Electrochemistry

CHE 3053

Applications of Special Interests

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Hydrogen evolution: importance

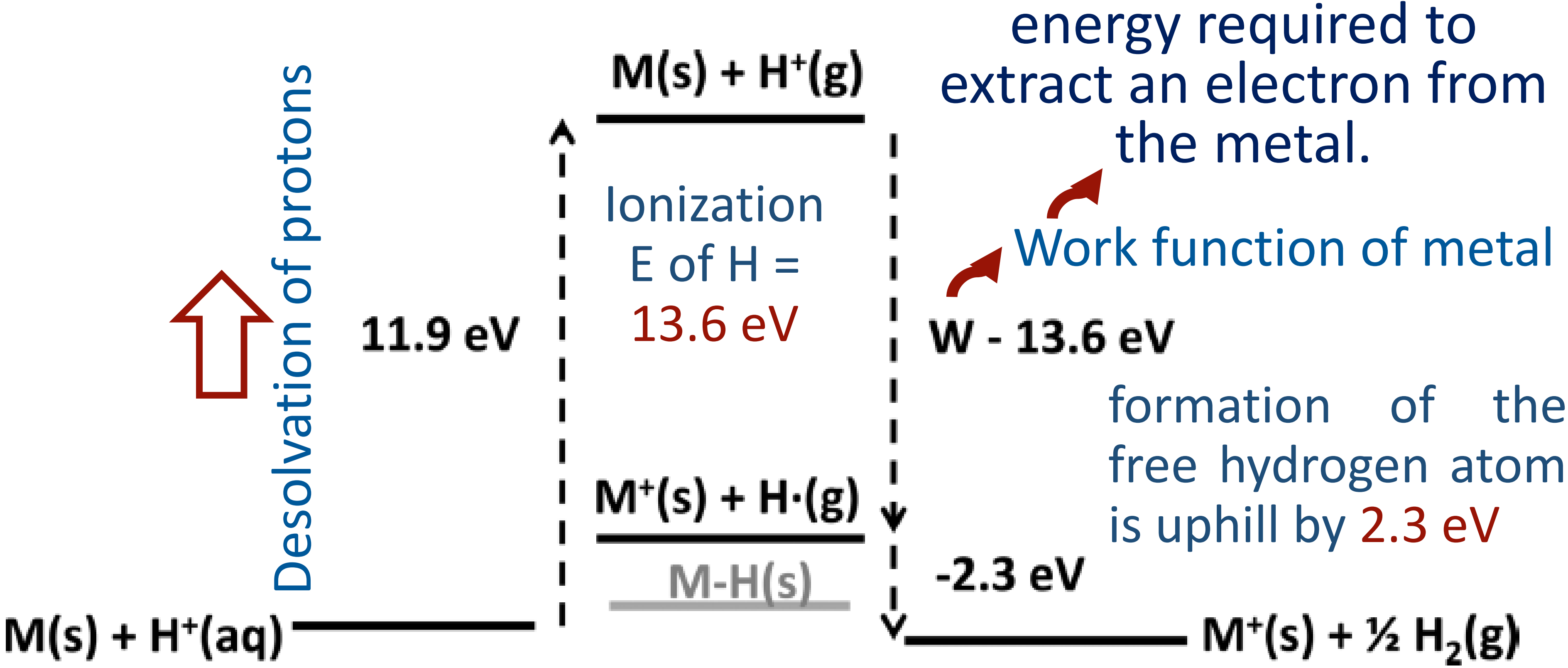
- **interferes** with the electrodeposition of metals.
- **represents** the electrochemical method of mass production of H_2.
- **represents** the main cathodic reaction in corrosion of metals in acid media.

Acid media ⇒ $$2H_3O^+ + 2e^- \rightleftharpoons H_2 + 2H_2O$$

H_2/O_2 Fuel

Alkaline/neutral media ⇒

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

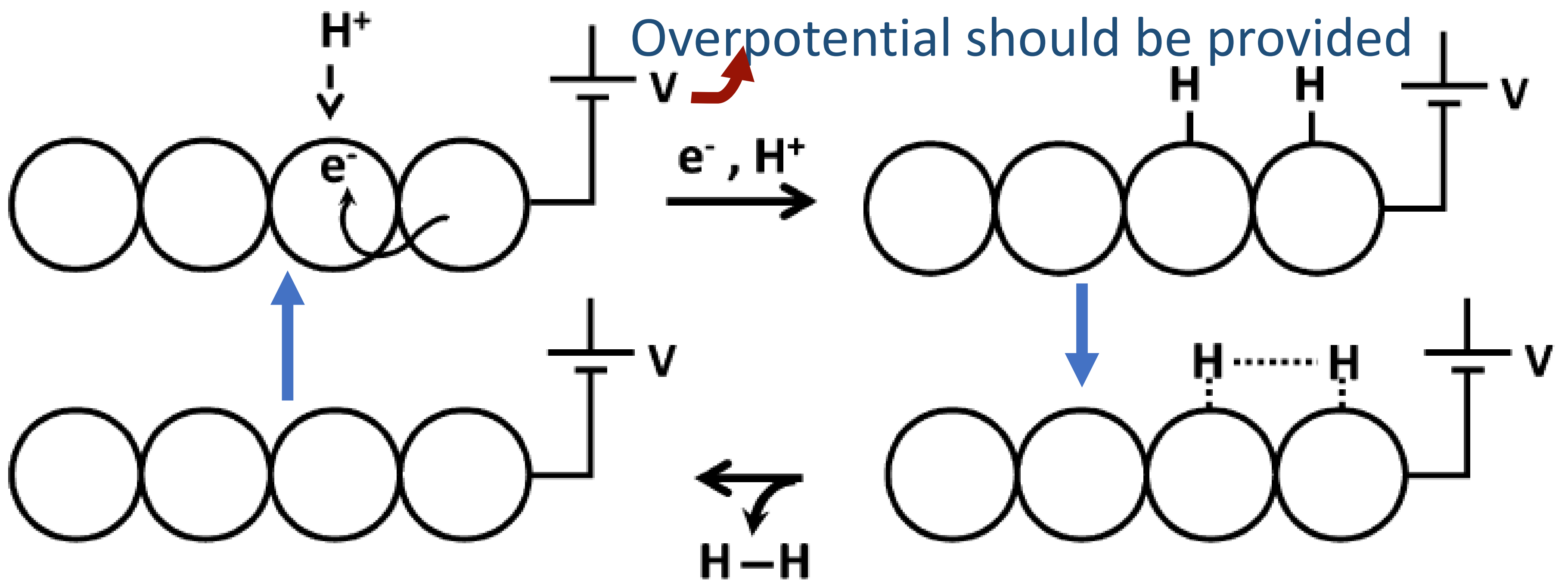


- Overall reaction is nevertheless feasible because H–H bond formation ultimately releases that much energy per atom of hydrogen.
- The kinetic barrier to reaction is prohibitively high for a pathway that involves the generation of the high energy H· intermediate.

http://dx.doi.org/10.1021/acs.jchemed.5b00189

Hydrogen evolution: Plausible mechanism

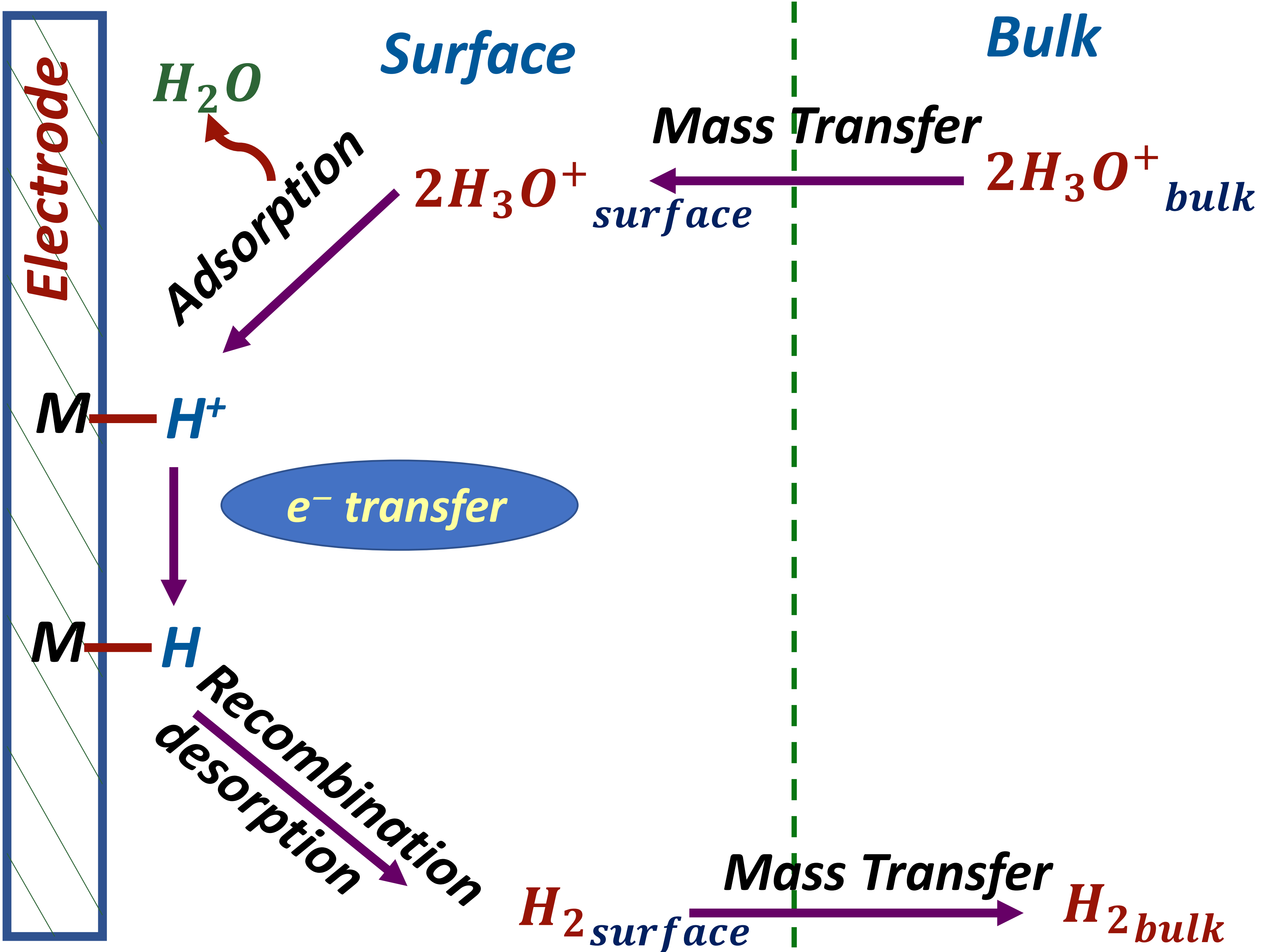
- Formation of M−H bond and avoiding formation of H·
- Each hydrogen atom could bind by bridging between two or more metal atoms on the surface.
- The electrode stabilizes "H atoms" by forming M−H bonds, paving the way to the formation of molecular hydrogen.



