1500	AZ® 1505 AZ® 1512 HS AZ® 1514 H AZ® 1518	≈ 0.5 µm ≈ 1.0 - 1.5 µm ≈ 1.2 - 2.0 µm ≈ 1.5 - 2.5 µm	AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® Developer	AZ® 100 Remover, TechniStrip® P1316 TechniStrip® P1331
			AZ® 4500	AZ® 4533 AZ® 4562	≈ 3 - 5 µm ≈ 5 - 10 µm	
		AZ® P4000	AZ® P4110 AZ® P4330 AZ® P4620 AZ® P4903	≈ 1 - 2 µm ≈ 3 - 5 µm ≈ 6 - 20 µm ≈ 10 - 30 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
			AZ® PL 177	AZ® PL 177	≈ 3 - 8 µm	
			AZ® 4999		≈ 1 - 15 µm	
		MC Dip Coating Resist		≈ 2 - 15 µm	AZ® 351B, AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
		AZ® ECI 3000	AZ® ECI 3007 AZ® ECI 3012 AZ® ECI 3027	≈ 0.7 µm ≈ 1.0 - 1.5 µm ≈ 2 - 4 µm	AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® Developer	
			AZ® 9200	AZ® 9245 AZ® 9260	≈ 3 - 6 µm ≈ 5 - 20 µm	
		AZ® 701 MiR	AZ® 701 MiR (14 cPs) AZ® 701 MiR (29 cPs)	≈ 0.8 µm ≈ 2 - 3 µm	AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® Developer	
Positive (chem. amplified)	Steep resist sidewalls, high resolution and aspect ratio for e. g. dry etching or plating	AZ® XT	AZ® 12 XT-20PL-05 AZ® 12 XT-20PL-10 AZ® 12 XT-20PL-20 AZ® 40 XT	≈ 3 - 5 µm ≈ 6 - 10 µm ≈ 10 - 30 µm ≈ 15 - 50 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF	AZ® 100 Remover, TechniStrip® P1316 TechniStrip® P1331
			AZ® IPS 6050	≈ 20 - 100 µm		
Image Re-versal	Elevated thermal softening point and undercut for lift-off applications	AZ® 5200	AZ® 5209 AZ® 5214	≈ 1 µm ≈ 1 - 2 µm	AZ® 351B, AZ® 326 MIF, AZ® 726 MIF	TechniStrip® Micro D2 TechniStrip® P1316 TechniStrip® P1331
		TI	TI 35ESX TI xLift-X	≈ 3 - 4 µm ≈ 4 - 8 µm		
Negative (Cross-linking)	Negative resist sidewalls in combination with no thermal softening for lift-off application	AZ® nLOF 2000	AZ® nLOF 2020 AZ® nLOF 2035 AZ® nLOF 2070	≈ 1.5 - 3 µm ≈ 3 - 5 µm ≈ 6 - 15 µm	AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	TechniStrip® NI555 TechniStrip® NF52 TechniStrip® MLO 07
			AZ® nLOF 5500	AZ® nLOF 5510		
	Improved adhesion, steep resist sidewalls and high aspect ratios for e. g. dry etching or plating	AZ® nXT	AZ® 15 nXT (115 cPs) AZ® 15 nXT (450 cPs)	≈ 2 - 3 µm ≈ 5 - 20 µm	AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	TechniStrip® P1316 TechniStrip® P1331 TechniStrip® NF52 TechniStrip® MLO 07
	AZ® 125 nXT	≈ 20 - 100 µm	AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF			

¹ In general, almost all resists can be used for almost any application. However, the special properties of each resist family makes them specially suited for certain fields of application.

² Resist film thickness achievable and processable with standard equipment under standard conditions. Some resists can be diluted for lower film thicknesses; with additional effort also thicker resist films can be achieved and processed.

³ Metal ion free (MIF) developers are significantly more expensive, and reasonable if metal ion free development is required.

Our Developers: Application Areas and Compatibilities

Inorganic Developers

(typical demand under standard conditions approx. 20 L developer per L photoresist)

AZ® Developer is based on sodium phosphate and –metasilicate, is optimized for minimal aluminum attack and is typically used diluted 1 : 1 in DI water for high contrast or undiluted for high development rates. The dark erosion of this developer is slightly higher compared to other developers.

