

Unit 1 – Deck 5

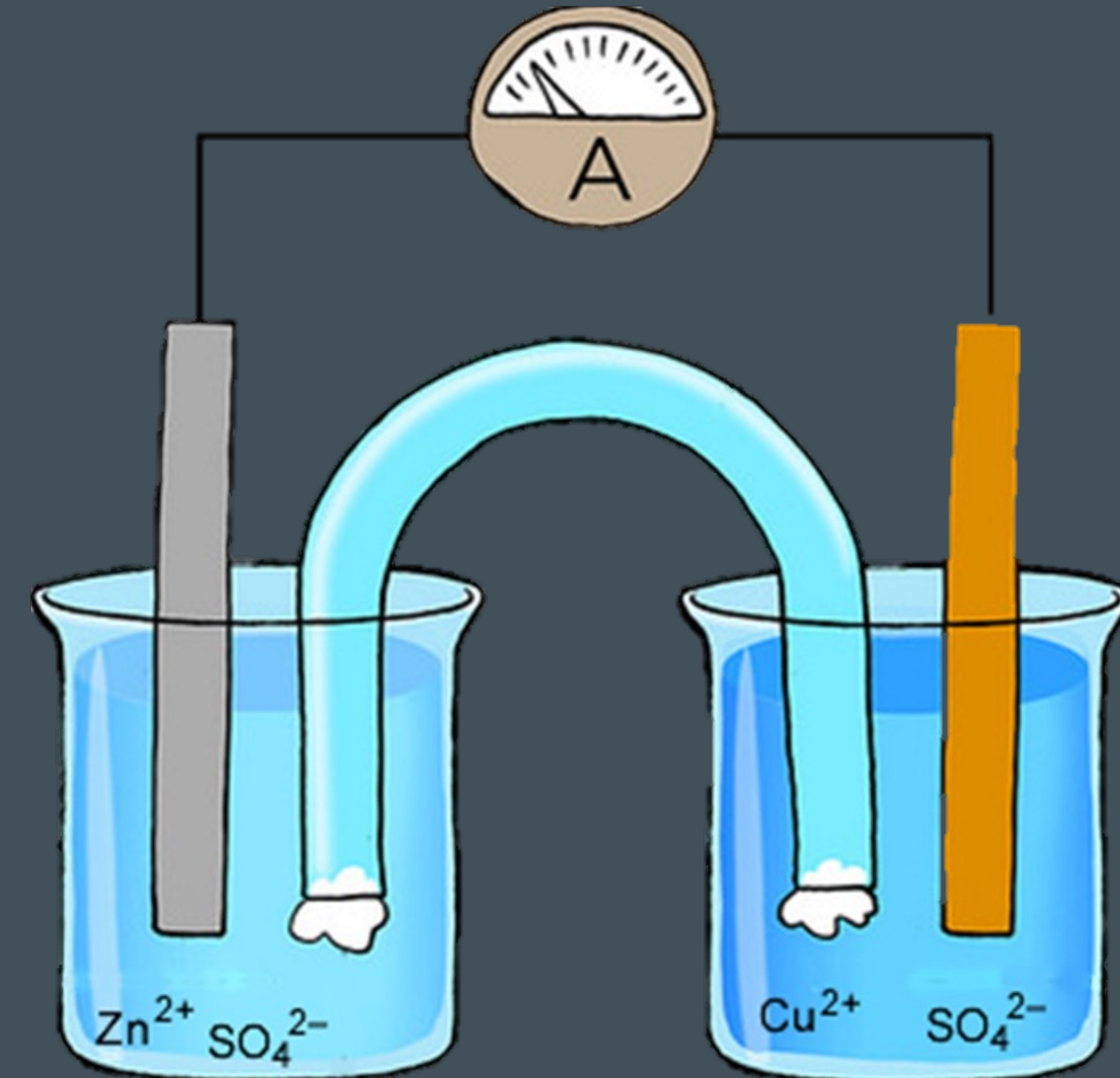
ELECTROCHEMISTRY

Pourbaix Diagrams & Applications of Electrolysis



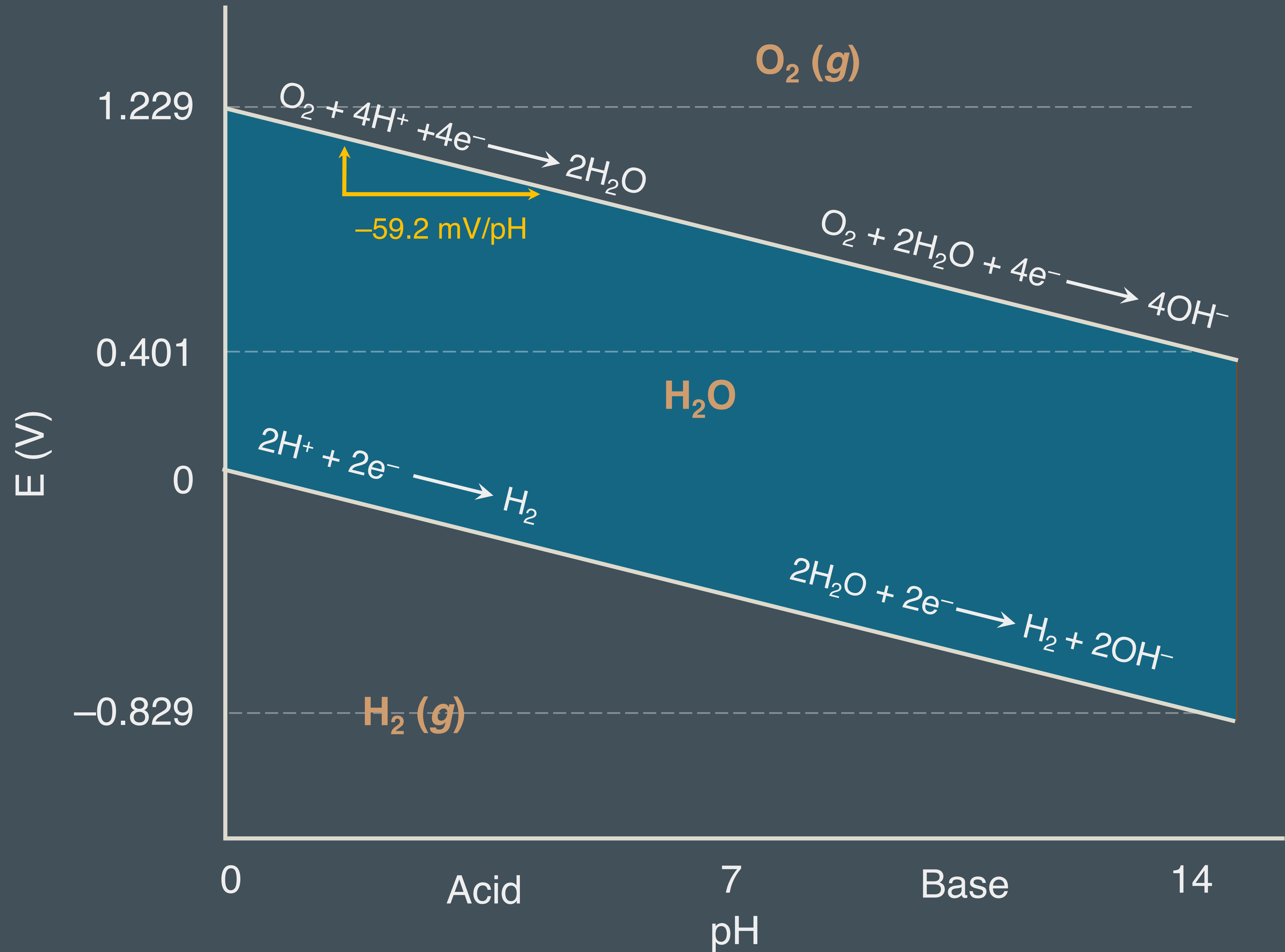
Topics – Electrolysis and Corrosion

- ① **Pourbaix**
- ② Corrosion