Hydrogen overpotential, η_{H_2}

- η is the potential required over that dictated by thermodynamics to induce a reaction to occur at a practicable rate.
- η_{H_2} is a special type of overpotential associating the H_2 evolution. The following parameters influence its value:

- ✓ The current density
- ✓ Temperature,
- ✓ Surface condition,
- ✓ H_2 pressure
- ✓ Type of metal cathode
- ✓ H^+ ion activity
- ✓ Surface impurities


Surface
Bulk
Electrode
H_2O
Adsorption
Mass Transfer
$2H_3O^+_{surface}$
$2H_3O^+_{bulk}$
M
H^+
e^- transfer
M
H
Recombination
desorption
Mass Transfer
$H_{2\,surface}$
$H_{2\,bulk}$

Hydrogen evolution

- Studies showed that the Rx is not controlled by mass transfer.
- Vigorous stirring has a limited effect on η_{H_2}.
- η_{H_2} depends on the nature of metal cathode.
- Activation enthalpy of η_{H_2} is close to typical activation overpotentials ($40 - 80$ kJ/mol) not to typical diffusion processes (≈ 20 kJ/mol).

Hydrogen evolution is a charge transfer-limited process

Hydrogen evolution mechanism

A) Volmer's/Tafel mechanisms

Very low surface coverage of H_2 $\theta_{H_2} \rightarrow 0$

Step I: Electron transfer concurrently with adsorption

➡ Volmer's mechanism if this step is limited

$$2H_3O^+ + 2M(e^-) \Rightarrow 2MH_{ads} + 2H_2O$$ acidic

$$2H_2O + 2M(e^-) \Rightarrow 2MH_{ads} + 2OH^-$$ Alkaline/ neutral

Step II: Chemical desorption $2MH_{ads} \rightarrow H_2 + 2M$

➡ Tafel's mechanism if this step is limited

B) Heyrovsky's mechanisms

High surface coverage of H_2 $\theta_{H_2} \rightarrow 1$

Step III: Electron transfer occurs on the adsorbed hydrogen atoms $\mathrm{MH_{ads}}$ in an electrodic desorption step (Heyrovsky's mechanism)

Heyrovsky's **mechanism** if this step is limited≡ RDS

$$H_3O^+ + MH_{ads} + e^- \Rightarrow H_2 + M + H_2O$$

Acidic

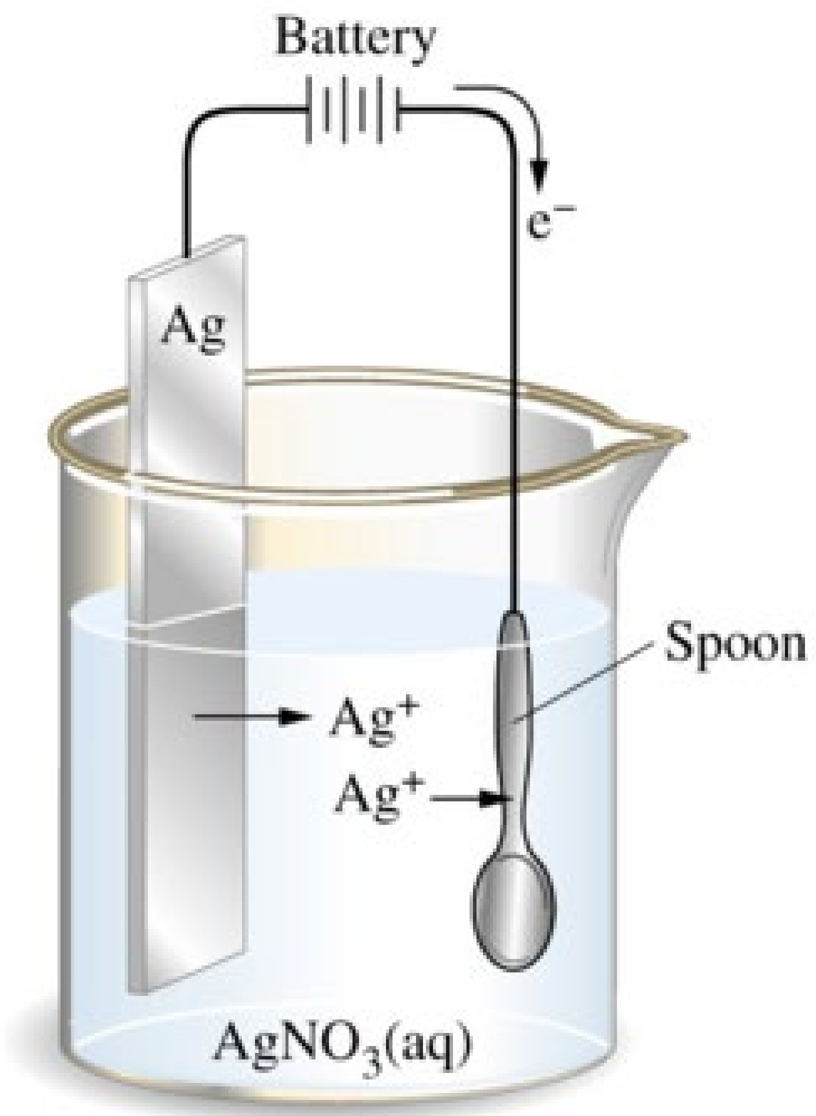
$$H_2O + MH_{ads} + e^- \Rightarrow H_2 + M + OH^-$$

Alkaline/ neutral

Metal	Log (i_0 / A cm^{-2}) 1M H_2SO_4	Mechanism
Platinum, Rhodium, Palladium	3.1 3.6 3.0	Fast electron transfer (I), Slow chemical desorption (II) Tafel's mechanism
Thallium, Lead, Mercury, Cadmium	11.0 12.0 12.3 10.8	Slow electron transfer (I), Fast electrodic desorption (III) Volmer's mechanism
Nickel	5.2	Fast electron transfer (I), Slow electrodic desorption (III) Heyrovesky's mechanism
Tungsten	5.9	Fast electron transfer (I), Slow electrodic desorption(III) at $\theta_{H_2} \rightarrow 1$ Heyrovesky's mechanism Slow electron transfer (I) Slow electrodic desorption (III)at $\theta_{H_2} \rightarrow 0$

Electroplating/Electrodeposition

- Cathodic deposition of metals is a principal method of extraction of active metals such as potassium, sodium, aluminum.
- A constant direct current is used as the source of electricity.
- When a thin layer of a metal as Au and Ag is electrodeposited on another metal, the process is called electroplating.



Crystallization (phase), overpotential, η_{Cryst}

- is a special type of overpotential associating electroplating.
- Assuming the typical crystalline nature of all metals, η_{Cryst} will represent the extra energy required to incorporate (via surface diffusion) the deposited metallic atom in a proper site in the crystal lattice of the metal.

Metals are expected to be deposited at more negative potentials than their reversible potentials !!!!!!!

Crystallization involves

- crystal nucleation
- crystal growth

- The mechanical stability and appearance of the electrodeposit depend on the relative rates of these steps during crystallization.
- The deposition current density, the composition of the deposition bath and temperature can influence/control the rate of both processes.

Good deposit

- Compact (non porous)
- Smooth
- bright
- Strong adherence

Fine-grained (smooth)/coarse (rough) deposits

- When the rate of crystal nucleation is faster than the rate of crystal growth, the deposition occurs in a layer by layer style with the formation of fine grained crystals, and consequently smooth surfaces are obtained.

- When the rate of crystal nucleation is slower than the rate of crystal growth: the formation of coarse large crystals is favored, and consequently rough surfaces are obtained .

Factors affecting electroplating

- Current Density.
- Bath (solution) composition
- Temperature.

Current density

- **Economically**, high current densities are preferred to save time. However, this will, in turn, increase the ohmic (IR) drop to
  - rise the temperature of the deposition bath (heating effect)
  - induct energy losses

Current density and deposit's structure

- **At low current densities,**
- the rate of crystal growth > Rate of nucleation

➡ **Coarsely crystalline deposits**

- **At high current densities,**
- the rate of crystal growth < Rate of nucleation

➡ **Fine grained crystals**

- **At very high current densities,**
- Depletion of metal cations in vicinity of cathode

➡ **Very rough deposits** (trees, nodules العقيدات , and protruding بروزات crystals)

At current densities > Limiting current density

- Maximum mass transfer current of deposition.
- Hydrogen evolves as bubbles concurrently with the metal deposition.
- Porous spongy deposits.
- Solution in the vicinity of the cathode becomes alkaline.
- Some oxides or basic salts of the metal cation may be precipitated and incorporated in the deposit to yield a dark fine grained deposit.

Bath (solution) composition

- The properties (morphology) of the deposit depend on the nature & concentration of metal salt & additives.