AZ® 351B is based on buffered NaOH and typically used diluted 1 : 4 with water, for thick resists up to 1 : 3 if a lower contrast can be tolerated.

AZ® 400K is based on buffered KOH and typically used diluted 1 : 4 with water, for thick resists up to 1 : 3 if a lower contrast can be tolerated.

AZ® 303 specifically for the AZ® 111 XFS photoresist based on KOH / NaOH is typically diluted 1 : 3 - 1 : 7 with water, depending on whether a high development rate, or a high contrast is required

Metal Ion Free (TMAH-based) Developers

(typical demand under standard conditions approx. 5 - 10 L developer concentrate per L photoresist)

AZ® 326 MIF is 2.38 % TMAH- (TetraMethylAmmoniumHydroxide) in water.

AZ® 726 MIF is 2.38 % TMAH- (TetraMethylAmmoniumHydroxide) in water, with additional surfactants for rapid and uniform wetting of the substrate (e. g. for puddle development)

AZ® 826 MIF is 2.38 % TMAH- (TetraMethylAmmoniumHydroxide) in water, with additional surfactants for rapid and uniform wetting of the substrate (e. g. for puddle development) and other additives for the removal of poorly soluble resist components (residues with specific resist families), however at the expense of a slightly higher dark erosion.

Our Removers: Application Areas and Compatibilities

AZ® 100 Remover is an amine solvent mixture and standard remover for AZ® and TI photoresists. To improve its performance, AZ® 100 remover can be heated to 60 - 80°C. Because the AZ® 100 Remover reacts highly alkaline with water, it is suitable for this with respect to sensitive substrate materials such as Cu, Al or ITO only if contamination with water can be ruled out.

TechniStrip® P1316 is a remover with very strong stripping power for Novolak-based resists (including all AZ® positive resists), epoxy-based coatings, polyimides and dry films. At typical application temperatures around 75°C, TechniStrip® P1316 may dissolve cross-linked resists without residue also, e.g. through dry etching or ion implantation. TechniStrip® P1316 can also be used in spraying processes. For alkaline sensitive materials, TechniStrip® P1331 would be an alternative to the P1316. Nicht kompatibel mit Au oder GaAs.

TechniStrip® P1331 can be an alternative for TechniStrip® P1316 in case of alkaline sensitive materials. TechniStrip® P1331 is not compatible with Au or GaAs.

TechniStrip® NI555 is a stripper with very strong dissolving power for Novolak-based negative resists such as the AZ® 15 nXT and AZ® nLOF 2000 series and very thick positive resists such as the AZ® 40 XT. TechniStrip® NI555 was developed not only to peel cross-linked resists, but also to dissolve them without residues. This prevents contamination of the basin and filter by resist particles and skins, as can occur with standard strippers. TechniStrip® NI555 is not compatible with GaAs.

TechniClean™ CA25 is a semi-aqueous proprietary blend formulated to address post etch residue (PER) removal for all interconnect and technology nodes. Extremely efficient at quickly and selectively removing organo-metal oxides from Al, Cu, Ti, TiN, W and Ni.

TechniStrip™ NF52 is a highly effective remover for negative resists (liquid resists as well as dry films). The intrinsic nature of the additives and solvent make the blend totally compatible with metals used throughout the BEOL interconnects to WLP bumping applications.

TechniStrip™ Micro D2 is a versatile stripper dedicated to address resin lift-off and dissolution on negative and positive tone resist. The organic mixture blend has the particularity to offer high metal and material compatibility allowing to be used on all stacks and particularly on fragile III/V substrates for instance.

TechniStrip™ MLO 07 is a highly efficient positive and negative tone photoresist remover used for IR, III/V, MEMS, Photonic, TSV mask, solder bumping and hard disk stripping applications. Developed to address high dissolution performance and high material compatibility on Cu, Al, Sn/Ag, Alumina and common organic substrates.

Our Wafers and their Specifications

Silicon-, Quartz-, Fused Silica and Glass Wafers

Silicon wafers are either produced via the Czochralski- (CZ-) or Float zone- (FZ-) method. The more expensive FZ wafers are primarily reasonable if very high-ohmic wafers (> 100 Ohm cm) are required.

