1 - Introduction to electrochemical syntheses

Brief history of electrochemical deposition:

1780's:	Galvani: birth of electrochemistry
1799:	Volta invented the first voltaic pile
1802:	Brugnatelli performed the first metal electroplating
1834:	Faraday law on the charge and matter quantities
1897:	J. J. Thomson discovers the electron
1905:	Tafel equation: $\eta = E - E_{eq} = a + b \cdot \log j$
1911:	Rutherford-Bohr model of the atom
1930:	Butler-Volmer model: $j = j_0 \cdot \left(exp^{\frac{\alpha_a zF\eta}{RT}} - exp^{-\frac{\alpha_c zF\eta}{RT}} \right)$
1935 – 1965:	Eyring: modern theory of electrochemical activation energy Burton-Cabrera-Frank model of real surfaces (surface defects)
1954:	Lorenz: surface diffusion of adions (adsorbed ions)
1958:	Bockris: surface site-dependent charge transfer
1965:	Dickson: microscopic study of nucleation and growth
1970-1980:	Hills: nucleation and growth models (Prog./Inst. – 2D/3D)

An important tool to process materials at the atomic scale:

Surface treatments

Separation and purification

Chemical synthesis

Additive manufacturing

Substrative manufacturing

Analyses (electrolytes and electrodes)

Electrochemical techniques can be classified as:

Substractive processes

Conversion processes

Additive processes

Analytical methods

Substractive processes

Electrolytic dissolution	EC-induced dissolution

A Faradaic current converts solid compounds from an electrode surface into solvated species.

Typically anodic / oxidation: $M^{0}_{(solid)} \rightarrow M^{z+}_{(solvated)} + z \cdot e^{-}$

Rarely cathodic / reduction: $M^{0}_{(solid)} + z \cdot e^{-} \rightarrow M^{z-}_{(solvated)}$

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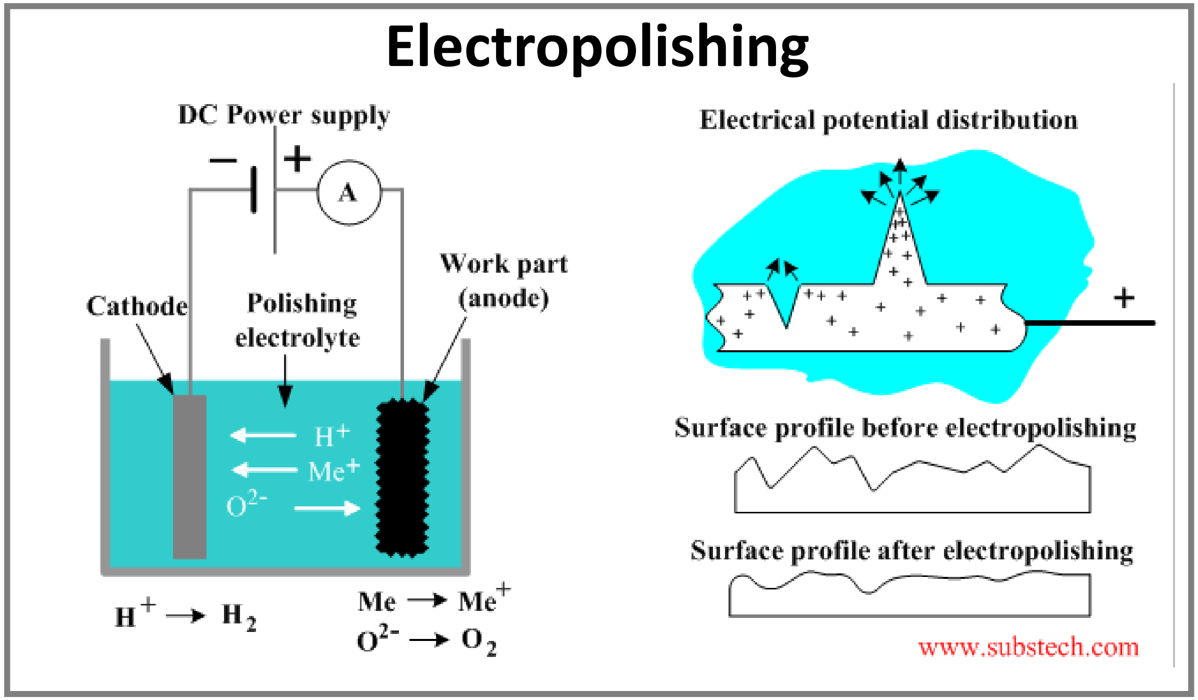

Applications: Electropolishing, electrochemical machining, electroleaching, dealloying, surface cleaning/activation

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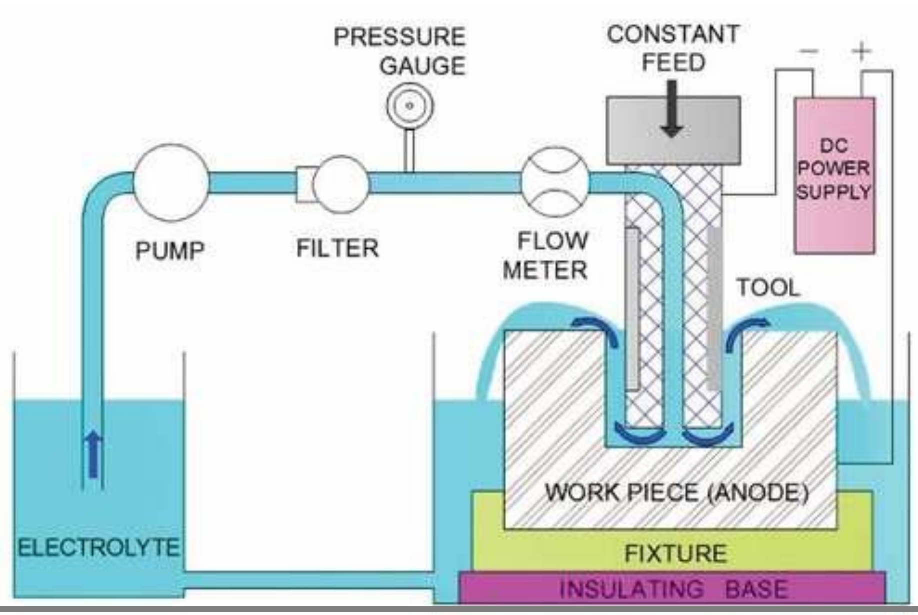
Electrochemical machining