A) Anion Type

Lead nitrate → rough lead deposits

lead silicofluoride → smooth lead deposits

Lead borofluoride → smooth lead deposits

B) Valence of the metal

Stannate (Sn^{4+}) → **Smooth deposits**

Stannite (Sn^{2+}) → Poor quality deposits

Plumbous (Pb^{+}) → Large crystals

Plumbic (Pb^{2+}) → Spongy deposits

C) Using metal complex ions

KAu(CN), $K_3Au(SO_3)_2$

- ¥ Always produce smooth deposits
- ¥ Cyanide baths are typical.
- ¥ Metal complexes with low coordination number (electron deficient) are bonded to the cathode & their bonds are replaced by metallic bonds with controlled inclusion of the deposited metal in the crystal lattice.

→ **smooth deposits**

D) Metal ions concentration

- ¥ The highest possible concentration of the metal salt is usually used to save time and to inspire:

  - Rate of nucleation > Rate of crystal growth since there are too many cations capable to start nucleation.

  - Crystals grow in two dimensions on the surface faster than grow perpendicularly.

➡ **Firm and Adherent deposits**

E) Additives (Brighteners)

- ¥ Surface active substances added in minute amounts to give a pronounced improvement (smoothening) in the morphology of the deposits.
- ¥ Specific for metal type and bath composition
- ¥ Examples: gelatin, casein, glues, gums, dyestuffs, alkaloids and sugars.

How it works ➡ **smooth deposits**

Get adsorbed on the crystal nuclei to inhibit a further crystal growth

F) Temperature

It has to be optimized to avoid the deterioration of deposits’ quality at high temperatures.

Temperature has two opposite effects

- Facilitation of diffusion of metal cations (inhibition of formation of coarse and spongy deposits at high current densities.
- Increasing the crystal growth rate which favors the formation of coarse crystals.
- Rising the rate of hydrogen evolution and hence the formation of spongy deposits and precipitation of basic salts in the deposits.

Simultaneous deposition of metals

Alloy deposition

- A metal is deposited if the equilibrium potential E_{rev} is shifted to a more negative potential.
- At a certain current density, E_{dep} is given by

$$E_{dep} = E_{rev} + \eta_{dep}$$

Deposition Overpotential

However

$$E_{rev} = E^0_{M^{n+}/M} + \frac{2.303RT}{nF}\log(a_{M^{n+}})$$

Standard electrode potential

Activity

$$E_{dep} = E^0_{M^{n+}/M} + \frac{2.303RT}{nF}\log(a_{M^{n+}}) + \eta_{dep}$$

At low current densities, $\eta_{dep} \rightarrow 0$ ➡ $E_{dep} \approx E_{rev}$

- In presence of more than one metal cation, the one having the most positive (least negative) E_{rev} should be deposited first. Note that η_{dep} is negative and potential is supposed to go from the +Ve to –Ve direction.
- Simultaneous deposition of metal cations is possible if their E_{rev} (function of $a_{M^{n+}}$)are made equal.

$$E_{rev,1} = E_{rev,2}$$

$$E^0_{M_1^{n+}/M_1} + \frac{2.303RT}{nF}\log\left(a_{M_1^{n+}}\right) = E^0_{M_2^{m+}/M_2} + \frac{2.303RT}{mF}\log\left(a_{M_2^{m+}}\right)$$

Example

- ¥ An alloy (Brass) of Cu ($E^0_{Cu^{2+}/Cu} = 0.34$ V) and Zn ($E^0_{Zn^{2+}/Zn} = -0.77$ V) is desired from a solution containing 0.1 M Zn^{2+}. Calculate the required concentration of Cu^{2+} to start a simultaneous deposition at the reversible potentials at 25 °C?

Solution

$$E^0_{Cu^{2+}/Cu} + \frac{2.303 \times 8.314 \times 298}{2 \times 96500} \log(a_{Cu^{2+}}) =$$

$$E^0_{Zn^{2+}/Zn} + \frac{2.303 \times 8.314 \times 298}{2 \times 96500} \log(a_{Zn^{2+}})$$

$$0.34\,V + 0.0295\log(a_{Cu^{2+}}) = -0.77\,V + 0.0295\log(0.1)$$

$$log(a_{Cu^{2+}}) = -50.15$$

$$a_{Cu^{2+}} = 7 \times 10^{-51}\ g.ion/L$$

¥ The extremely low value of $a_{Cu^{2+}}$ is impractical to obtain an alloy of Cu and Zn. In practice the problem is solved by considering the complex formation via adding excess CN^- ions to a suitable Zn^{2+} and Cu^{2+} mixture:

$$Cu^{2+} + 4CN^- \rightleftharpoons [Cu(CN)_4]^{2-}$$

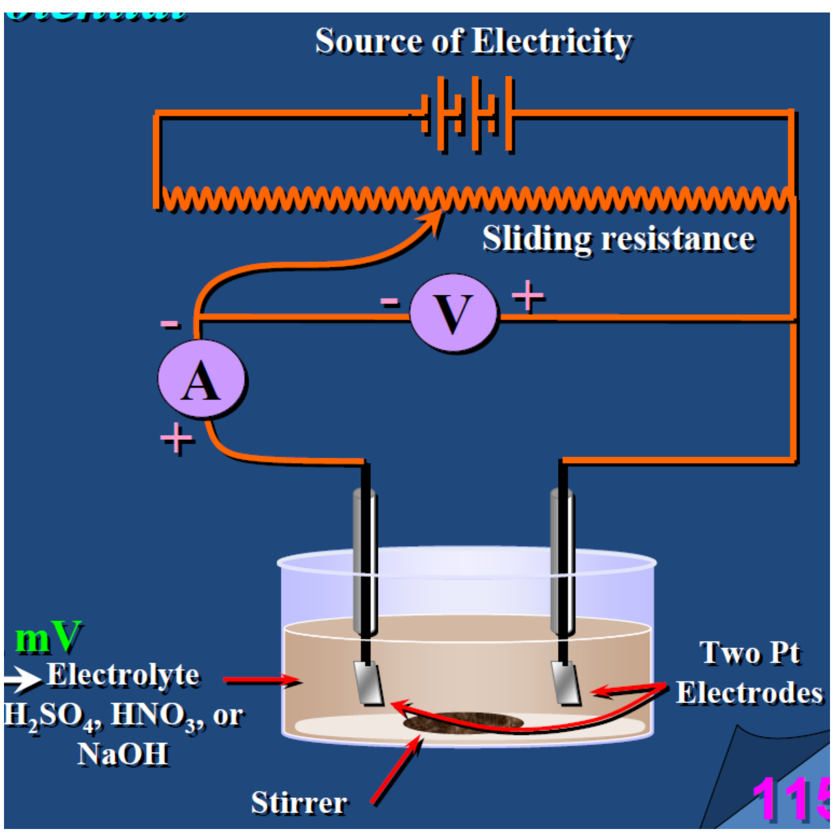
$$Zn^{2+} + 6CN^- \rightleftharpoons [Zn(CN)_6]^{4-}$$

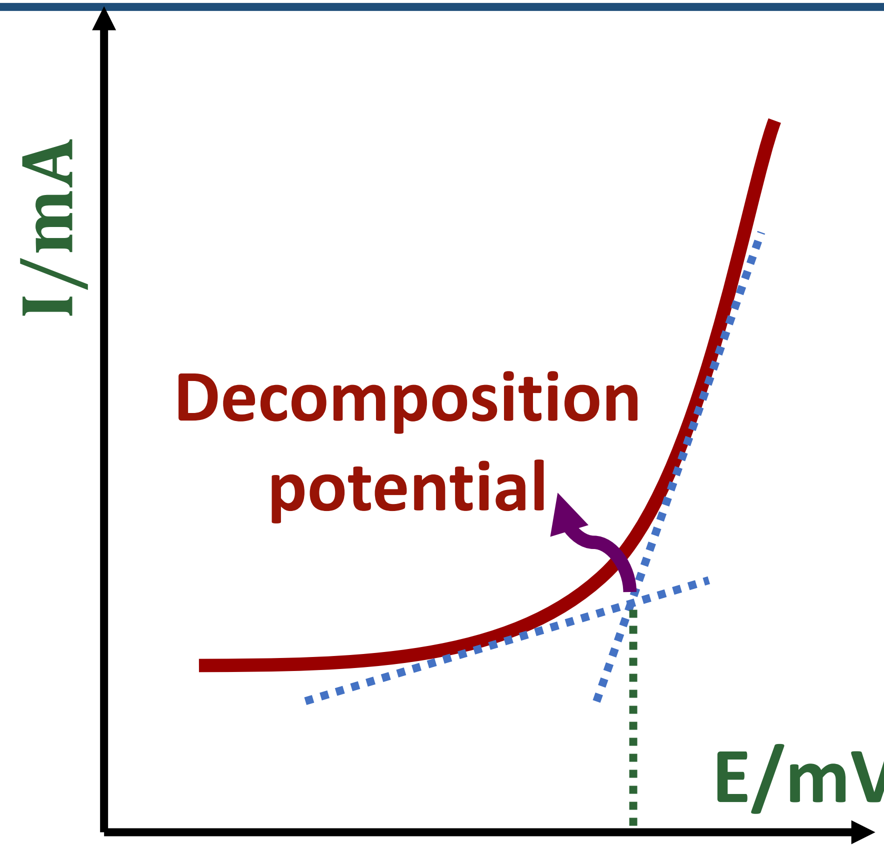
The large Stabilities of the resulting complex ions make it possible to simultaneously deposit Cu and Zn in reasonable proportions at sufficiently larger negative potentials than $E^0_{Zn^{2+}/Zn}$ (≈ -1.1 V)

Electrolysis

Decomposition Potential

- The minimum applied voltage required to start and to maintain continuous electrolysis in an electrolyte.





$$D_i = D_0 + \eta$$

$$D_0 = E_{cathode} - E_{anode}$$

$$\eta = \eta_{cathode} + \eta_{anoode} + \mathrm{IR}$$

D_i: is the irreversible decomposition potential

D_0: is the reversible decomposition potential

η: is the decomposition overpotential needed to start and maintain the process. It represents the total overvoltage at the anode, cathode and also the ohmic potential drop.

$E_{cathode}$: is the reversible potential of the cathode

E_{anode}: is the reversible potential of the anode.