- ③ Electrolysis



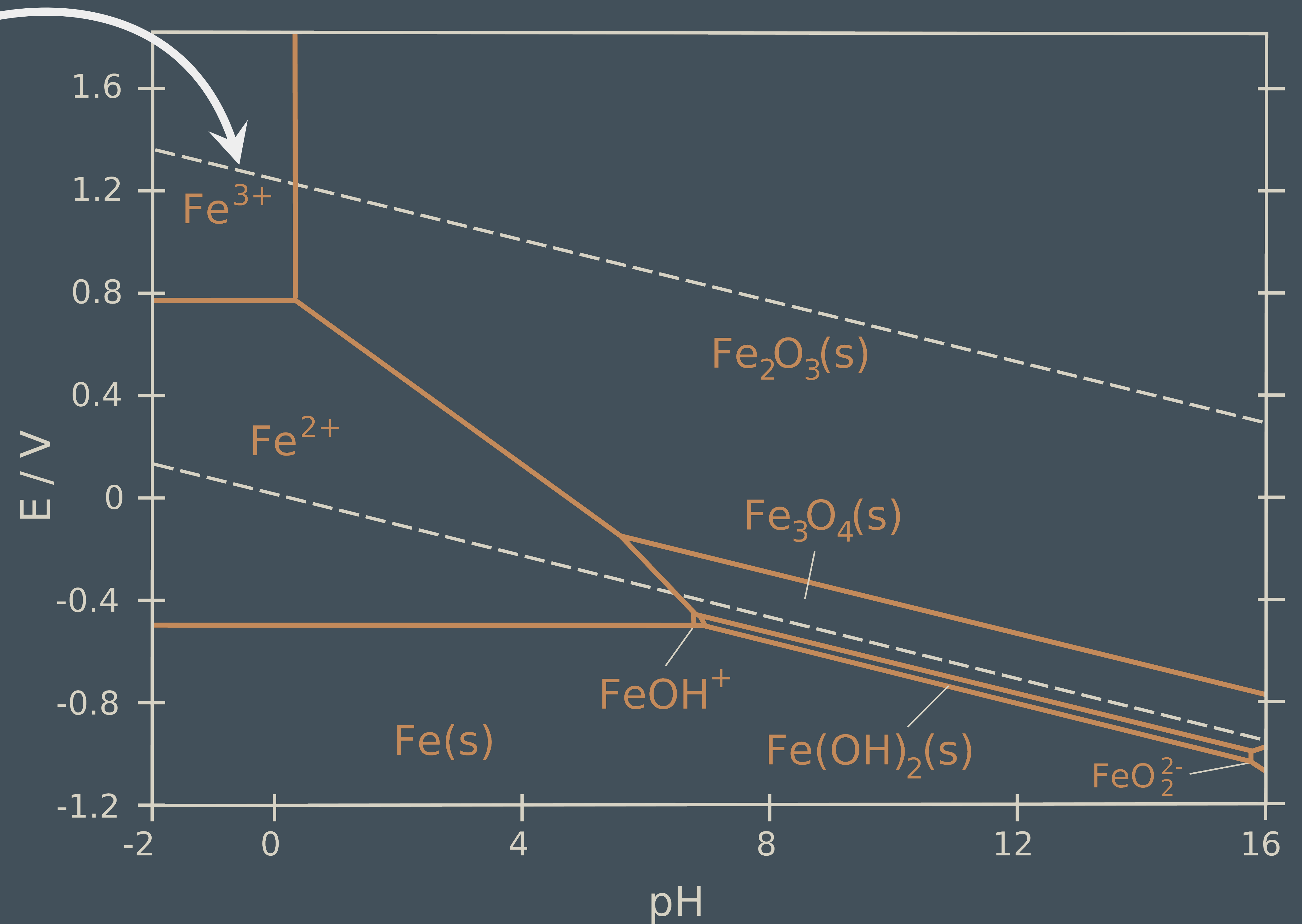
A visual approach: Pourbaix diagrams

Also called an *E-pH* diagram



A typical Pourbaix diagram

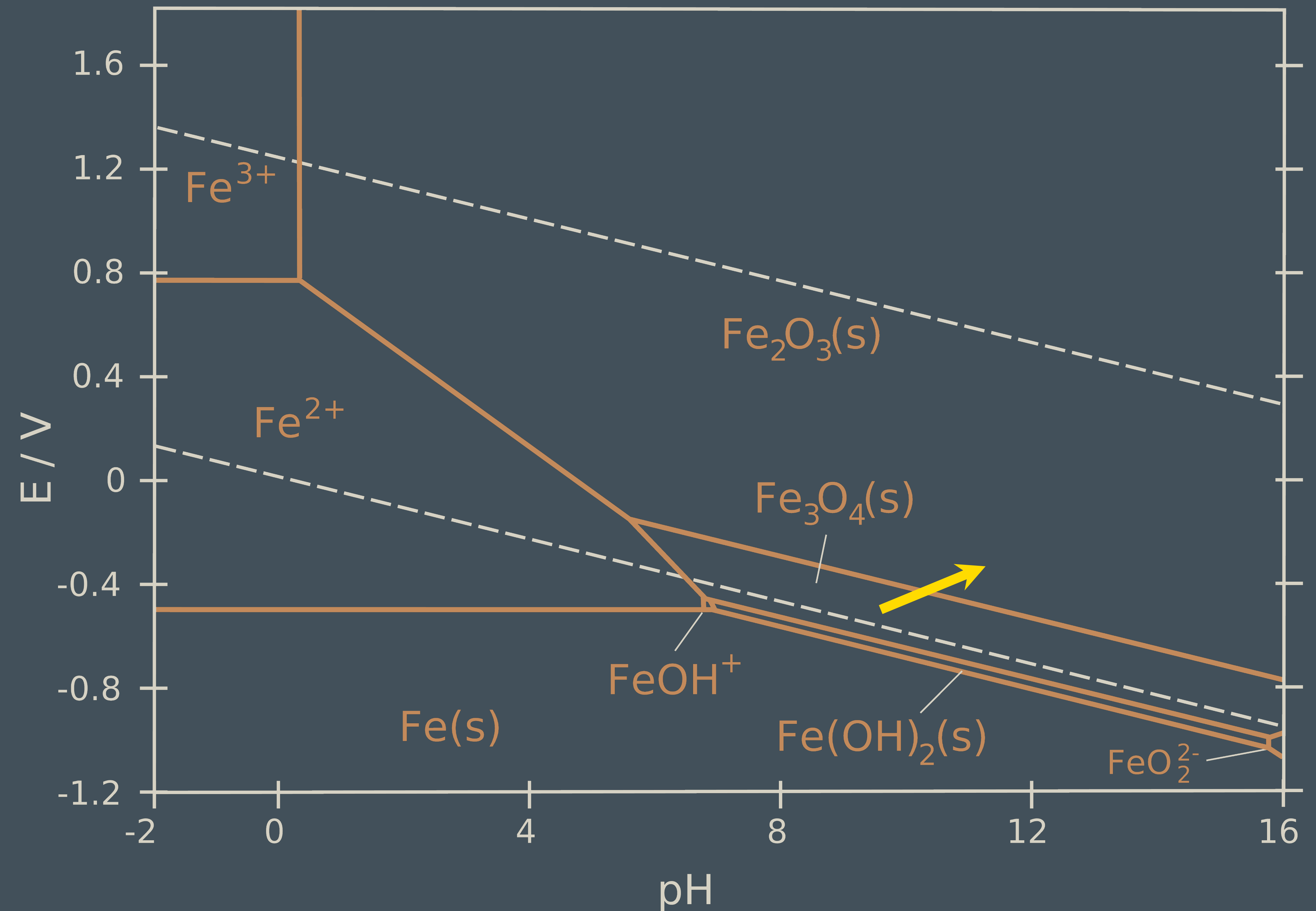
Pourbaix diagram for water is always overlaid.