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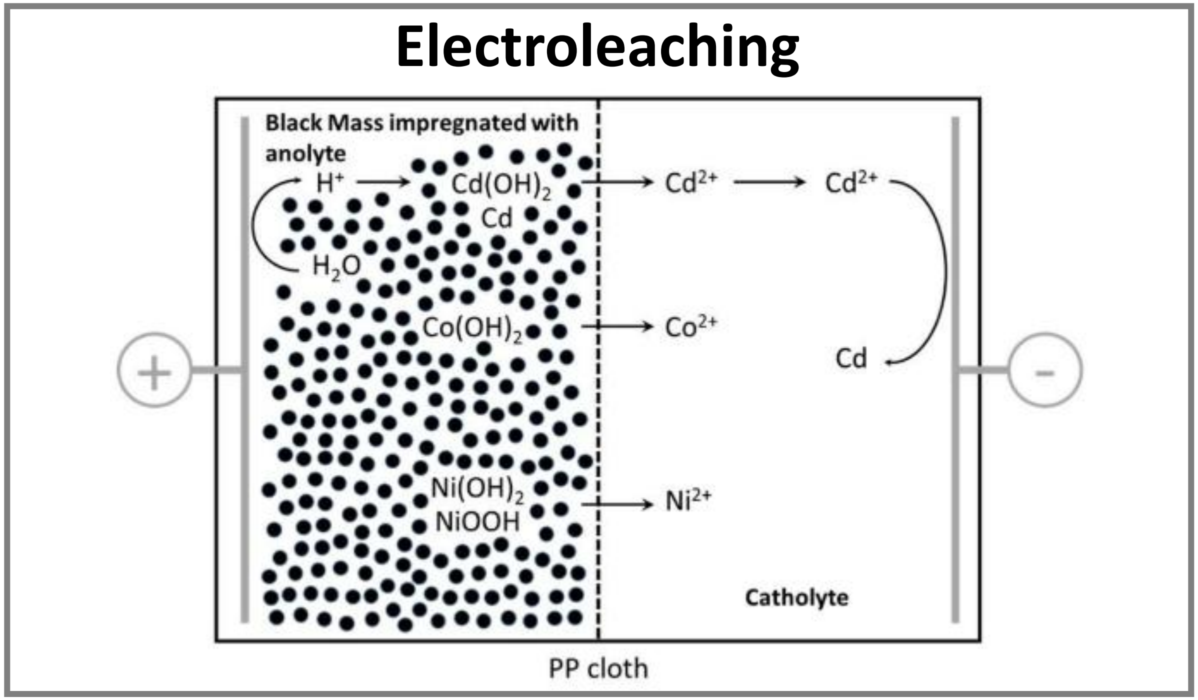

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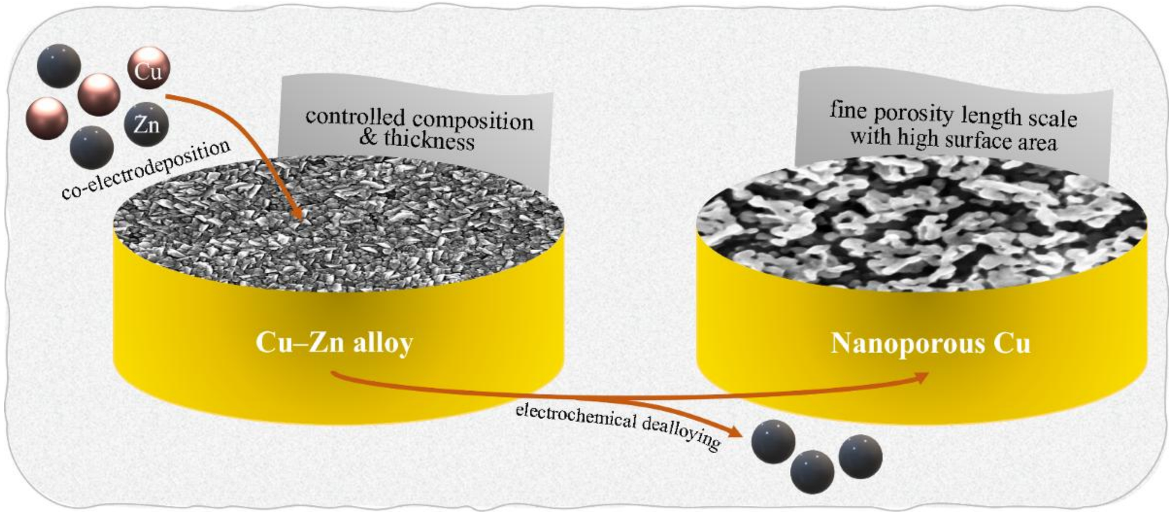
Dealloying



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A Faradaic current converts solid compounds from an electrode surface into solvated species.

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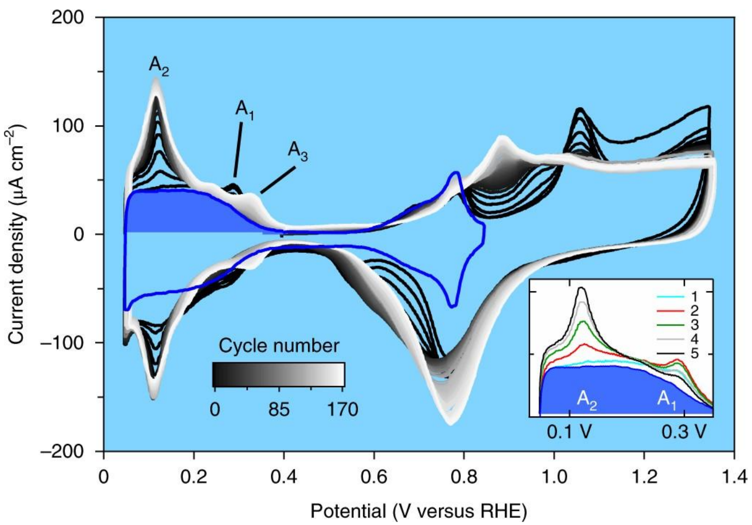
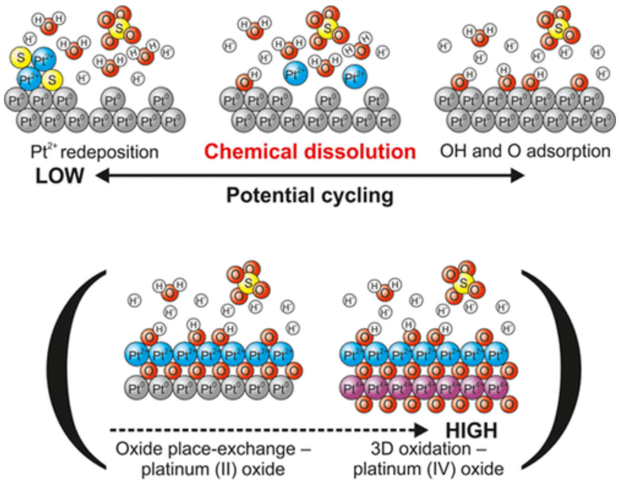
Cleaning and activation of surfaces



Red/Ox of contaminants

Surface restructuring



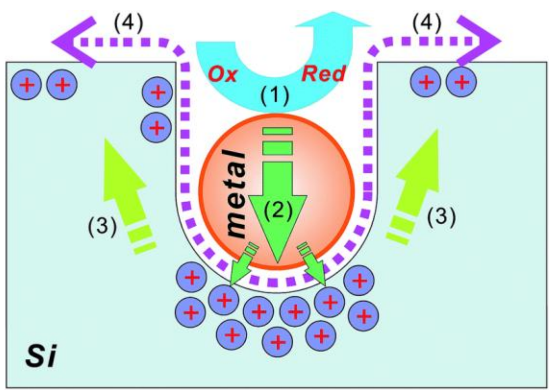
Applications: Electropolishing, electrochemical machining, electroleaching, dealloying, surface cleaning/activation

Substractive processes

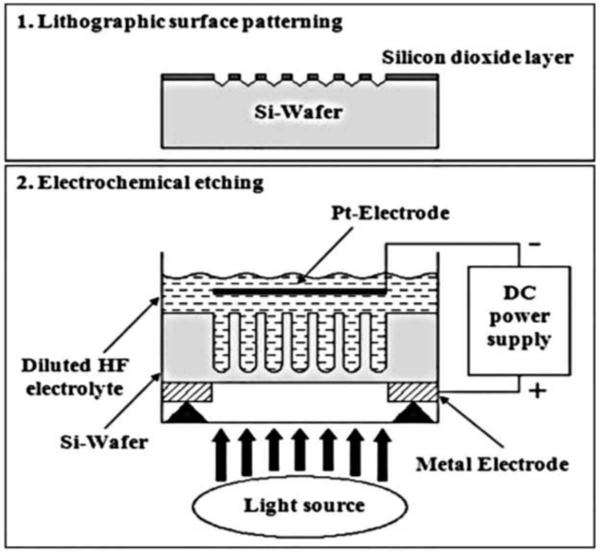
Electrolytic dissolution	EC-induced dissolution

Electrochemical reactions induce local changes of chemical conditions leading to the dissolution of solid species.