Decomposition Potential, DP

- The DP of dilute solutions of acids, e.g., H_2SO_4 , HNO_3 , H_3PO_4 , ... (except halogen acids) or bases, e.g., NaOH, KOH, . . ., etc is approximately equal to 1.7 V.

- This is because the electrolysis products of these solutions are always the same: cathodic evolution of H_2 and anodic evolution of O_2.

$$2H_2O_{sol} \rightarrow 2H_{2_{gas}} + O_{2_{gas}}$$

Decomposition Potential, DP

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$$2H_2O_{sol} \rightarrow 2H_{2_{gas}} + O_{2_{gas}}$$

DP of halogen acids

- The DP of dilute halogen acids is typically less than 1.7 V.

$$2HCl_{sol} \rightarrow H_{2_{gas}} + Cl_{2_{gas}}$$

- This is because The electrolysis products of these solutions are: cathodic evolution of H_2 and anodic evolution of Cl_2.

- Although Cl_2 evolution is thermodynamically less favorable than O_2 evolution, it is much kinetically easier, i.e., needs less η to evolve.

$$Cl_2 + 2e^- \rightarrow 2Cl^- \qquad E^0 = 1.36\,V$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E^0 = 1.23\,V$$

DP of metal salts

- Metal salts having M^{n+}/M reversible potentials less negative than that of hydrogen (such as $CuSO_4$, $AgNO_3$) show: $D_i \neq 1.7V$ due to the metal deposition is the main cathodic process.

DP of neutral solutions

- In unstirred sulphates, nitrates, . . . , solutions $D_i > 1.7V$ due to the non-buffering action (increasing the pH in the vicinity of the cathode and decreasing the pH in the vicinity of the anode relative to the bulk solution's pH) which increases the concentration overpotential.

Cathode

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

Basic

Neutral Bulk

Anode

$$2H_2O \rightarrow O_2 \uparrow + 4H^+ + 4e^-$$

acidic

$$D_0 = E_{oxygen} - E_{hydrogen}$$

$$D_0 = \left(E^0_{oxygen} - 0.059\,pH_{cathode}\right) - \left(E^0_{hydrogen} - 0.059\,pH_{anode}\right)$$

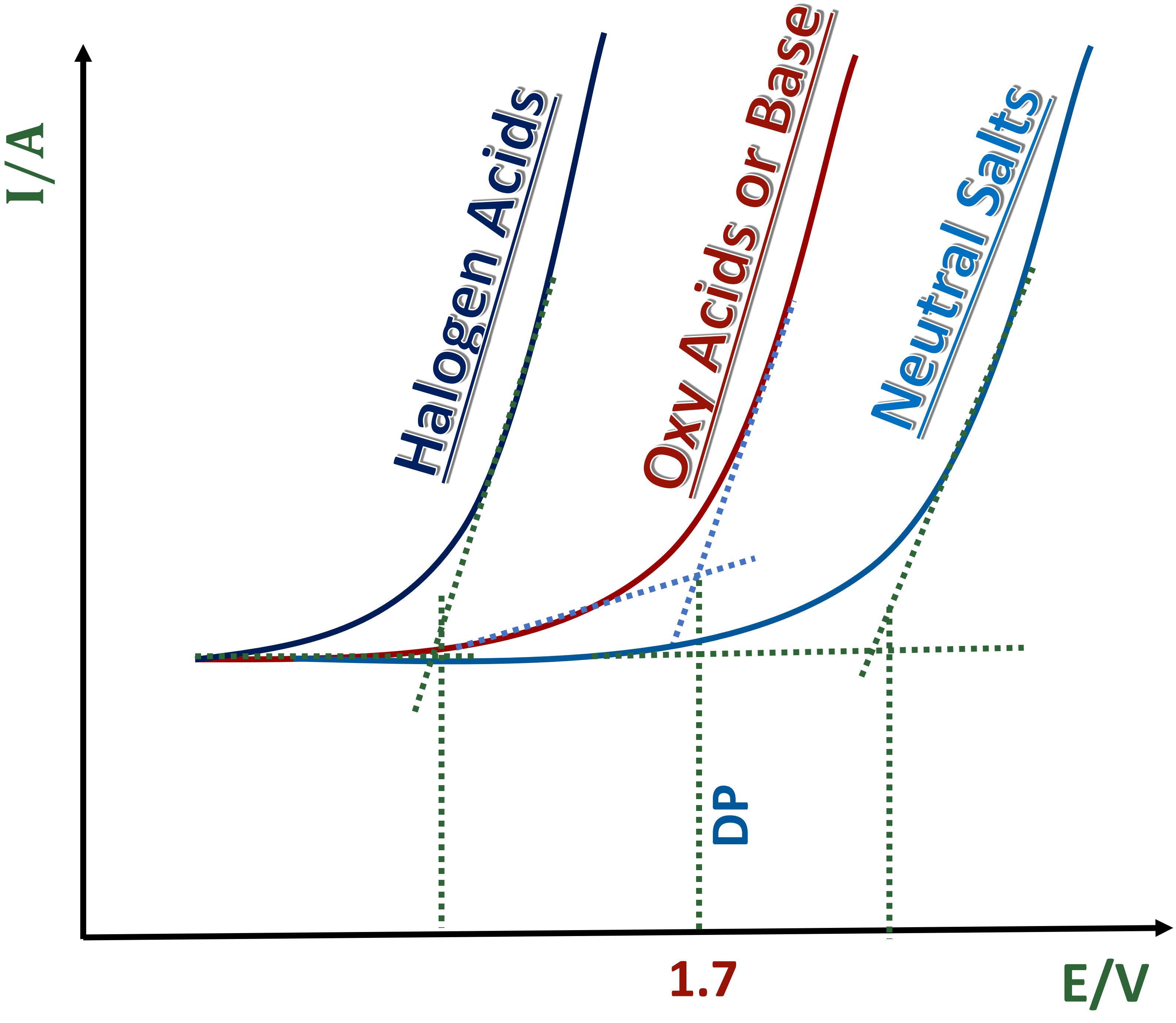
$$E^0_{oxygen} - E^0_{hydrogen} = 1.23\text{ V}$$

Buffered solutions: pH is same at the cathode and anode

$$D_0 = 1.23 - 0.059\,pH_{cathode} + 0.059\,pH_{anode} = 1.23\,V$$

Non-buffered solutions: pH is different at the cathode and anode. Eg., pH= 10 at the cathode and pH=3 at the anode

$$D_0 = 1.23 - 0.059\,pH_{cathode} + 0.059\,pH_{anode} = 1.23 - 0.059(10) + 0.059(3) \neq 1.23$$


I/A
Halogen Acids
Oxy Acids or Base
Neutral Salts
DP
1.7
E/V


Corrosive damage in materials - 2
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Corrosion


Corrosive damage in materials
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Corrosion

- is a natural decay (dissolution) of metals and alloys due to the reaction with environment (air, water, and soils).
- involves oxidation of metals and can be viewed as the process of returning metals to their natural state—the ores from which they were originally obtained.
- Metals (except gold) which are commonly used for structural and decorative purposes all have standard reduction potentials less positive (more negative) than that of oxygen gas.

- When any of these half-reactions is reversed (to show oxidation of the metal) and combined with the reduction half-reaction for oxygen, the result is a positive E^0 (spontaneous process).

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E^0_{red} = 1.23\ V$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad E^0_{red} = 0.68\ V$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad E^0_{red} = 0.40\ V$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad E^0_{red} = 0.00\ V$$

$$Fe^{3+} + 3e^- \rightarrow Fe \qquad E^0_{red} = -0.036\ V$$

$$Fe^{2+} + 2e^- \rightarrow Fe \qquad E^0_{red} = -0.44\ V$$

$$Cr^{3+} + 3e^- \rightarrow Cr \qquad E^0_{red} = -0.73\ V$$

$$Zn^{2+} + 2e^- \rightarrow Zn \qquad E^0_{red} = -0.76\ V$$

$$Al^{3+} + 3e^- \rightarrow Al \qquad E^0_{red} = -1.66\ V$$

- Thus the oxidation of most metals by oxygen is spontaneous (although we cannot tell from the potential how fast it will occur).
- Since corroded metal often loses its structural integrity and attractiveness, this spontaneous process has great economic impact (the annual global cost of corrosion is $2.5 trillion, equivalent to roughly 3.4% of the world's gross domestic product).
- Approximately one-fifth of the iron and steel produced annually is used to replace rusted metal.

Corrosion is an electrochemical process

- **Anode** $Fe \rightarrow Fe^{2+} + 2e^-$ $E^0_{oxid.} = 0.44\,V$
- **Wiring** (electronic conduction

  e^- that are released from the anodic region flow through anode (steel), as they do through the wire of a galvanic cell, to a cathodic region, where they react with oxygen

- **Cathode**

  $2H^+ + 2e^- \rightarrow H_2$ $E^0_{red} = 0.00\,V$

  $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $E^0_{red} = 1.23\,V$

- **Salt bridge** (ionic conduction): Moisture

Spontaneous Corrosion

- The equilibrium electrode potential of the M/M^{n+} is negative to the equilibrium potential of the reducible species (H^+, O_2).

- Active metals as Mg, Zn, and Fe corrode with the H_2 evolution and O_2 reduction.

- Noble metals as Cu and Ag corrode with O_2 reduction only.

Does Corrosion prevent the use of metals in air ?

- Most metals (e.g., Al) develop a thin oxide coating, which tends to protect their internal atoms against further oxidation.

$$Al^{3+} + 3e^- \rightarrow Al \qquad\qquad E^0_{red} = -1.66\,V$$

- **Thermodynamically**, an aluminum airplane should dissolve in a rainstorm. !!!!!!!!
- Corrosion of Al leads to the formation of a thin, adherent layer of aluminum oxide (Al_2O_3), more properly represented as $Al_2(OH)_6$, which greatly inhibits further corrosion.
- The potential of the "passive," oxide–coated aluminum is –0.6 V, a value that causes it to behave much like a noble metal.

Iron also forms a protective oxide coating

- However, this coating is not a perfect shield against corrosion. When steel is exposed to oxygen in moist air, the oxide coat tends to scale off and expose new metal surfaces to corrosion.