Example



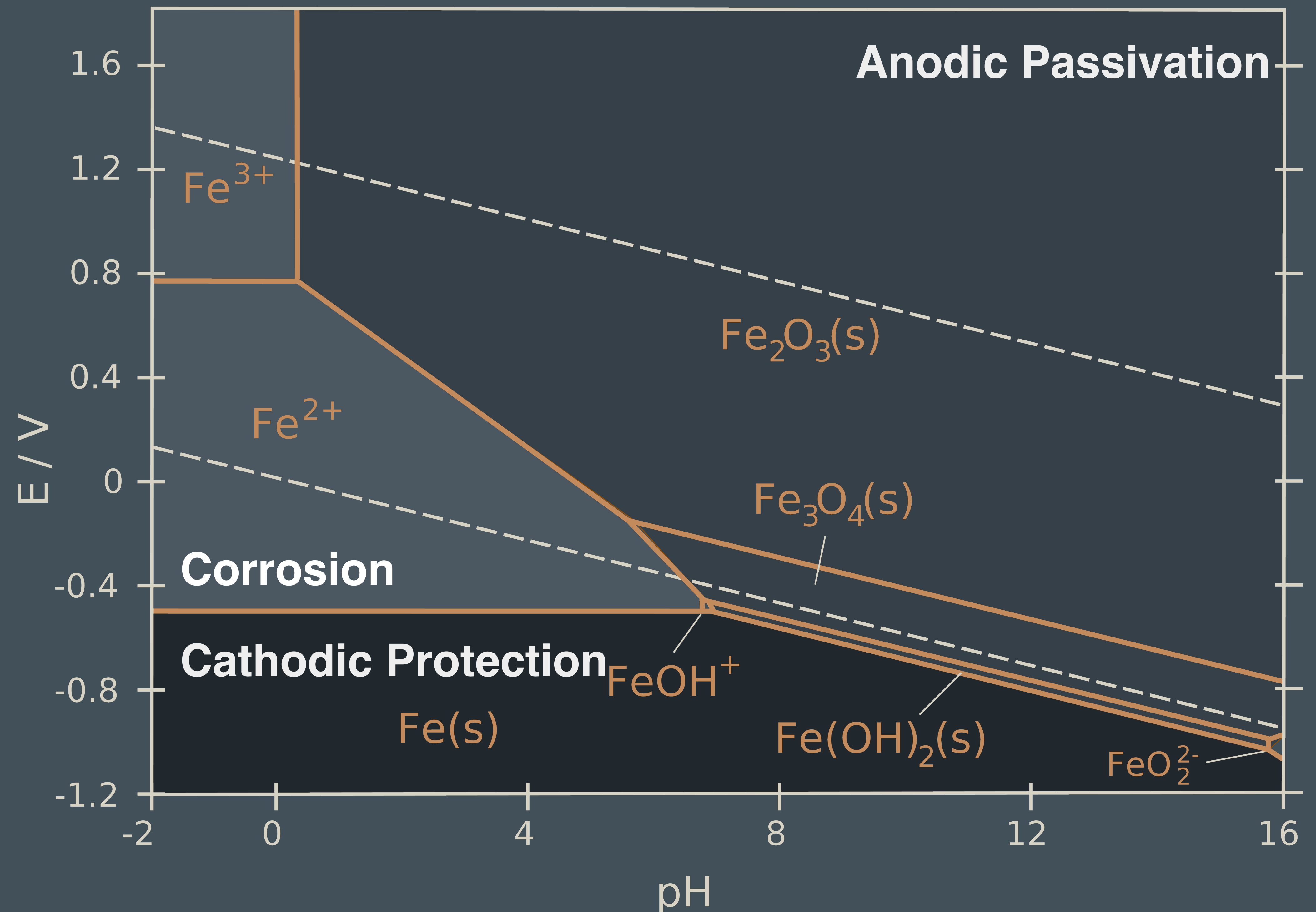
Write a balanced half reaction for that described by the change in position in the E-pH diagram as indicated by \rightarrow .



A typical Pourbaix diagram

With an iron electrode. The construction of the Pourbaix diagram provides useful information

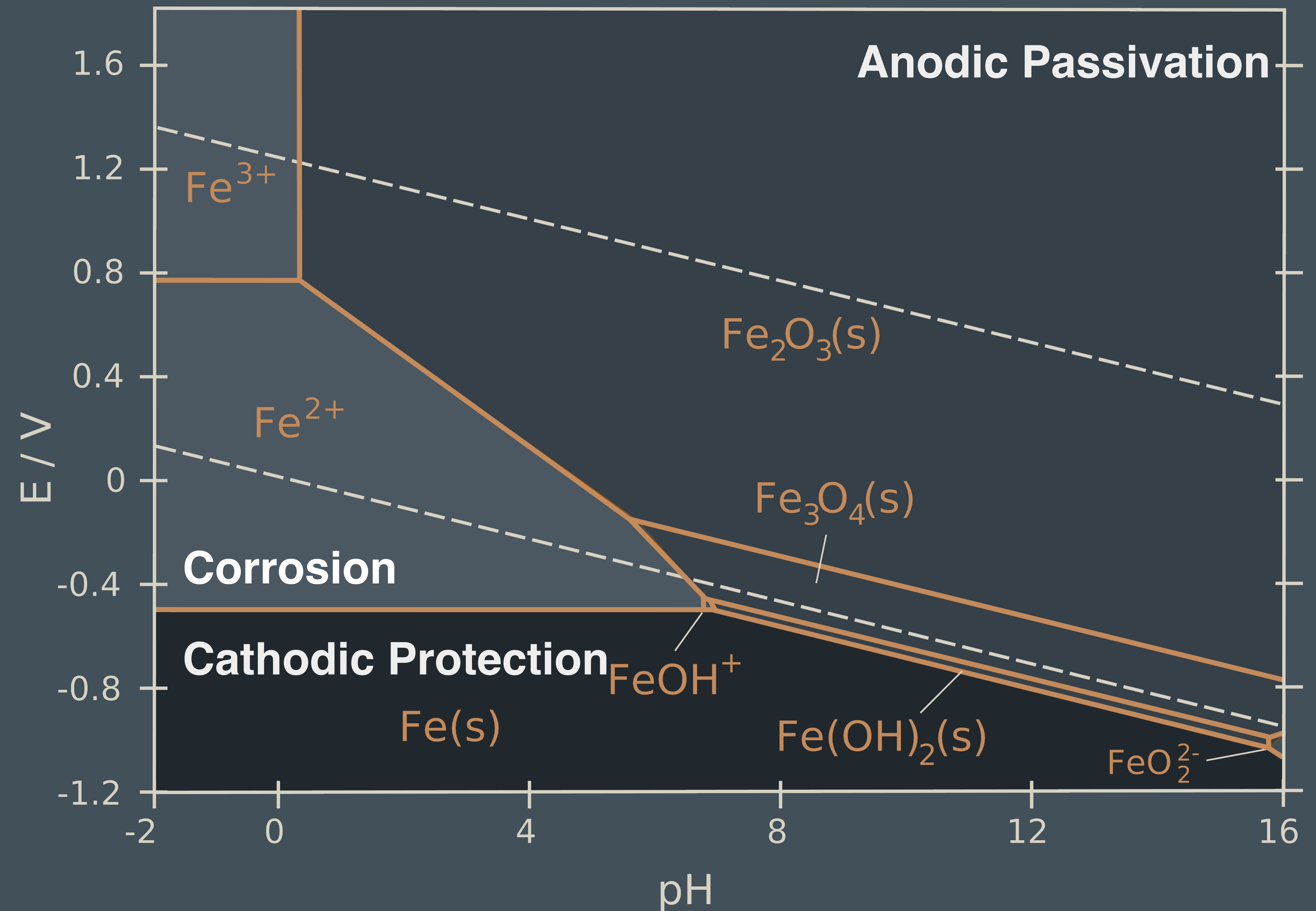
- ① E-pH ranges we can use to prevent corrosion (as in galvanization)
- ② E-pH ranges where we can avoid precipitation of iron ions from solution as oxides or metallic deposits