Electrochemical etching of silicon



e.g., H_2O_2 reduction on silver particles



Applications: Silicon microcomponents and surface nanostructuring, surface cleaning

Conversion processes

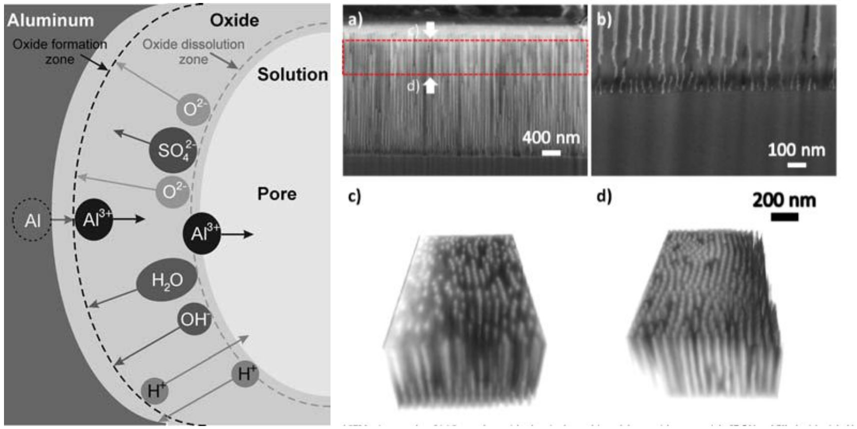
Anodisation	Electrosynthesis	Energy conversion and storage	Ion transfer

Growth of an oxide layer onto a metal electrode by anodic oxidation.

$$xM^0_{(solid)} + yH_2O \rightarrow M_xO_y + 2y\,H^+ + 2y\,e^-$$

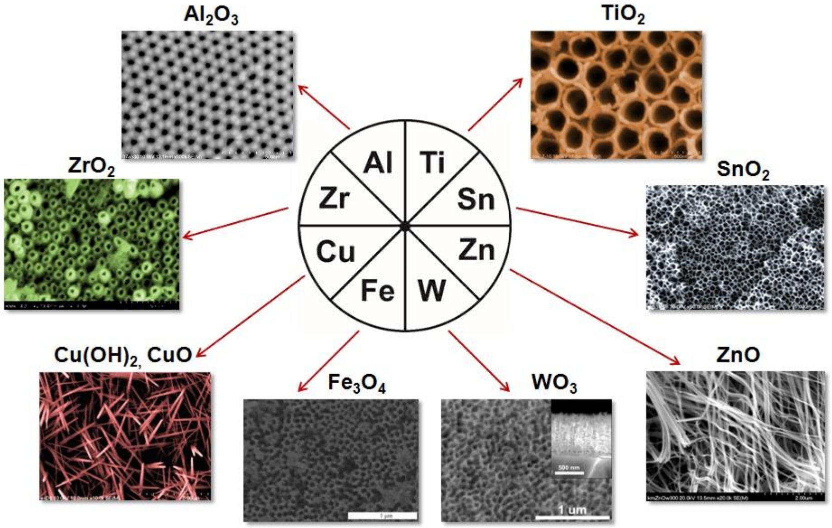
Anodic coatings

Anodisation of aluminum



Highly ordered nanopore arrays

Other examples



Applications: Protective coatings, nanoporous oxides, decorative, tribology, nanostructures

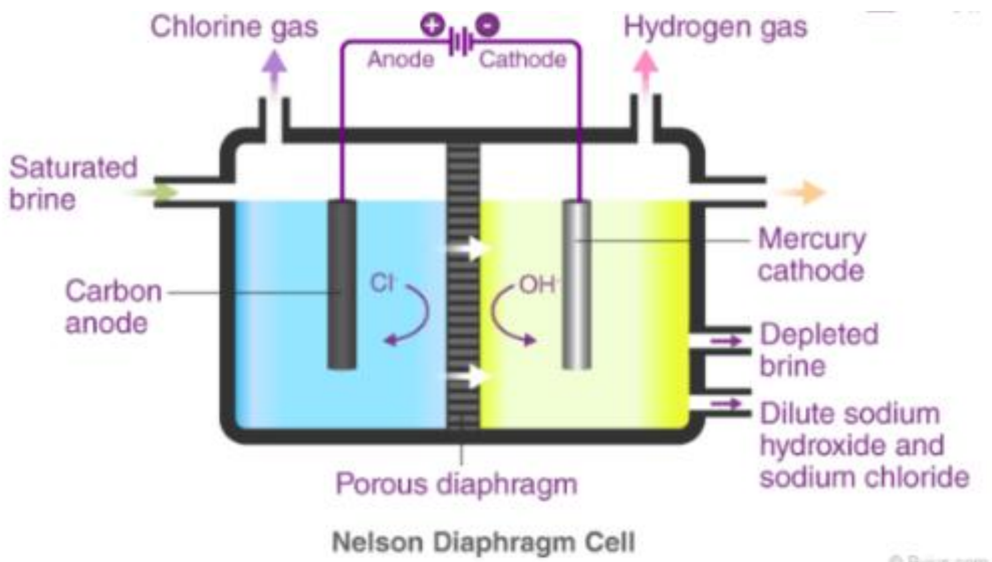
Conversion processes

Anodisation	Electrosynthesis	Energy conversion and storage	Ion transfer

Chemical transformation where electrodes are used to assist electron transfer reactions.

Anodic, cathodic, EC & C coupled reactions

Electrosynthesis of NaOH



Applications: Synthesis of added-value products (acids & bases, energy vectors, organics)

Conversion processes

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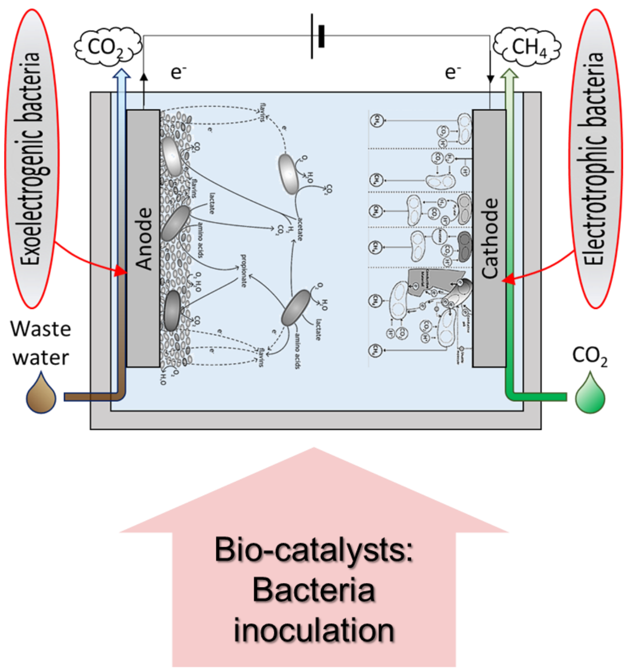