Corrosion products of noble metals are complex

- This affects their use as decorative materials.
- Copper forms an external layer of greenish copper carbonate called patina.
- Silver tarnish is silver sulfide (Ag_2S), which in thin layers gives the silver surface a richer appearance.
- Gold, with a positive standard reduction potential of 1.50 V, significantly larger than that for oxygen (1.23 V), shows no appreciable corrosion in air.

Corrosion of iron

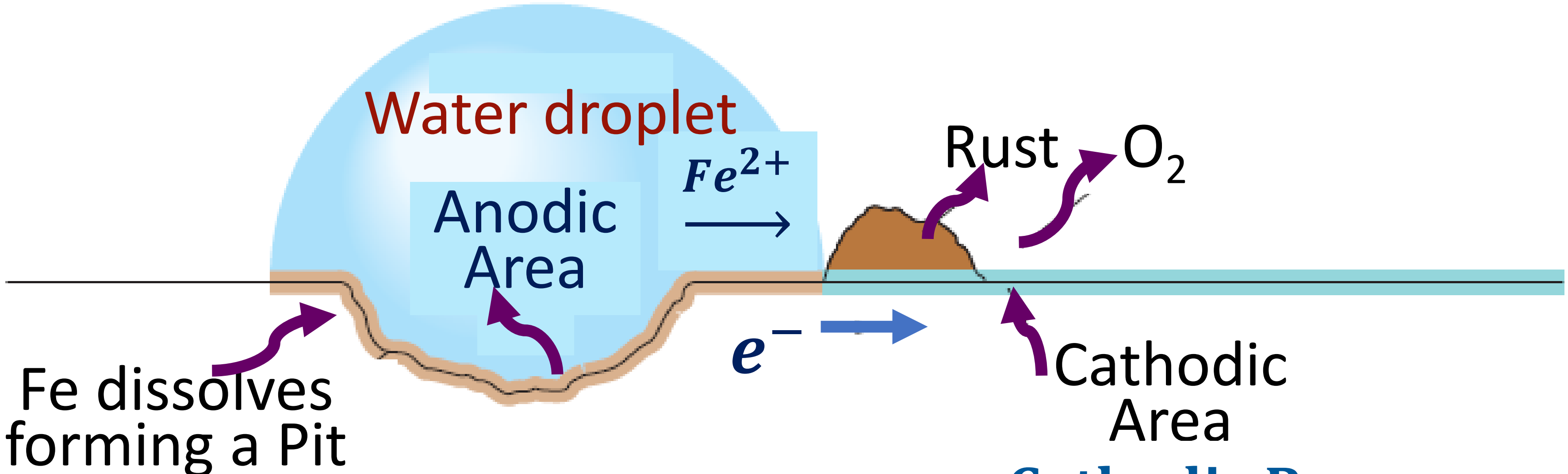
- Steel has a non-uniform surface because the chemical composition is not completely homogeneous. Also, physical strains leave stress points in the metal.
- These non-uniformities cause areas where the iron is more easily oxidized (anodic regions) than it is at others (cathodic regions).
- In the anodic regions each iron atom gives up two electrons to form the Fe^{2+} ion:

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad E^0_{oxid.} = 0.44\ V$$

- The electrons that are released flow through the steel, as they do through the wire of a galvanic cell, to a cathodic region, where they react with oxygen:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E^0_{red} = 1.23\ V$$

- The Fe^{2+} ions (from the anodic regions) travel to the cathodic regions through the moisture on the surface of the steel, just as ions travel through a salt bridge in a galvanic cell.
- In the cathodic regions Fe^{2+}, ions react with oxygen to form rust, which is hydrated iron(III) oxide of variable composition:



Cathodic Rx

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

Anodic Rx: $Fe \rightarrow Fe^{2+} + 2e^-$

Overall Rx

$$4Fe^{2+}(aq) + O_2(g) + (4+2n)H_2O(l) \rightarrow$$
$$2Fe_2O_3.nH_2O(s) + 8H^+\ (aq)$$

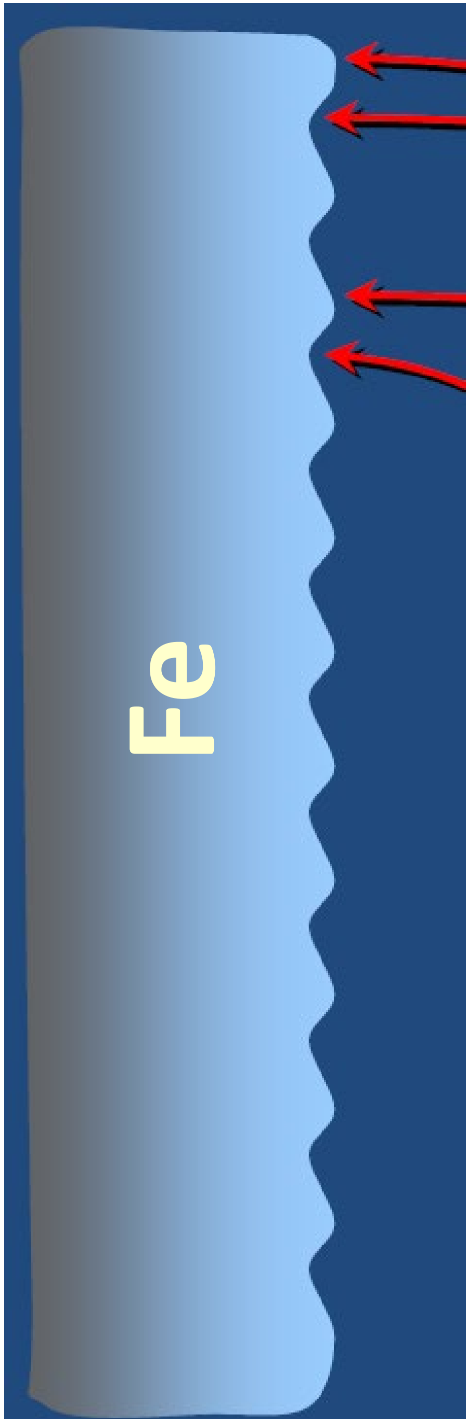
Rust

Rusting

- Because of the migration of ions and electrons, rust often forms at sites that are remote from those where the iron dissolved to form pits in the steel.
- The degree of hydration of the iron oxide affects the color of the rust, which may vary from black to yellow to the familiar reddish brown.
- The electrochemical nature of the rusting of iron explains the importance of moisture (acts as a salt bridge) in the corrosion process.
- Steel does not rust in dry air, a fact that explains why cars last much longer in the arid Southwest than in the relatively humid Midwest.

Salts accelerate Rusting

- a fact that is realized in snowing areas where salts are used on roads to melt snow and ice.
- The severity of rusting is greatly increased because the dissolved salt on the moist steel surface increases the conductivity of the aqueous solution formed there and thus accelerates the electrochemical corrosion process.
- Chloride ions also form very stable complex ions with Fe^{3+}, and this encourages the dissolution of iron; again accelerating the corrosion.



Local microelectrochemical cells

Cathodic Process – Low energetic (smooth, bottoms)

Anodic Process – High energetic (edges, tips, tops)

The distribution of anodic and cathodic areas on the surface depends on:

- ✓ the chemical composition,
- ✓ the roughness,
- ✓ the geometry of the surface.

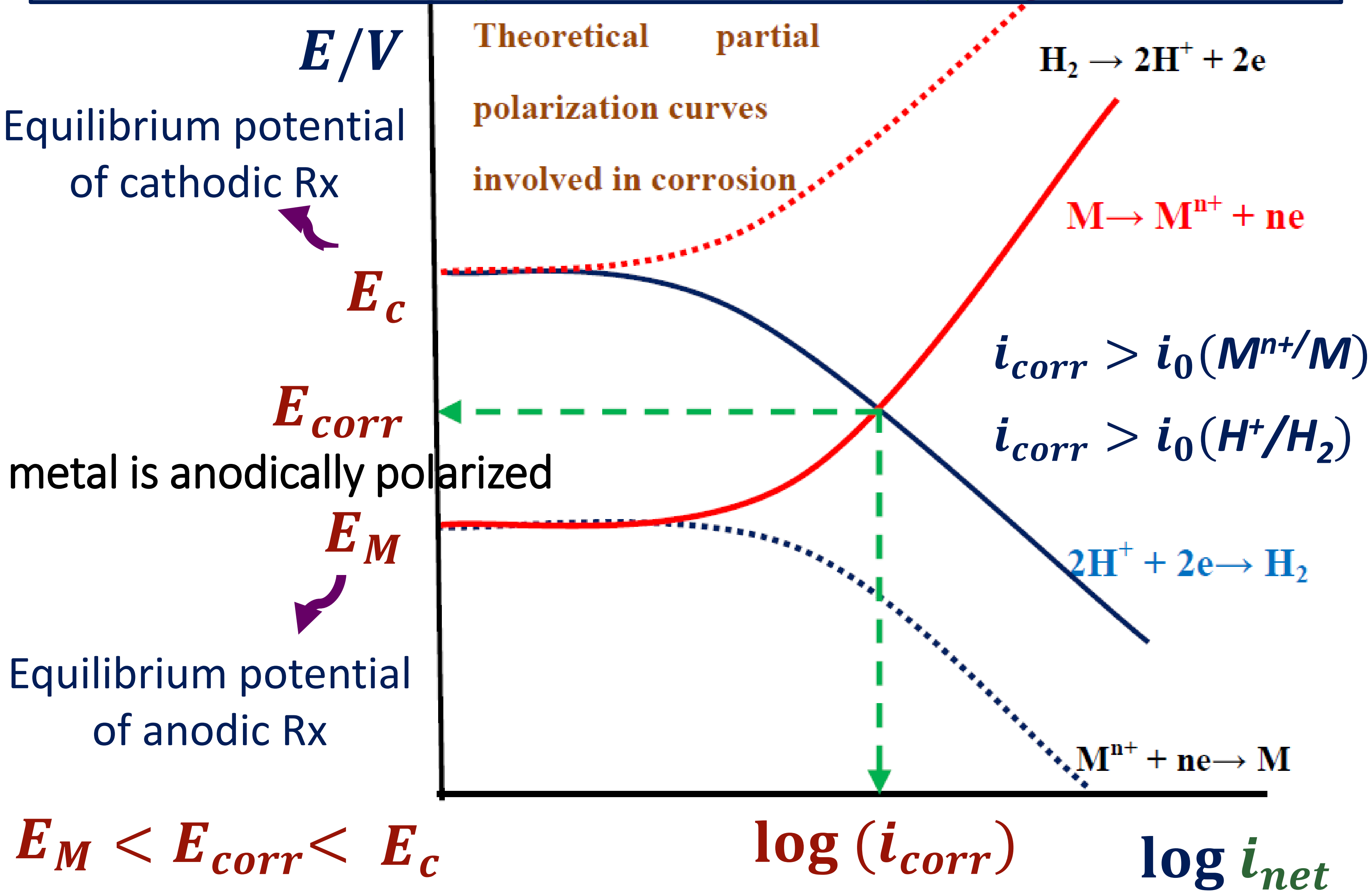
Corrosion rate is low for smooth ultrapure metals and is increased with the surface's roughness and heterogeneity