A typical Pourbaix diagram

With a few experimental E° values describing the aqueous electrochemistry of an element you have all you need to construct these diagrams on your own.

Note: E-pH diagrams are dependent on the concentrations of ions in solution. Using the Nernst equation a different E-pH diagram can be calculated for each concentration.



Corrosion vs Passivation

Unstable Iron Oxidation to Fe_2O_3



Stable Iron Oxidation to Fe_2O_3 (passivation)



COR-TEN
Steel-Copper alloy
Other minor alloyed elements



Protection via passivation and cathodic protection

Passivation:

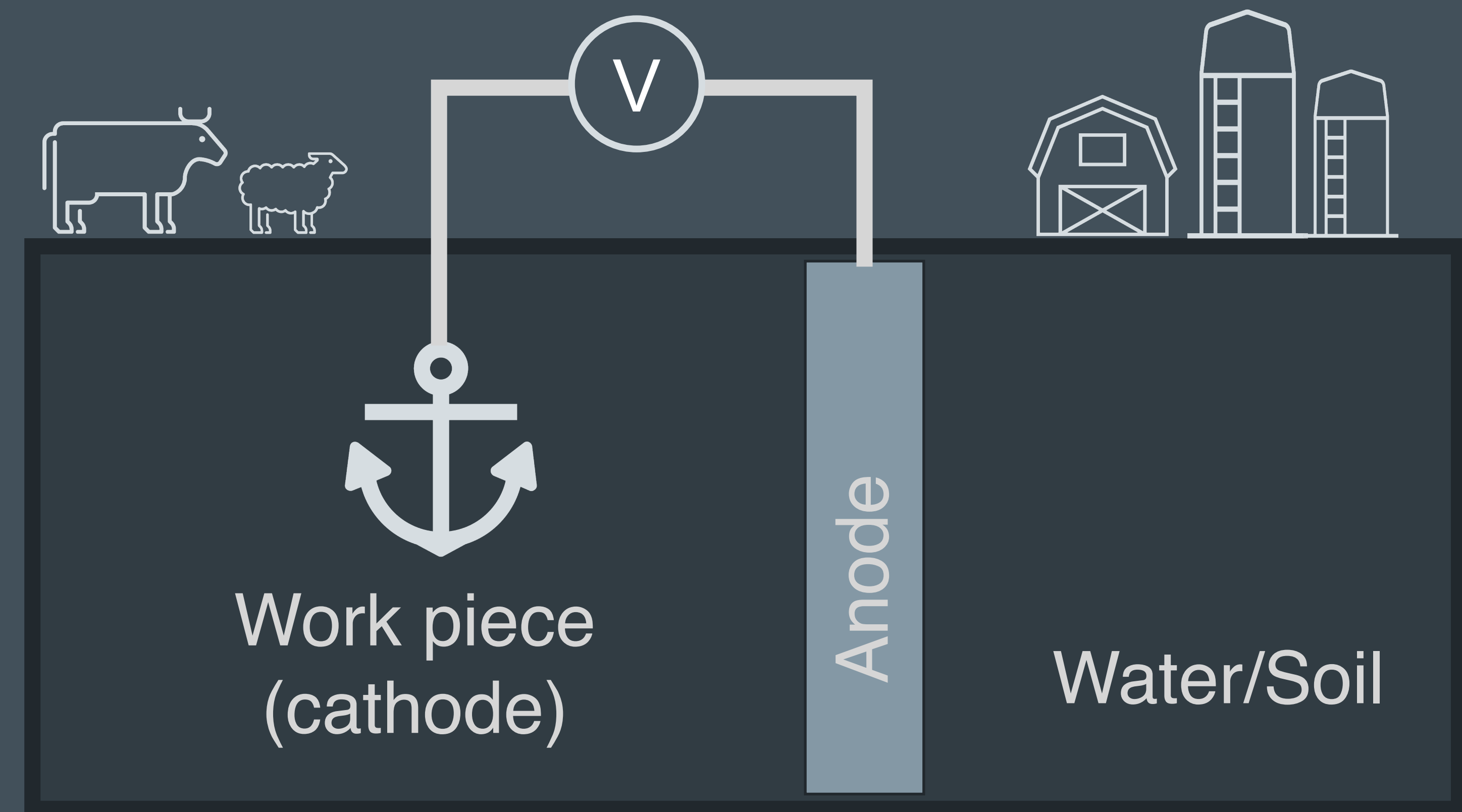
Cathodic Protection:

Cathodic Protection

Galvanic Cathodic Protection



Impressed Current Cathodic Protection



Passivation vs Anodization

Anodization: the deliberate electrochemical growth of a passivation layer on an electrode surface