Bio-Electrolysis cells:

- Electrodes are activated with electroactive bacteria
- Bacteria metabolisms unlock complex reactions
- Anodic biofilm: ***organic waste oxidation***
- Cathodic biofilm: ***CO_2 reduction***

Some applications:

- *Wastewater treatment:* COD, total nitrogen, phosphate, sulfates, micropollutants
- *CO_2 valorization:* pure biomethane, methanol, acetate, formate, …

Applications: Synthesis of added-value products (acids & bases, energy vectors, organics)

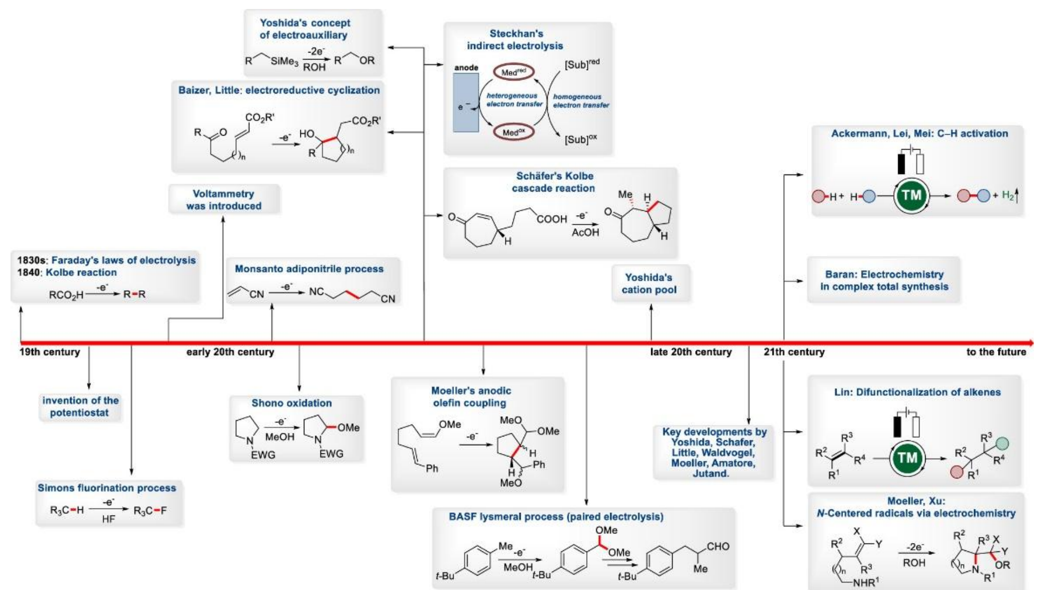
Conversion processes

Anodisation	**Electrosynthesis**	Energy conversion and storage	Ion transfer

Chemical transformation where electrodes are used to assist electron transfer reactions.

Anodic, cathodic, EC & C coupled reactions

Organic electrochemistry



Applications: Synthesis of added-value products (acids & bases, energy vectors, organics)

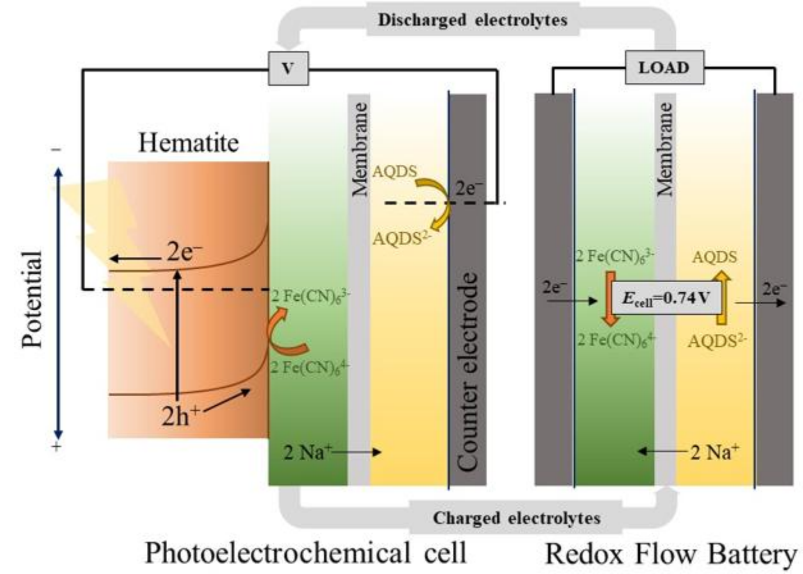
Conversion processes

Anodisation	Electrosynthesis	Energy conversion and storage	Ion transfer

Conversion of chemical potential into electrical energy and vice versa.

Anodic + cathodic, photons, phonons

Photoelectrochemical redox flow battery



Applications: Batteries, fuel cells, redox flow, light and heat harvesting, synthetic fuels

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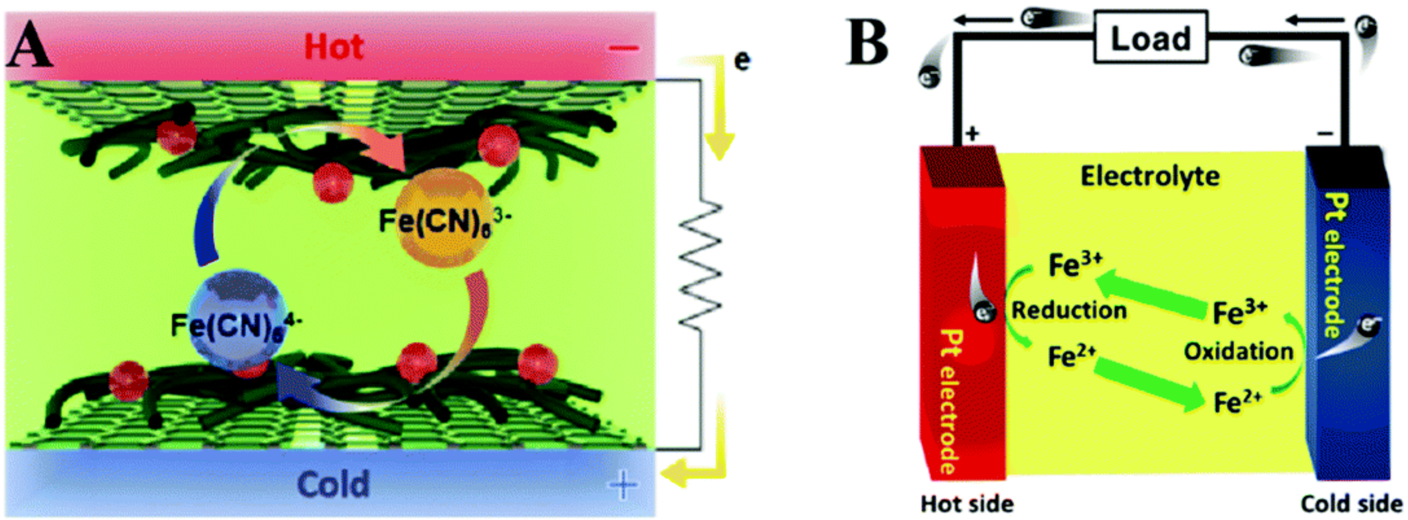
Thermoelectrochemical cells