Polarization Curves

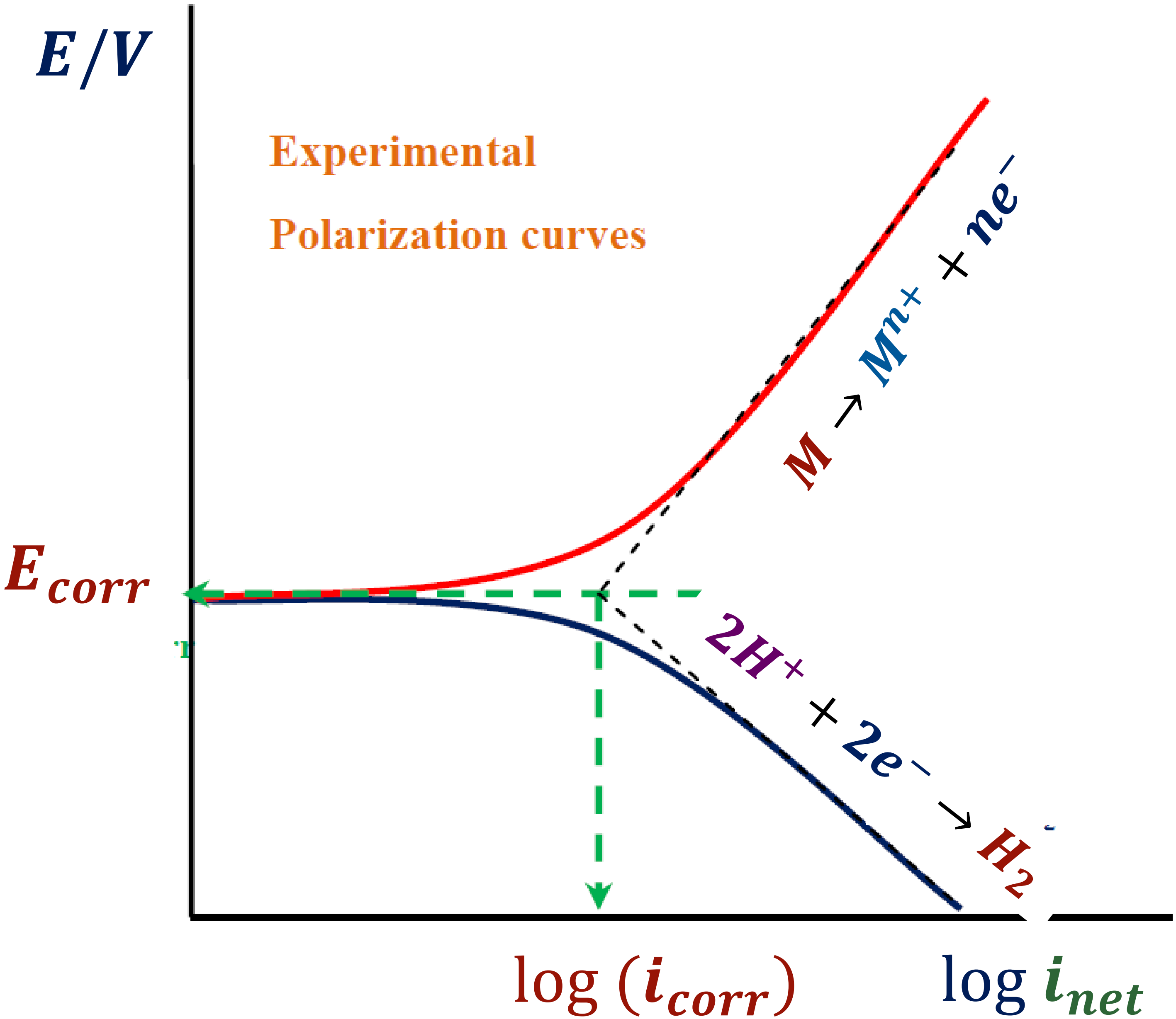
- Each of the electrochemical reactions involved in corrosion has its own partial theoretical polarization curves.

- The point of intersection of these polarization curves denotes the corrosion potential (E_{corr}: experimentally is the open circuit potential where $E_{\mathrm{I=0}}$).

$$\eta = \frac{-2.303\, RT \log i_0}{(1-\alpha)nF} + \frac{2.303\, RT}{(1-\alpha)nF}\log(i_{net})$$



Experimental polarization curves



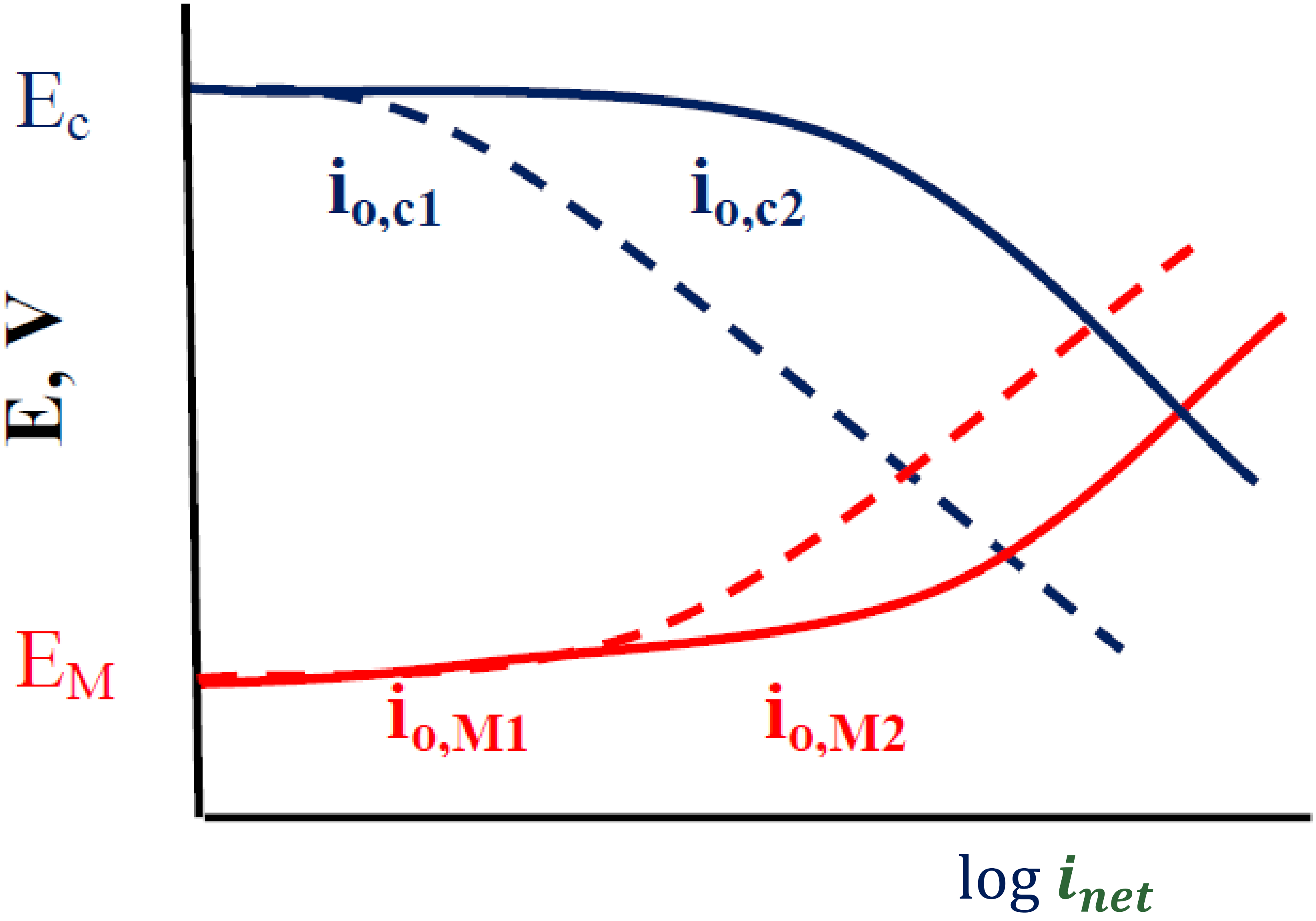
Parameters affecting E_{corr} and i_{corr}