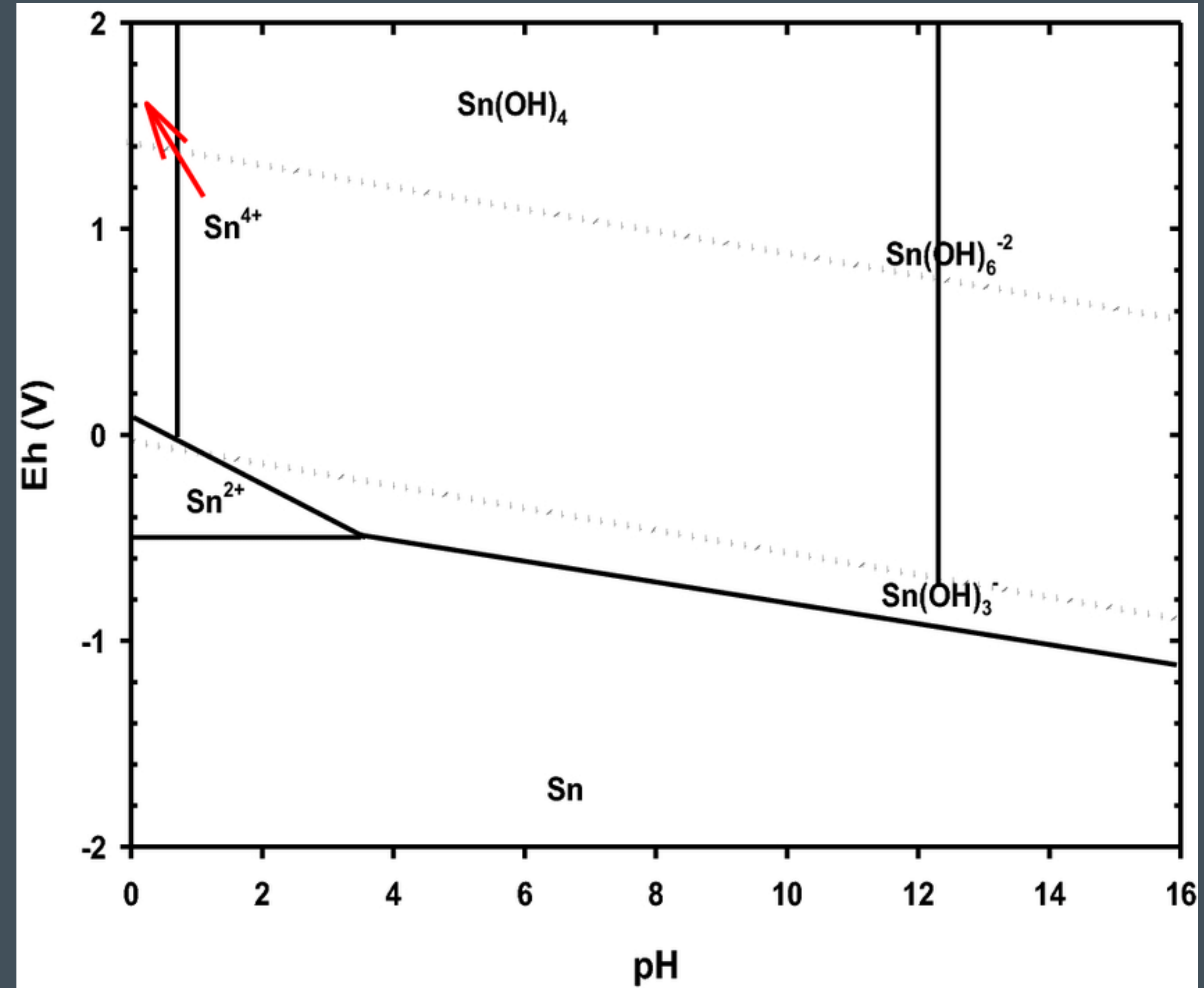




Example

What does process is active in the indicated region?

- A. Anodic Passivation
- B. Cathodic Protection
- C. Stable diffusion
- D. Corrosion

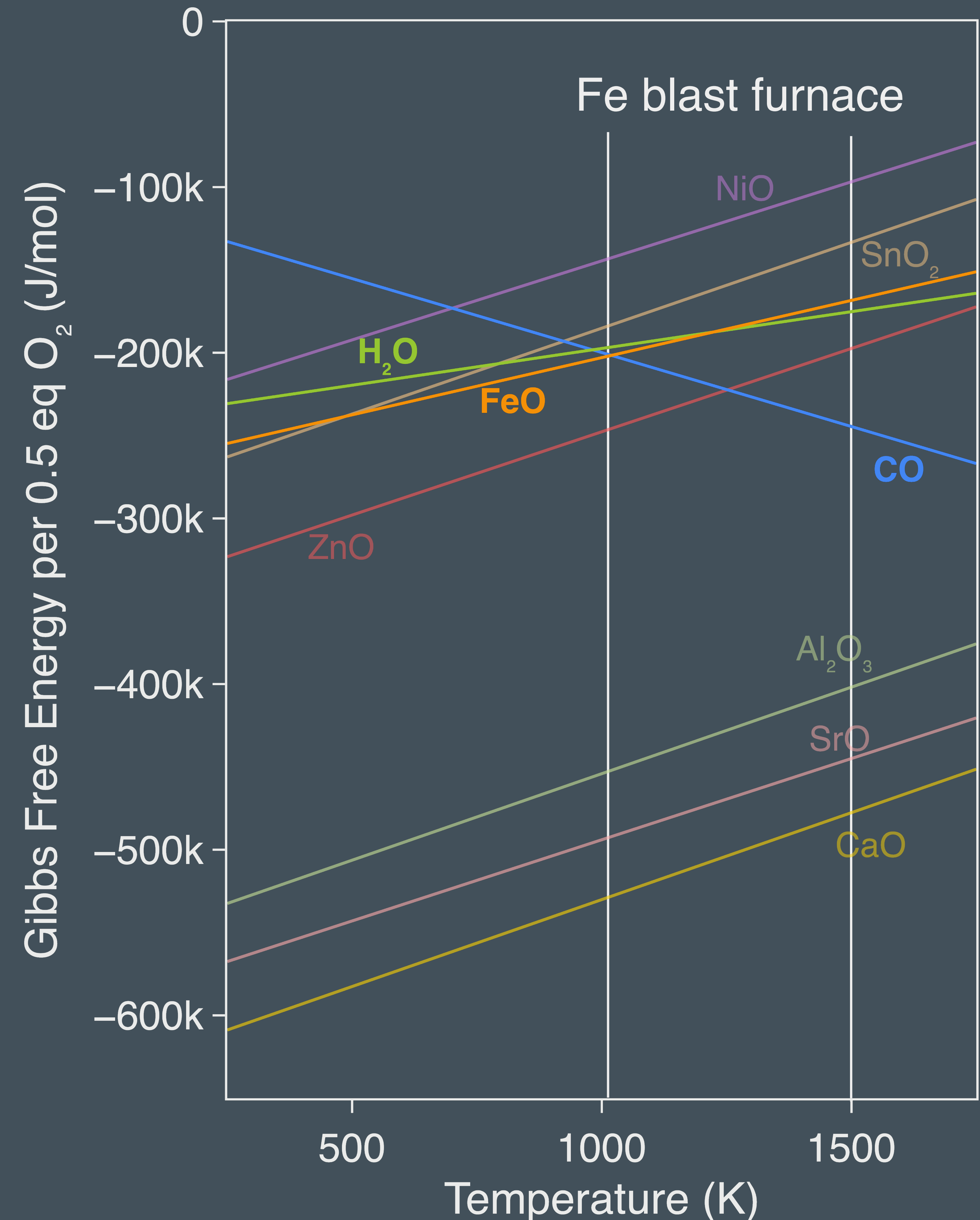


Temperature dependance: Ellingham Diagram

$$\Delta G = \Delta H - T\Delta S$$

Decarbonization of iron smelting using H₂ as fuel

“Direct [Hydrogen] Reduction”



For example see $C + \frac{1}{2} O_2 \rightarrow CO$

Kinetic overpotential

Kinetic overpotential



Given the following electrolytic reaction at which applied potential would the reaction proceed at the fastest rate?