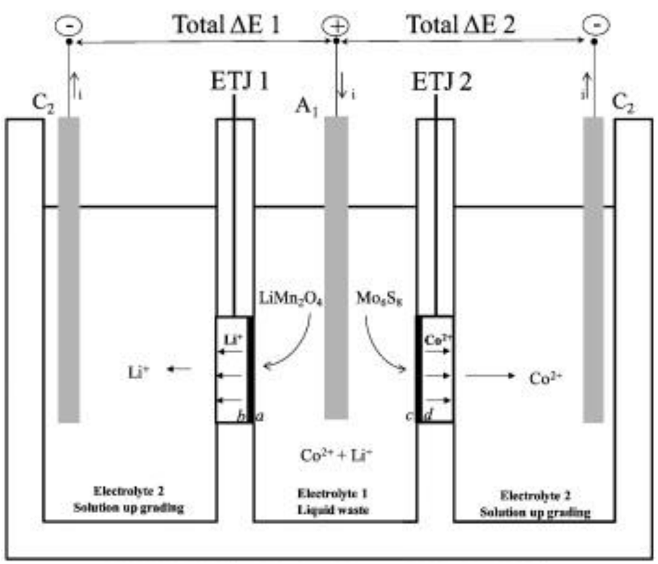
Applications: Batteries, fuel cells, redox flow, light and heat harvesting, synthetic fuels

Conversion processes

Intercalation and extraction of ions.

Separation membrane

Electrochemical transfer junction



Interface a : $x\,Li^+ + x\,e^- + Li_{1-x}Mn_2O_4 \rightarrow Li_1Mn_2O_4$

Interface b : $Li_1Mn_2O_4 \rightarrow x\,Li^+ + x\,e^- + Li_{1-x}Mn_2O_4$

Interface c : $1Co^{2+} + 2e^- + Mo_6S_8 \rightarrow Co_1Mo_6S_8$

Interface d : $Co_1Mo_6S_8 \rightarrow Co^{2+} + 2\,e^- + Mo_6S_8$

Applications: deionization, ion separation, waste treatment and recycling

Additive processes

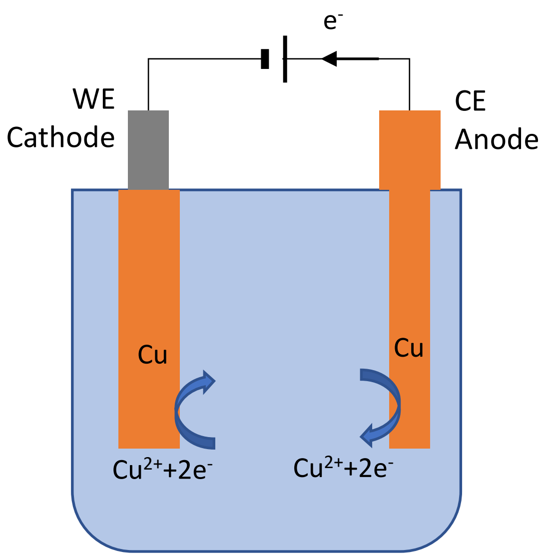
Electrolytic deposition	Electroless deposition	EC-induced precipitation	Electrophoretic deposition

A Faradaic current converts solvated ions (e- acceptor) into a solid deposit onto an electrode surface (e- donor).

Typically cathodic / reduction: $M^{z+}_{(solvated)} + z \cdot e^{-} \rightarrow M^{0}_{(solid)}$

Rarely anodic / oxidation (*e.g.*, selenium, tellurium, polyaniline, polypyrrole)

Cathodic deposition of copper



All features must be electrically connected

Electrodeposit properties controlled by the electrolyte and electrode potential

Applications: functional coatings (metals

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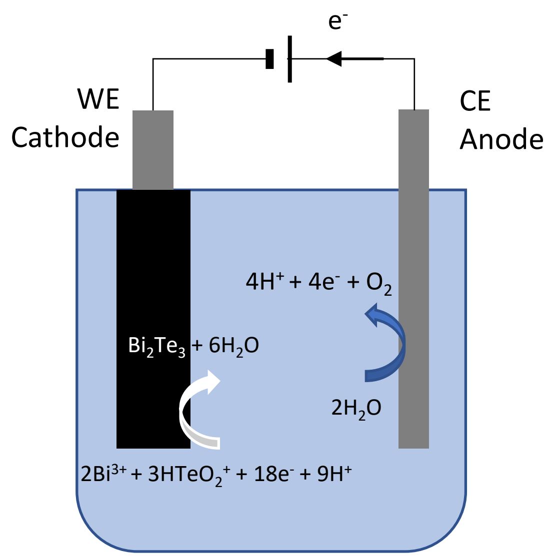
Cathodic deposition of Bi_2Te_3



All features must be electrically connected

Electrodeposit properties controlled by the electrolyte and electrode potential

Applications: functional coatings (metals, alloys, supersaturated solid solutions

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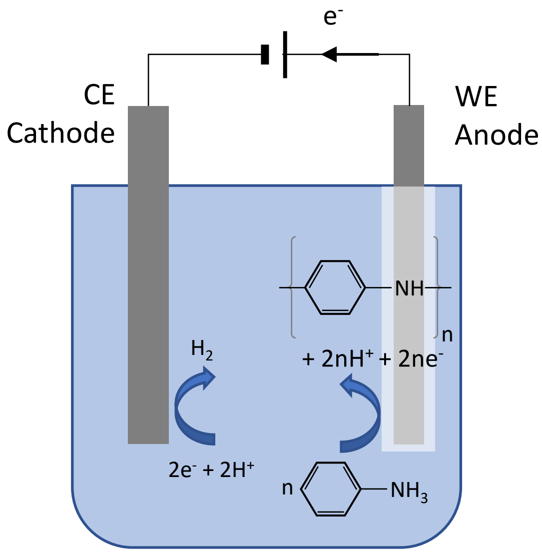
Electropolymerization



All features must be electrically connected

Electrodeposit properties controlled by the electrolyte and electrode potential

Conductive polymers: polyaniline, polypyrrole, polyfuran

→ Protective coatings, supercaps …

Applications: functional coatings (metals, alloys, supersaturated solid solutions, polymers)

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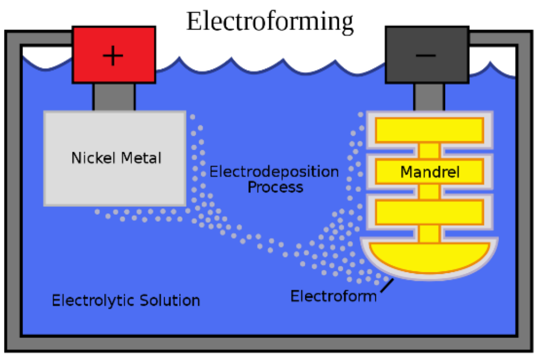
Electroforming



All features must be electrically connected

Electrodeposit properties controlled by the electrolyte and electrode potential

Electrodeposition is conformal

Applications: functional coatings (metals, alloys, supersaturated solid solutions, ceramics, polymers), surface texturing, 3D parts, microcomponents, nanostructures