Metal type

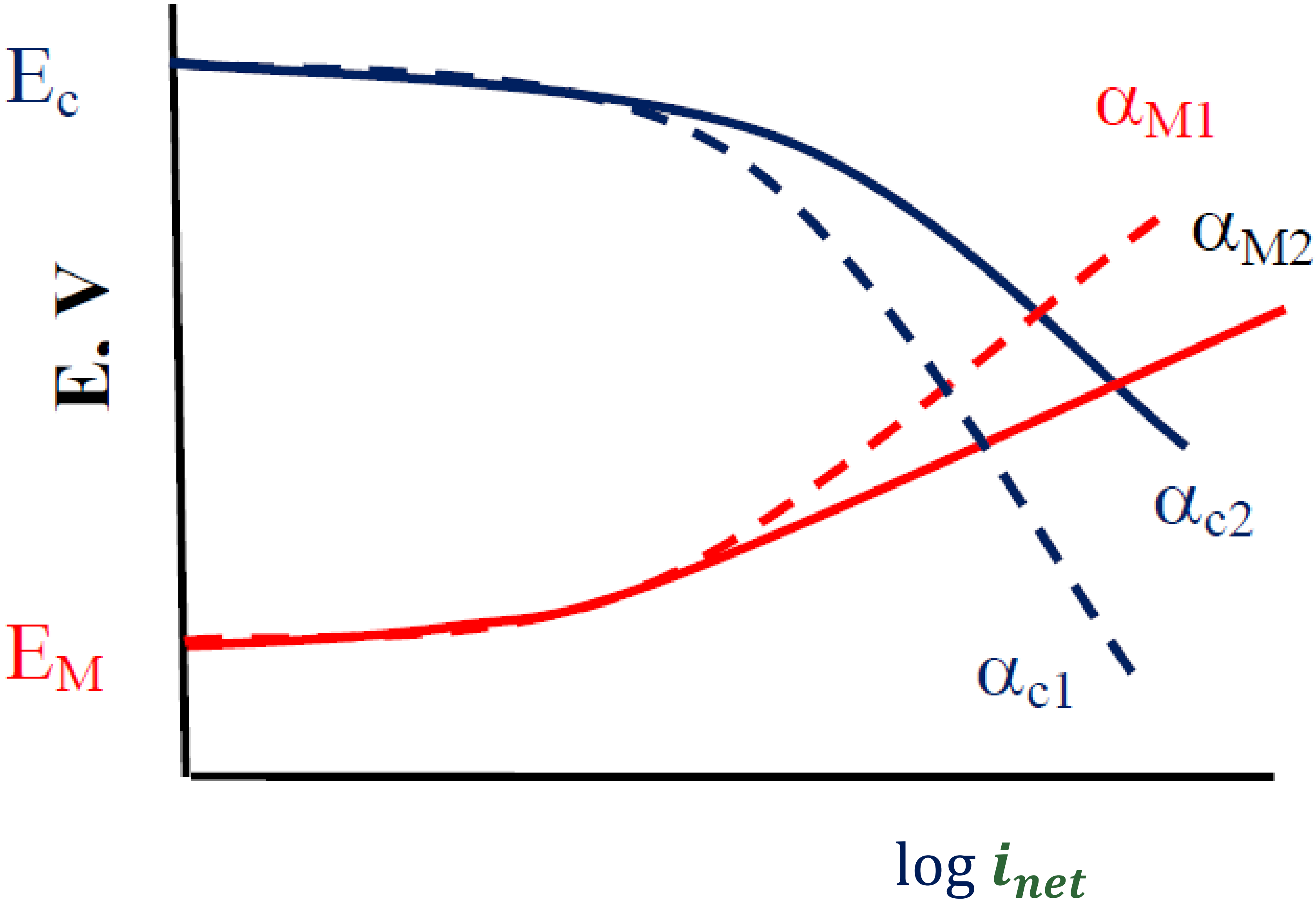
- is reflected in E_M, $i_0(M^{n+}/M)$ and the transfer coefficient α.

$$b = \text{Tafel slope} = \frac{2.303\,RT}{\alpha nF}$$

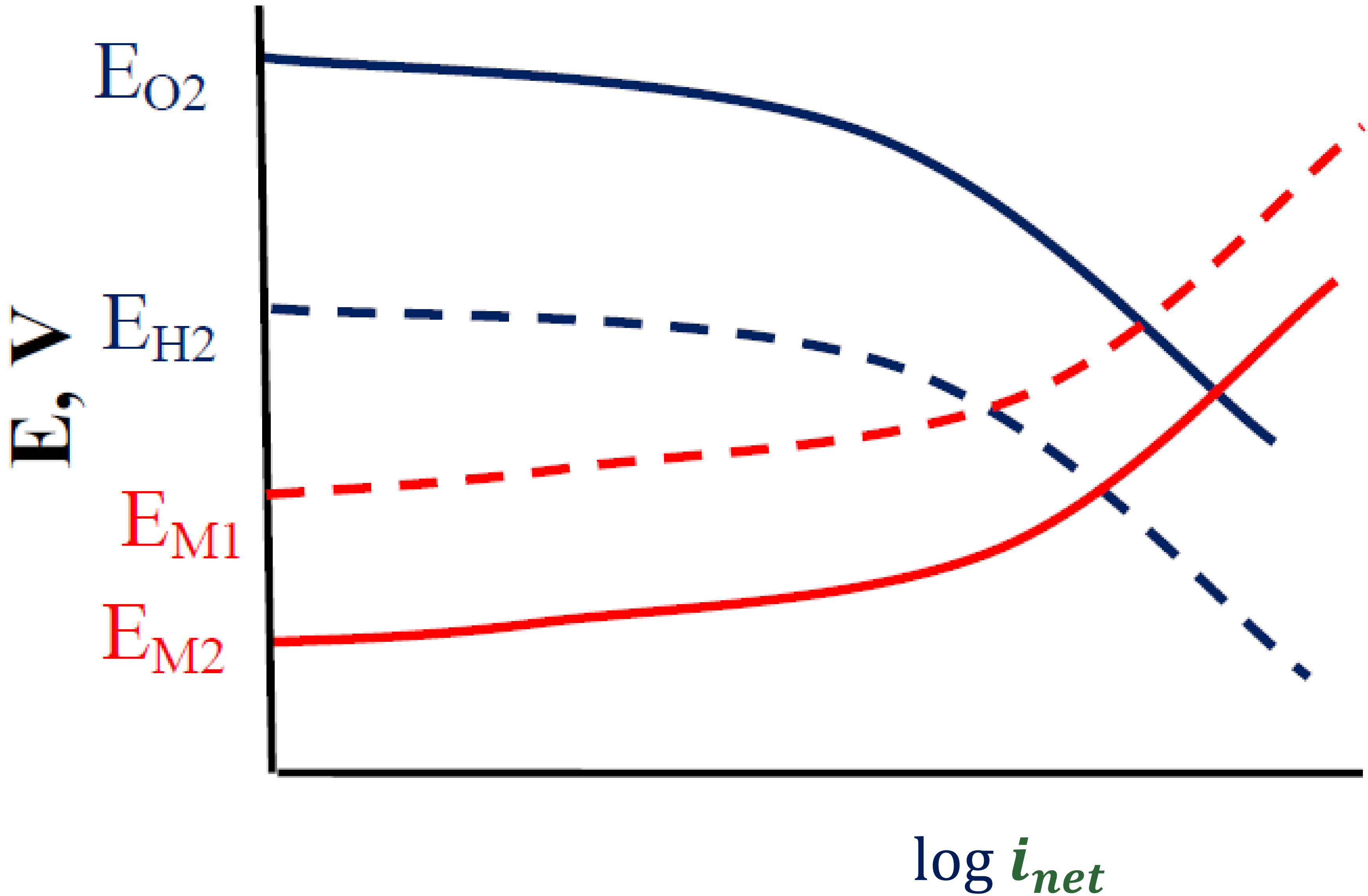
Effect of i_0



Effect of α



Effect of E_c and E_M

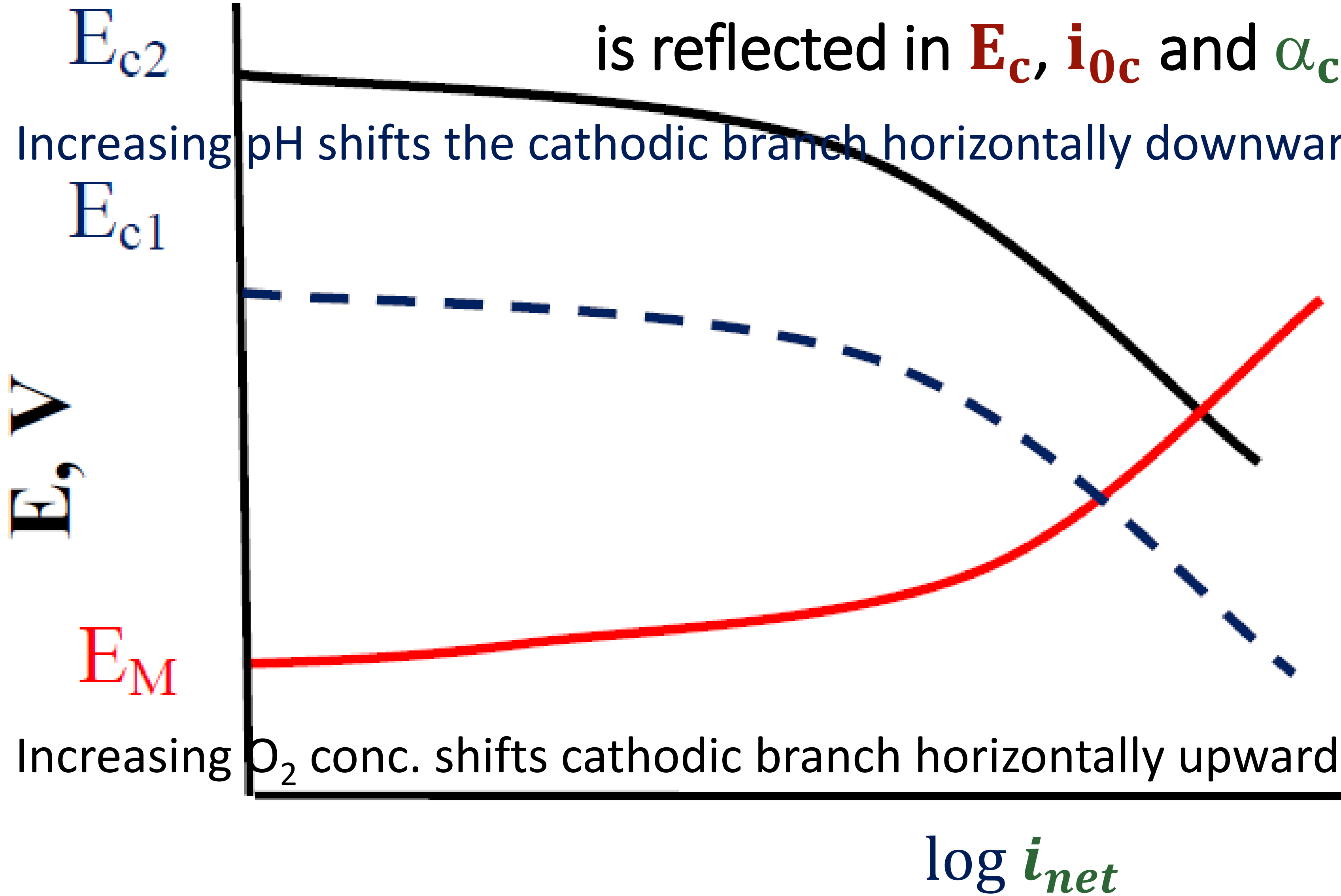


Effect of $[O_2]$ or $[H_+]$; $C_2 > C_1$

Reducible species type and concentration

is reflected in E_c, i_{0c} and α_c.