- A. 5.1 V
- B. -5.1 V
- C. 4.9 V
- D. 7.2

Electrolysis of water

Chloralkali reaction



PRODUCT STREAMS

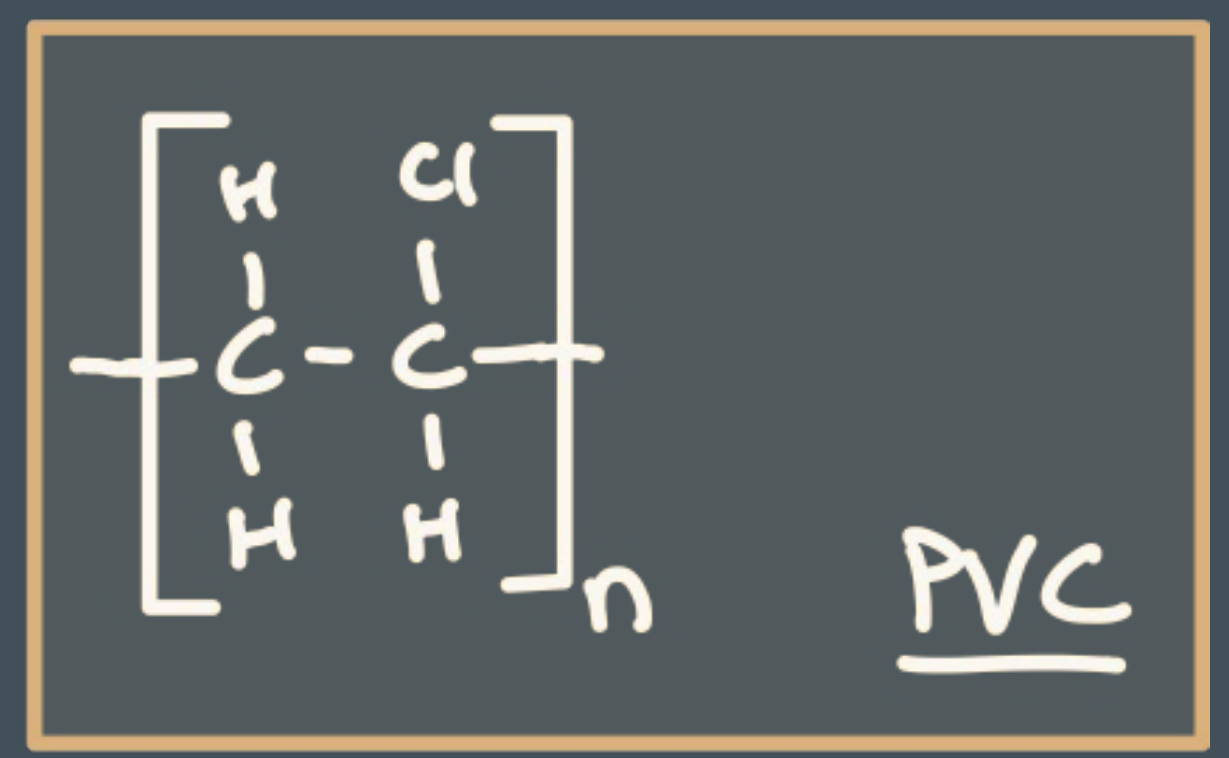
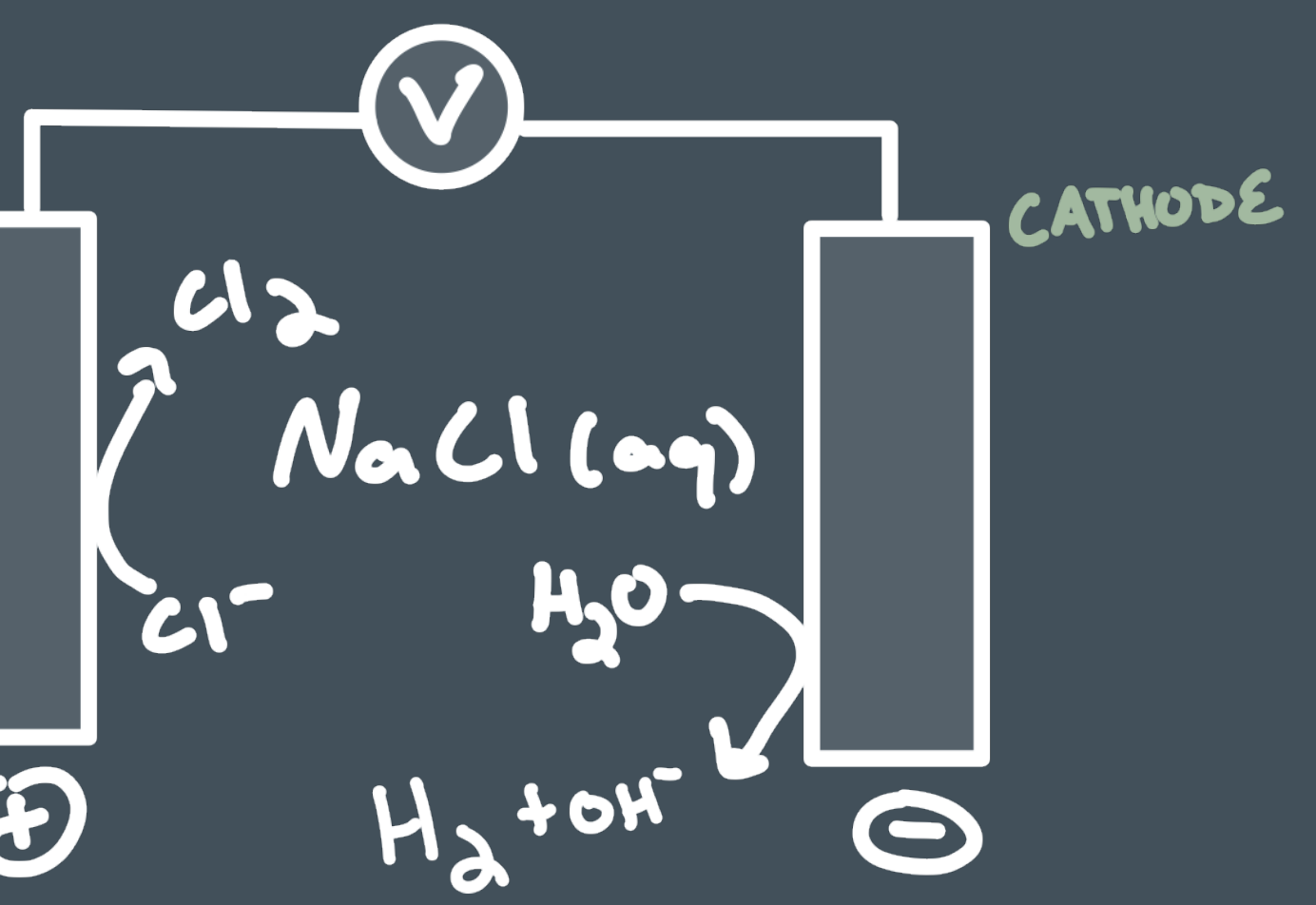
① NaOH

50% SOLN
OR SOLID PELLETS

- DRILLING MUD
- DESULFURIZATION CRUDE OIL
 $\text{H}_2\text{S} + 2\text{NaOH} \rightarrow \text{Na}_2\text{S} + 2\text{H}_2\text{O}$
- NEUTRALIZE ACID WASTE
- WATER TREATMENT → PRECIPITATE METALS
- PULPING (15%)
WOOD CHIPS + NaOH + Na₂S → WOOD PULP
- BAYER PROCESS
BAUXITE + 2NaOH → 2NaAlO₂ (aq) → Al₂O₃
Al₂O₃ ORE CaSiO₄(s)
- SAPONIFICATION

② Cl₂ (g) - COMPRESSED GAS

- $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$
- $\text{Cl}_2 + \text{H}_2\text{C}=\text{CH}_2 \xrightarrow[\text{CAT.}]{\text{FeCl}_3} \text{H}_3\text{C}-\text{CH}_2-\text{Cl}$ DICHLOROETHANE
- $2\text{HCl} + \text{H}_2\text{C}=\text{CH}_2 + \frac{1}{2}\text{O}_2 \xrightarrow[\text{"OXYCHLORINATION"}]{\text{CuCl}_2 \text{ cat.}}$
- $\text{H}_3\text{C}-\text{CH}_2-\text{Cl} \xrightarrow[\text{ETHANOL}]{\text{KOH}} \text{H}_2\text{C}=\text{CH}-\text{Cl} \xrightarrow[\text{POLYMERIZATION}]{\text{RADICAL}}$



- 15,000 OTHER COMPOUNDS
 - 63% ORGANIC
 - 18% INORGANICS
 - 19% BLEACH ↙ EXCLUDING

Chloralkali reaction



Water oxidation to dioxygen gas proceeds slowly in dilute NaCl solutions. At higher NaCl concentrations, the reaction is faster but toxic Cl_2 (g) gas is produced at the anode instead.