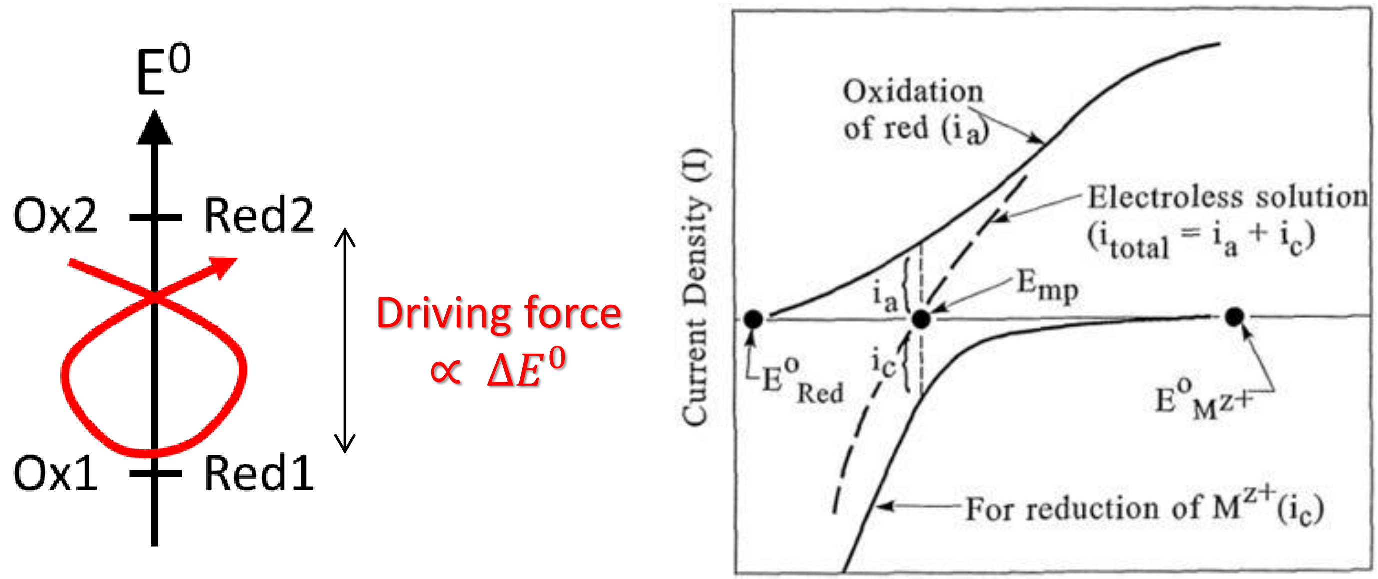
Additive processes

Electrolytic deposition	Electroless deposition	EC-induced precipitation	Electrophoretic deposition

Deposition is mediated by redox reactions between a reductant (e- donnor) and an oxidant (e- acceptor).

No external polarization needed, no counter electrode needed

Redox reaction



Applications: metallization of insulating parts, conformal coatings on complex geometries

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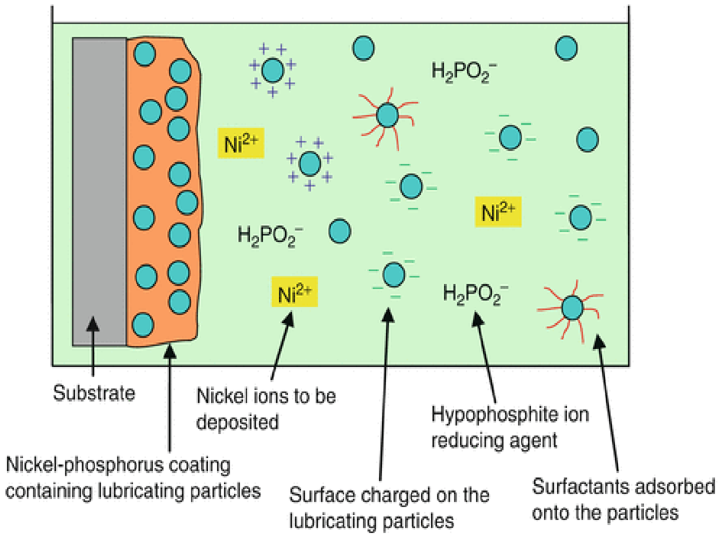
Autocatalytic plating

Red and Ox are both solvated species

$Ni^{2+} + 2e^- \rightarrow Ni^0{}_{(solid)}$ (E⁰ = -257 mV/NHE)

$\Delta E^0 = -242\ mV$

$H_2PO_3{}^- + 2H^+ + 2e^- \rightarrow H_2PO_2^- + H_2O$ (E⁰ = -499 mV/NHE)



Phosphorous is codeposited (amorphous)

Possible to incorporate particles (hardness, friction)

→ Used for hard amagnetic coatings

Applications: metallization of insulating parts, conformal coatings on complex geometries, modification of surface chemistry, nanocomposites

Additive processes

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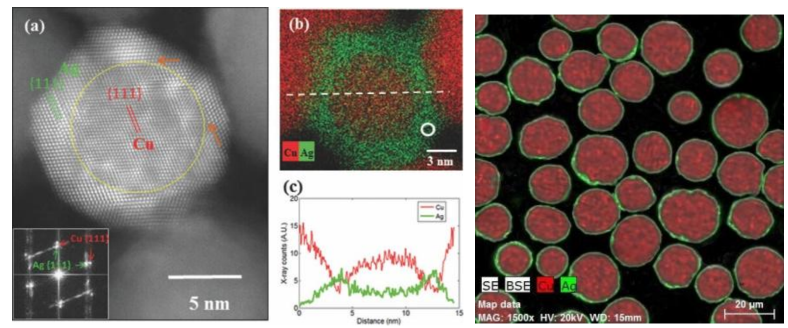
Galvanic displacement

The reducing agent is the solid substrate

$Ag^+ + e^- \rightarrow Ag^0{}_{(solid)}$ (E0 = +799.6 mV/NHE)

$\Delta E^0 = -457.7\ mV$

$Cu^{2+} + 2e^- \rightarrow Cu^0{}_{(solid)}$ (E0 = +341.9 mV/NHE)



The more noble metal displaces the less noble metal

Self-limiting process

→ Modification of the surface chemistry, core-shell structures

Applications: metallization of insulating parts, conformal coatings on complex geometries, nanocomposites, corrosion and tarnishing protection, core-shell structures

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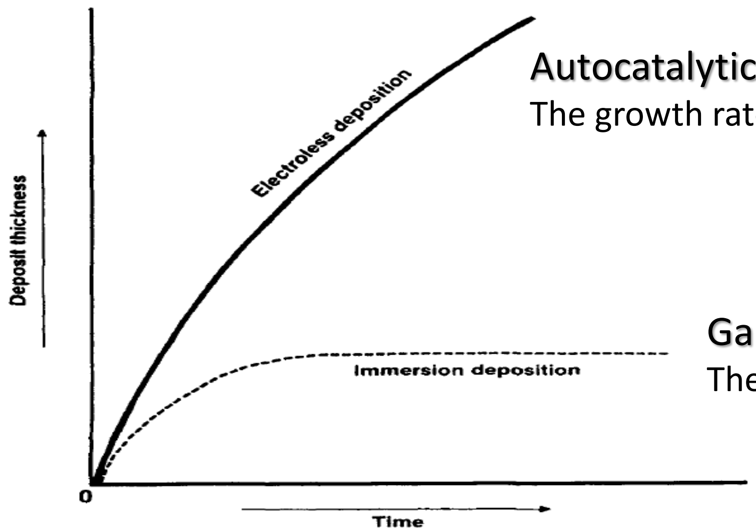
Rate of electroless plating

Autocatalytic vs galvanic displacement



Autocatalytic plating:
The growth rate depends on the bath chemistry

Galvanic displacement:
The growth rate depends on the surface chemistry

Applications: metallization of insulating parts, conformal coatings on complex geometries, nanocomposites, corrosion and tarnishing protection, core-shell structures