Quartz wafers are made of monocrystalline SiO₂, main criterion is the crystal orientation (e. g. X-, Y-, Z-, AT- or ST-cut)

Fused silica wafers consist of amorphous SiO₂. The so-called JGS2 wafers have a high transmission in the range of ≈ 280 - 2000 nm wavelength, the more expensive JGS1 wafers at ≈ 220 - 1100 nm.

Our glass wafers, if not otherwise specified, are made of borosilicate glass.

Specifications

Common parameters for all wafers are diameter, thickness and surface (1- or 2-side polished). Fused silica wafers are made either of JGS1 or JGS2 material, for quartz wafers the crystal orientation needs to be defined. For silicon wafers, beside the crystal orientation (<100> or <111>) the doping (n- or p-type) as well as the resistivity (Ohm cm) are selection criteria.

Prime-, Test-, and Dummy Wafers

Silicon wafers usually come as „Prime-grade“ or „Test-grade“, latter mainly have a slightly broader particle specification. „Dummy-Wafers“ neither fulfill Prime- nor Test-grade for different possible reasons (e. g. very broad or missing specification of one or several parameters, reclaim wafers, no particle specification) but might be a cheap alternative for e. g. resist coating tests or equipment start-up.

Our Silicon-, Quartz-, Fused Silica and Glass Wafers

Our frequently updated wafer stock list can be found here: www.microchemicals.com/products/wafers/waferlist.html

Further Products from our Portfolio

Plating

Plating solutions for e. g. gold, copper, nickel, tin or palladium: www.microchemicals.com/products/electroplating.html

Solvents (MOS, VLSI, ULSI)

Acetone, isopropyl alcohol, MEK, DMSO, cyclopentanone, butylacetate, ... www.microchemicals.com/products/solvents.html

Acids and Bases (MOS, VLSI, ULSI)

Hydrochloric acid, sulphuric acid, nitric acid, KOH, TMAH, ... www.microchemicals.com/products/etchants.html

Etching Mixtures

for e. g. chromium, gold, silicon, copper, titanium, ... www.microchemicals.com/products/etching_mixtures.html

Further Information

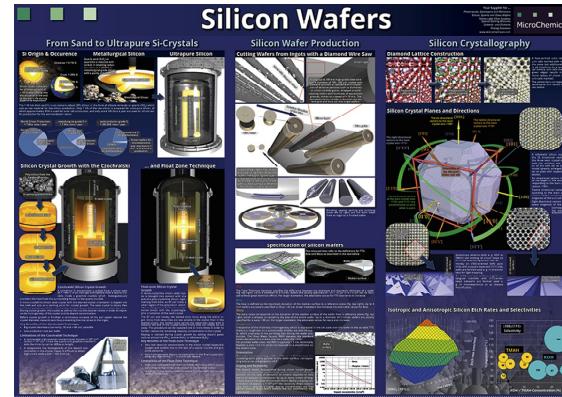
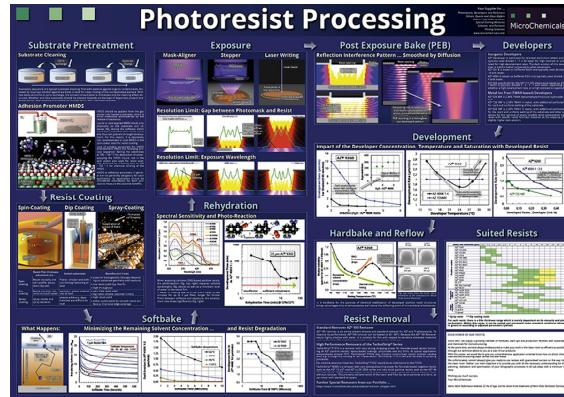
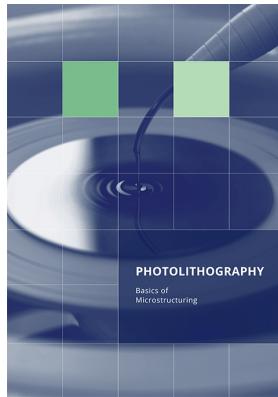
Technical Data Sheets:

www.microchemicals.com/downloads/product_data_sheets/photoresists.html

Material Safety Data Sheets (MSDS):

www.microchemicals.com/downloads/safety_data_sheets/msds_links.html

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