Why?

- A. All of the chlorine is converted to perchlorate at low concentrations and does not react at the anode
- B. The much larger concentration of water at low NaCl concentrations allows the oxidation of water to occur at a much faster rate so very little Cl_2 is ever produced.
- C. Water is stabilized by salt solutions and is not reactive as a component of an electrolyte
- D. In a concentrated NaCl solutions water oxidation is only possible at the cathode.

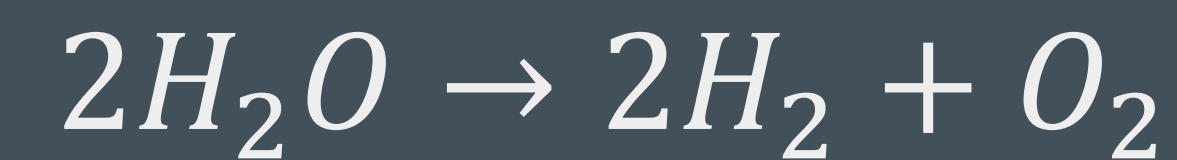
Hydrogen production



How much hydrogen would need to be produced electrolytically to replace the 120,000 TWh of fossil fuels burned each year?

$$1 \text{ W h} = 1 \text{ A h V}$$

$$1 \text{ Faraday} = 26.8 \text{ A h / mol}$$



$$E^\circ_{\text{cell}} = 1.23 \text{ V (theoretical minimum)} \quad \eta^\circ = 1.2 \text{ V (industrial)}$$

Combustion of H_2 gas



A. 1 million moles **B.** 1 billion moles **C.** 1 trillion moles **D.** 1 quadrillion moles

Smelting

The industrial extraction of a pure metal by chemical or electrochemical reduction

Electrochemically: Al, Zn, Na, Li, Cu (pure), K, Mg, Ca, Ag

Aluminum smelting

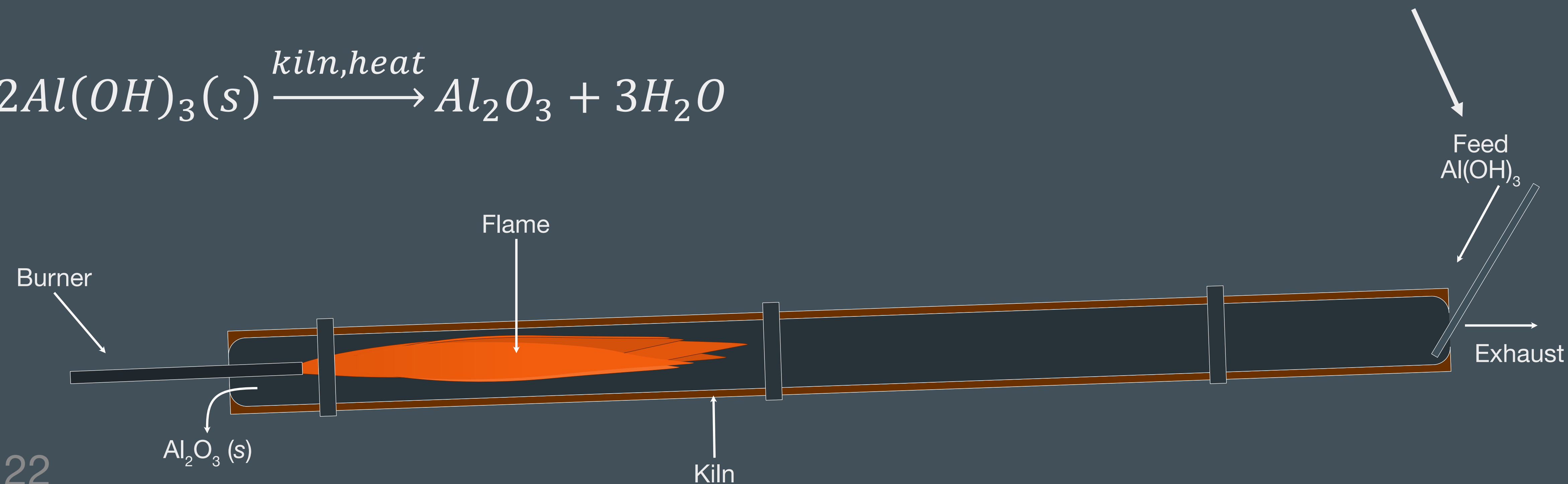
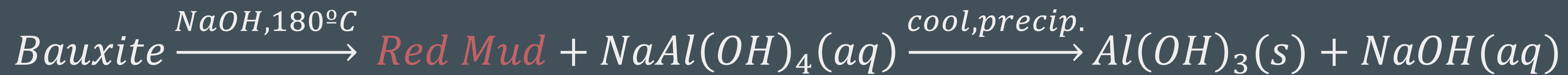
① Mine Bauxite

Impurities

Gibbsite + Boehmite + Diaspore + Goethite + Hematite
 $Al(OH)_3 + \gamma-AlO(OH) + \alpha-AlO(OH) + FeO(OH) + Fe_2O_3$



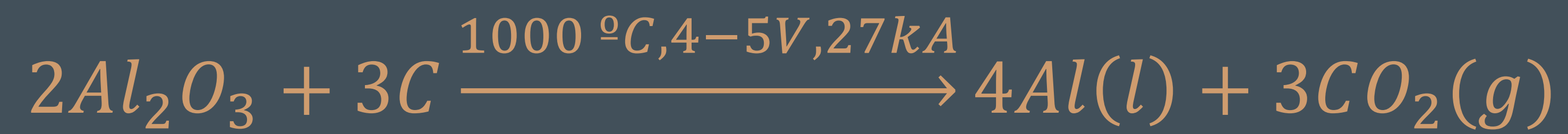
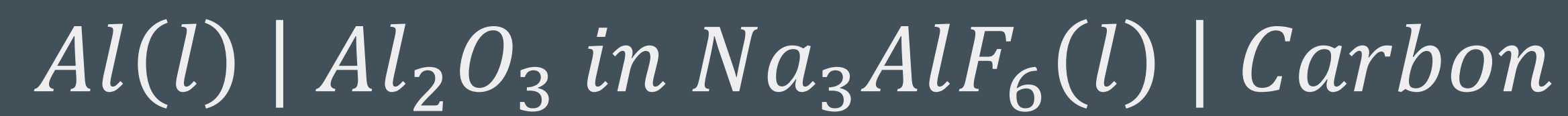
② Bayer Process