Additive processes

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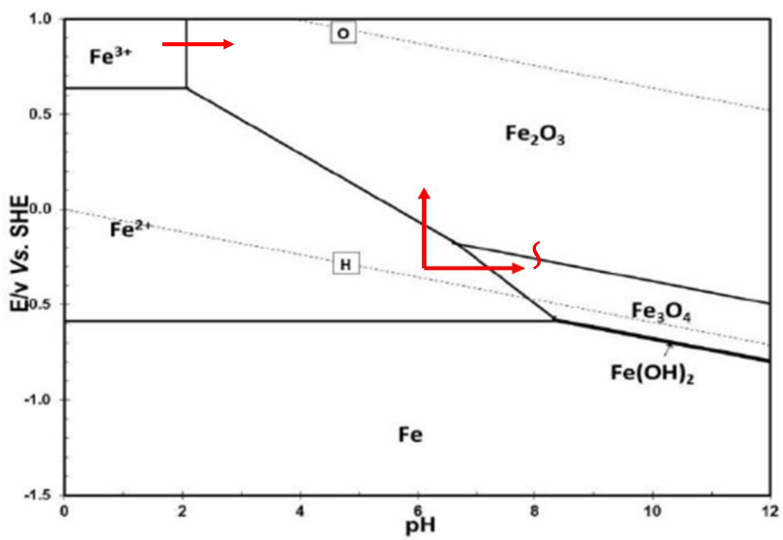
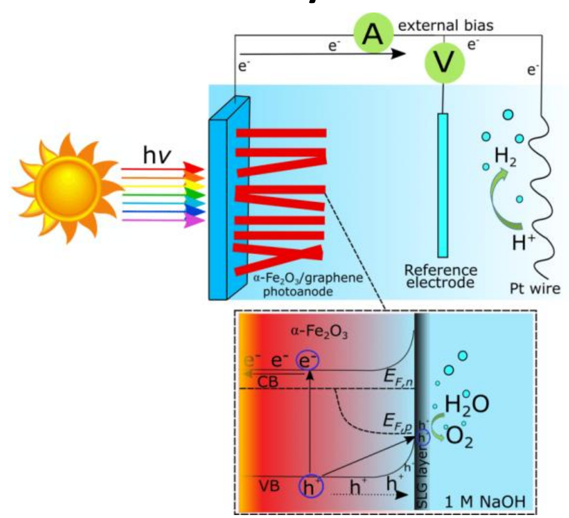
Electrochemical reactions induce local changes of chemical conditions leading to the precipitation of solvated species.

A local increase of ionic strength leads to metal oxide/hydroxide precipitates.
Typically the pH but also the oxidation state or coordination

Three ways of precipitating Fe_xO_y





Hematite photoelectrocatalyst decorated nanostructures for solar water splitting

Applications: electroplating of oxides, catalysis

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Precipitation of ZnO nanorods

Production of OH^- (V_{imp}=-1 V vs SCE)

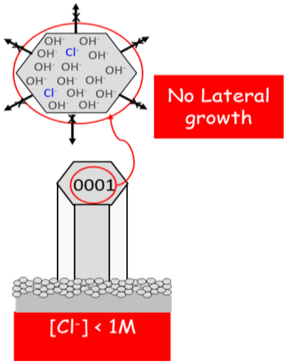
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$$

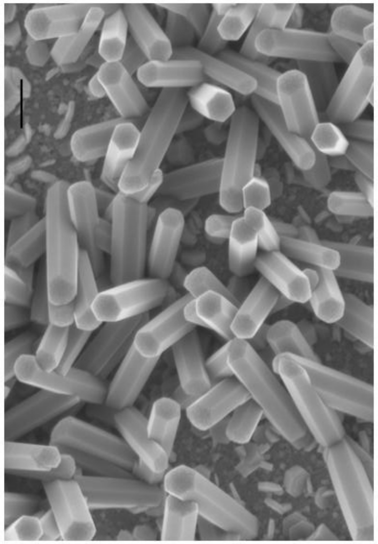
Chemical precipitation

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \rightarrow ZnO + H_2O$$

Internal structure of ZnO

Anisotropic growth along [0001] direction





Applications: electroplating of oxides, catalysis, functional coatings (photonics, hydrophobicity,

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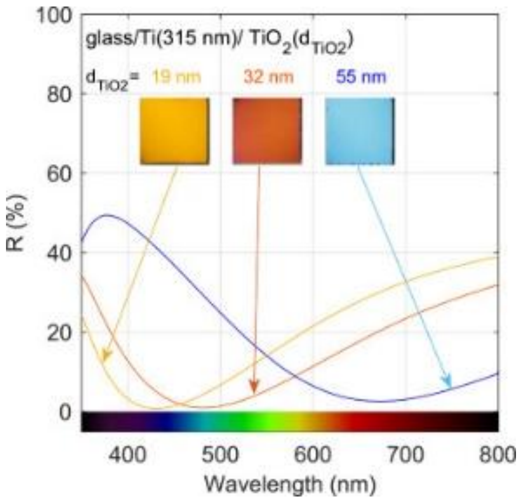
Precipitation of TiO_2 nanolayers

1) Reduction of the oxygen precursor:
   1. $O_2+2H_2O+4e^- \rightarrow 4OH^-$
   2. $H_2O_2+2e^- \rightarrow 2OH^-$
   3. $NO_3^-+H_2O+2e^- \rightarrow NO_2^-+2OH^-$
   4. $NH_2OH + 2H_2O + 2e^- \rightarrow NH_4^+ + 2OH^-$
2) Precipitation of titanium peroxo-complex into titanium hydroxide, to TiO_2:

$$TiO(X)_2^{2-} + 2OH^- \rightarrow TiO(OH)_2 \rightarrow TiO_2 + H_2O$$

Interference colors



Applications: electroplating of oxides, catalysis, functional coatings (photonics, hydrophobicity, dichroic, biocompatibility…)