Increasing pH shifts the cathodic branch horizontally downward



Increasing O_2 conc. shifts cathodic branch horizontally upward.

Increase in	E_{corr}	i_{corr}
α_c	Decreases	Decreases
α_a	Increases	Decreases
E_M	Increases	Decreases
E_c	Increases	Increases
$i_0(M^{n+}/M)$	Increases	Increases
$i_0(reducible\ spec.)$	Increases	Increases
$[O_2]$	Increases	Increases
pH	Decreases	Decreases

Corrosion rate

- Assuming a uniform corrosion, the rate of corrosion can be expressed as the mass loss per unit surface area per unit time.
- **Technical corrosion unit.**
  - mdd (mg per decimeter square per day). The corrosion rate can be evaluated from the value of i_{corr}.
  - mmy the reduction in thickness (mm) per (year).

$$mmd = \frac{10^3 \times i_{corr}(A\,cm^{-2}) \times 10^2 \times 60 \times 60 \times 24 \times A_w}{nF}$$

$$mmy = \frac{10 \times i_{corr}(A\,cm^{-2}) \times 60 \times 60 \times 24 \times 365.5 \times A_w}{nFd\,(g\,cm^{-3})}$$

density

Atomic mass of metal

Forms of Corrosion

Uniform Corrosion

- A uniform attack and thinning of the metal pieces occurs. It is easy to predict, evaluate and avoid

Galvanic Corrosion

- Two dissimilar metals are connected. Such as Fe and Cu; the active metal (Fe) corrodes while reducible species is reduced on the surface of the nobler metal (Cu).

Anodic Rx: $Fe \rightarrow Fe^{2+} + 2e^{-}$

Cathodic Rx $2H^{+} + Cu + 2e^{-} \rightarrow H_2 + Cu$

Localized Corrosion

serious forms because they are difficult to predict and evaluate

- Occurs only on a small fraction of the metal surface area exposed to the medium.
- Heterogeneity of the metals and most alloys surfaces can promote localized corrosion.
- Examples:
  - Trans- and Inter-granular corrosion
  - Selective Dissolution.
  - Crevice and Pitting corrosion: in presence of aggressive anions, especially Cl^- ions.
  - Stress Corrosion Cracking (internal & external stress).
  - Erosion corrosion: Fast flow of medium

Corrosion Prevention

Design and installation

- Good planning and application help avoiding corrosion, such as, dissimilar junctions, stress corrosion, erosion, etc.

Coating

- **Metallic**: coating of a metal (Fe) with a more active one (Zn).
- **Isolating**: polymers as plastics or paints insolate the metal.
- **Mixed**: paints containing fine particles of active metal as Zn.

Inhibitors and Passivators

- Inhibitors are substances added in very small amounts to the environment to form a barrier layer on the corroding metal or to be adsorbed on the surface to isolate the metal from the corrosive attack.

- Passivators (chromate, carbonate) help promoting a passive layer (mostly oxide) on the metal surface.

- Substance, such as, hydrazines or sulphites remove O_2 from the medium and thus reduce the corrosion rate.

Cathodic Protection

- Either sacrificial anodes (like Mg, Zn) are connected to the metal to be protected or external power (potential) is applied between the metal (connected as cathode) and an inert cheap anode.

Anodic Protection

- It is applied only for passive metals.
- External potential is applied between the metal to be passivated (as the anode) and a cheap cathode.
- The passivity current of the passivated metal should be much lower than its i_{corr} without anodic protection

Coating

- The primary means of protection is the application of a coating, most commonly paint or metal plating, to protect the metal from oxygen and moisture.
- Chromium and tin are often used to plate steel because they oxidize to form a durable, effective oxide coating.
- Zinc, also used to coat steel in a process called galvanization, where a mixed oxide–carbonate coating forms. Since zinc is a more active metal than iron, as the potentials for the oxidation half-reactions show, any oxidation that occurs dissolves zinc rather than iron.

$$Fe^{2+} + 2e^- \rightarrow Fe \qquad E^0_{red} = -0.44\,V$$

$$Zn^{2+} + 2e^- \rightarrow Zn \qquad E^0_{red} = -0.76\,V$$

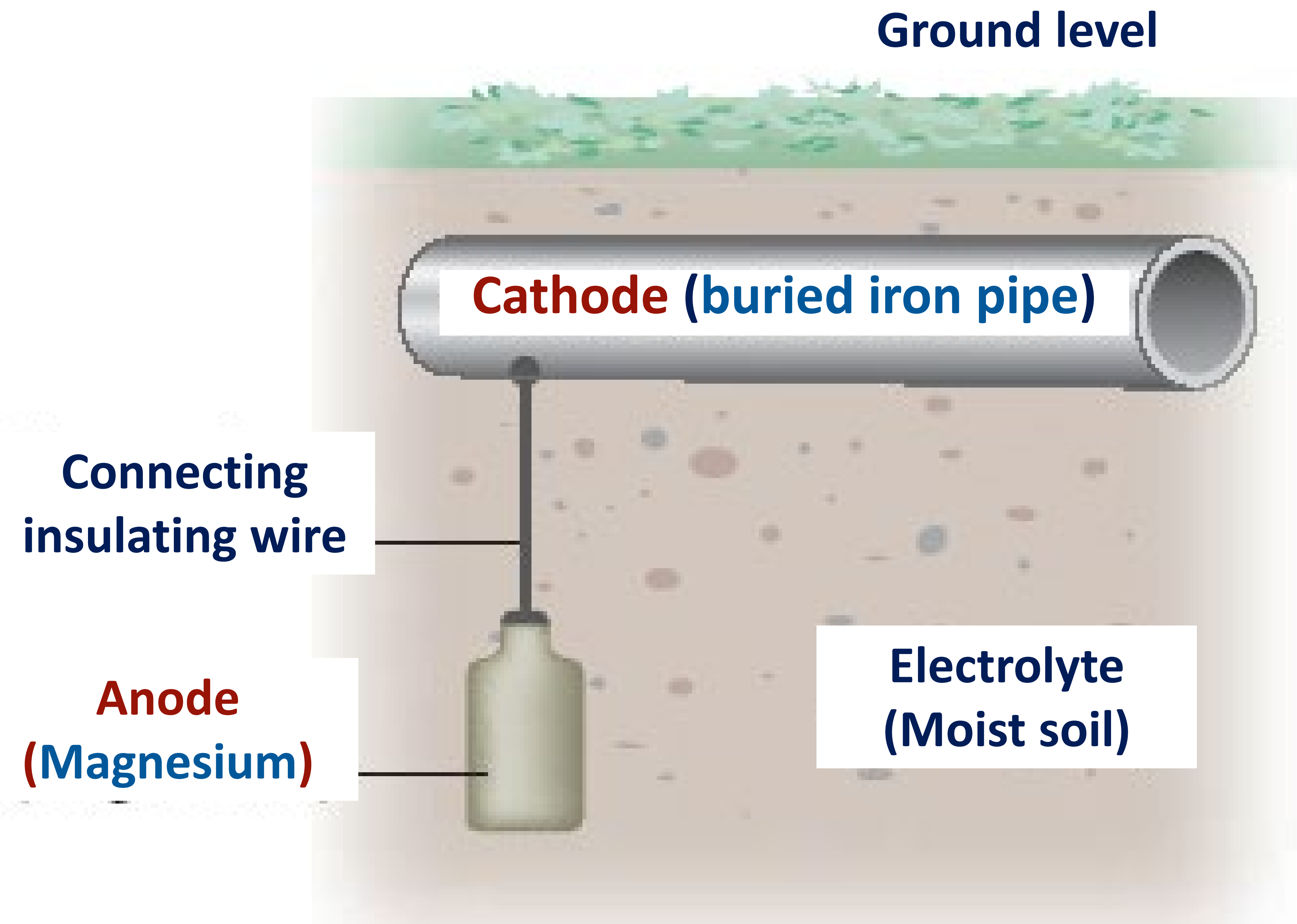
Alloying

- Stainless steel contains chromium and nickel, both of which form oxide coatings that change steel's reduction potential to one characteristic of the noble metals.

- A new technology is now being developed to create surface alloys. Instead of forming a metal alloy such as stainless steel, which has the same composition throughout, a cheaper carbon steel is treated by ion bombardment to produce a thin layer of stainless steel or other desirable alloy on the surface.

Cathodic Protection

- protects steel in buried fuel tanks and pipelines.
- An active metal, such as Mg, is connected by a wire to the pipeline or tank to be protected.
- Because Mg is a better reducing agent than iron, electrons are furnished by Mg rather than by iron, keeping iron from being oxidized.
- As oxidation occurs, Mg anode dissolves, and so it must be replaced periodically.
- Ships' hulls are protected in a similar way by attaching bars of titanium metal to the steel hull. In salt water the titanium acts as the anode and is oxidized instead of the steel hull (the cathode).



Ground level
Cathode (buried iron pipe)
Connecting insulating wire
Anode (Magnesium)
Electrolyte (Moist soil)

End of Course

بالتوفيق