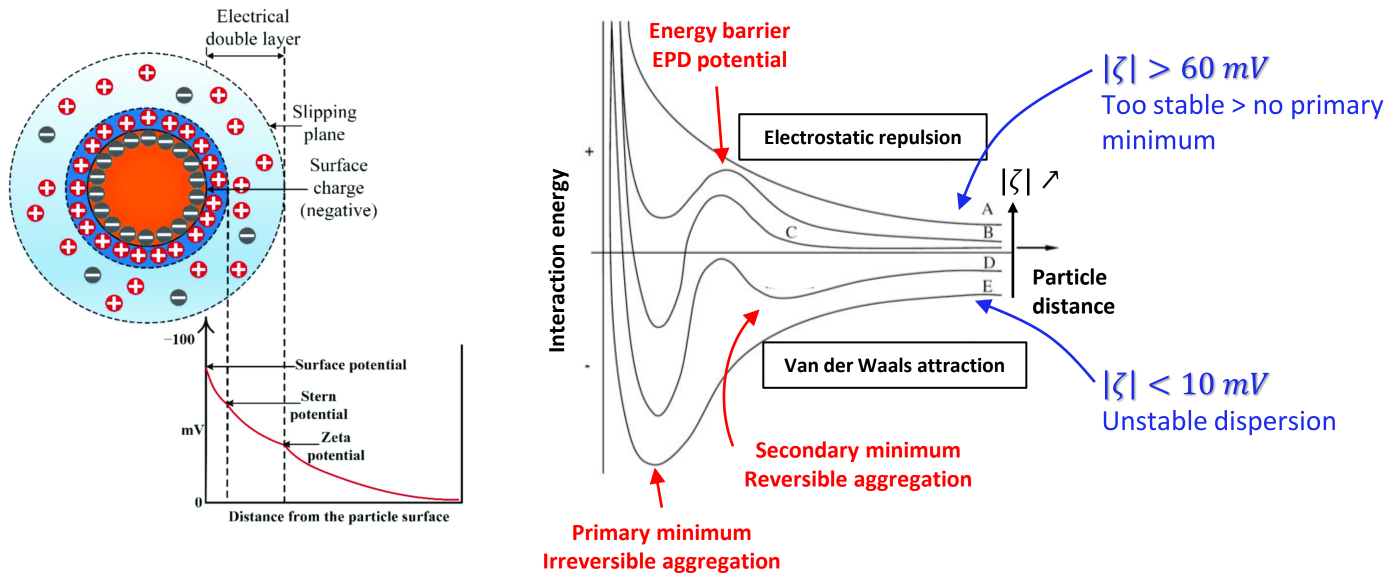
Additive processes

Electrolytic deposition	Electroless deposition	EC-induced precipitation	Electrophoretic deposition

Forced migration and desolvation of charged particles (colloids) in an electric field.

Charged particles dispersed in an electrolyte (low ionic conductivity)
Any material that can develop a surface charge (zeta-potential)

Charged particles and colloids: the DLVO theory

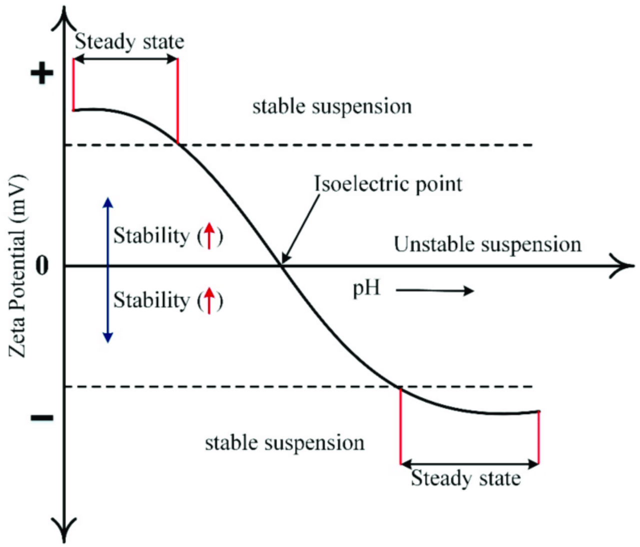


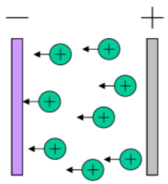
Applications: dielectric coatings

Forced migration and desolvation of charged particles (colloïds) in an electric field.

Charged particles dispersed in an electrolyte (low ionic conductivity)
Any material that can develop a surface charge (zeta-potential)

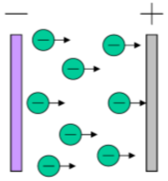
Electrophoretic deposition: cathodic or anodic





Particles with $\zeta > 0$ mV migrate towards the cathode

➢ **Cathodic EPD**



Particles with $\zeta < 0$ mV migrate towards the anode

➢ **Anodic EPD**

Applications: dielectric coatings, paints, nanocomposite materials, separation of colloids (by size or chemical nature)

Additive processes

Electrolytic deposition	Electroless deposition	EC-induced precipitation	Electrophoretic deposition

Forced migration and desolvation of charged particles (colloïds) in an electric field.

Charged particles dispersed in an electrolyte (low ionic conductivity)
Any material that can develop a surface charge (zeta-potential)

Electrophoretic vs electrolytic deposition

Property	**Electroplating**	**Electrophoretic deposition**
Moving species	Ions	Solid particles
Deposition mechanism	Charge transfer Electrocrystallization	Solvation sphere displacement Particle aggregation
Electrolyte conductivity	High	Low
Preferred solvent	Water	Organic solvents
Voltage	Few hundreds mV	Several tens V
Growth rate	< 50 µm/h	Hundreds of µm/h possible
Deposited materials	Only conductive materials	Any colloidal solid
Deposit morphology	Compact	Powder / need binding

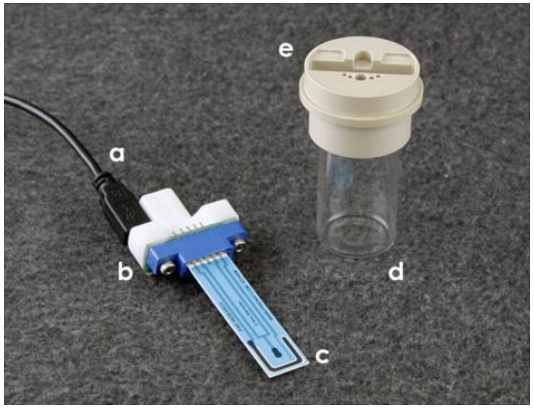
Applications: dielectric coatings, paints, nanocomposite materials, separation of colloids (by size or chemical nature)

Applications of electrodeposition (electroplating)

Functional coatings, bulk materials, microcomponents, nanostructures, nanocomposites, and metamaterials

Advantages:

- Versatility, ambient and near-ambient conditions
- Relatively cheap and simple
- Electrodeposits are conformal: possible to electroplate or electroform 3D parts
- Electrodeposition only occurs on conductive surfaces: masking process/localized ECD
- Possible to electrodeposit alloys and solid solution in a single step
- Possible to electroplate complex materials (multilayers, nanocomposites…)
- Easy to scale-up

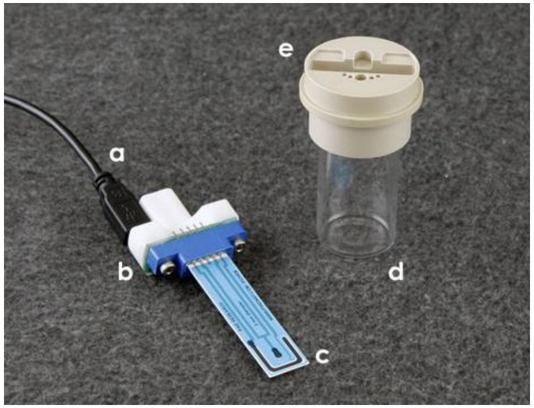


Applications of electrodeposition (electroplating)

Functional coatings, bulk materials, microcomponents, nanostructures, nanocomposites, and metamaterials

Drawbacks:

- Limited to conductive substrates
- Sometime complex to get the desired coating properties
  - Electrolyte formulation
  - Physical parameters optimization
- Chemical wastes might be hazardous
- Medium growth rate (rarely more than several µm/h)



Applications of electrodeposition (electroplating)

Functional coatings, bulk materials, microcomponents, nanostructures, nanocomposites, and metamaterials

Materials selection:

- Mechanical and tribological properties *(e.g., hardness, wear resistance, friction)*
- Corrosion protection
- Optical properties (reflectivity, colors (intrinsic, structural), metamaterials)
- Electrical properties (semiconductors, electronic boards, MEMS)
- Magnetic properties (diamagnetic, paramagnetic (…) gigantic magnetoresistance,)
- (Photo-)(electro-)catalysts
- Thermoelectric materials

Select the material for your application
→ can it be electrodeposited?