Aluminum smelting

③ Hall-Heroult Process

90% Al smelting today



② Green Alternative: "Inert" Anodes

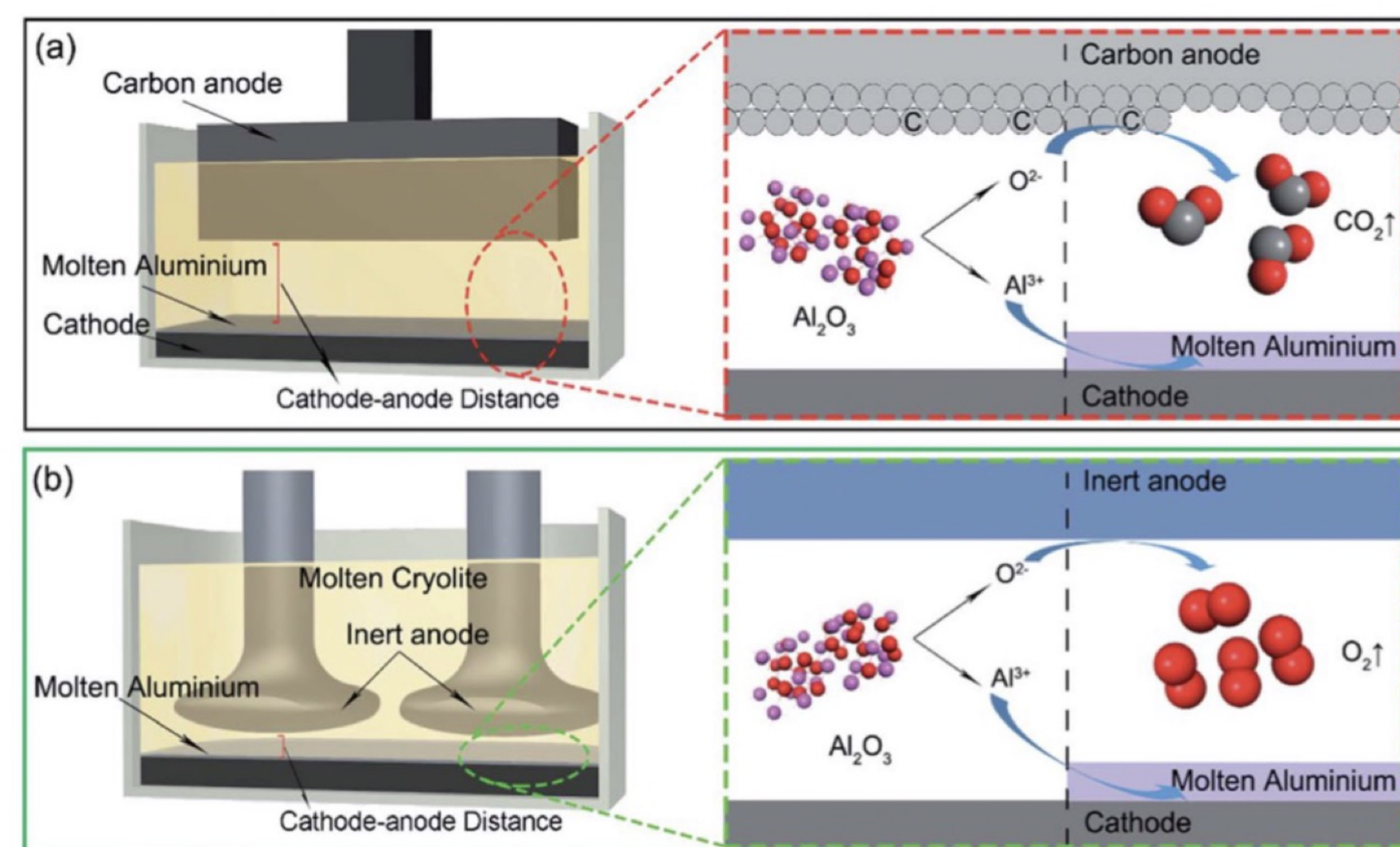
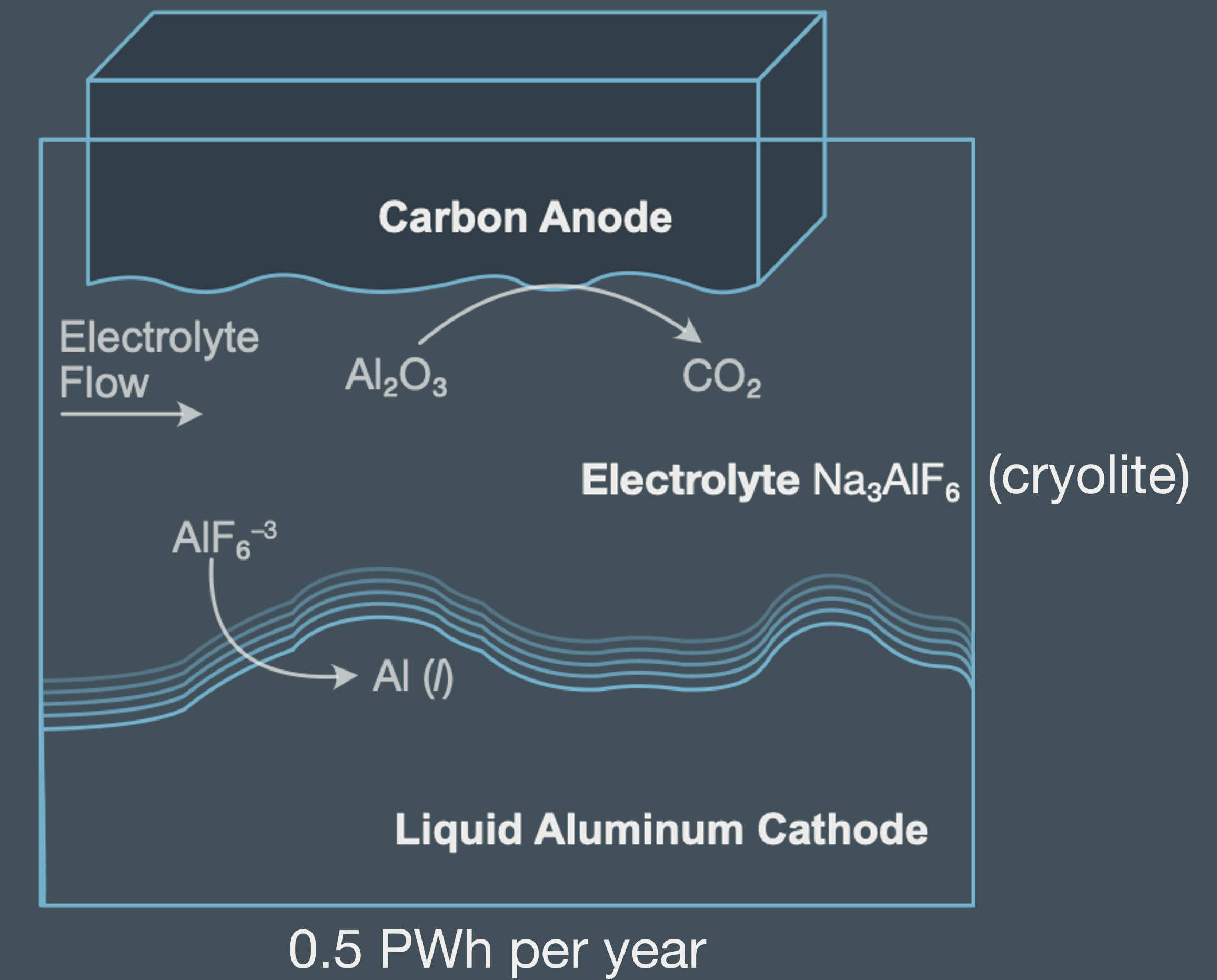
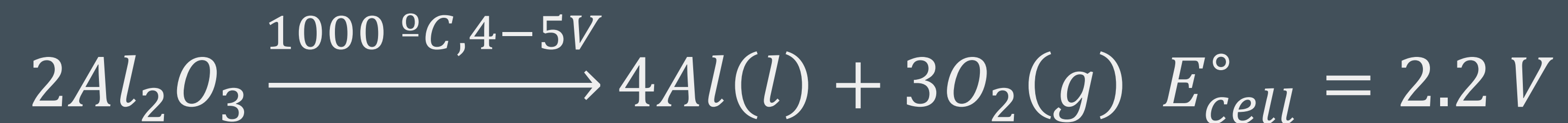


Fig. 1 Aluminium electrolysis cells and their reaction mechanisms using (a) carbon anodes and (b) inert anodes.

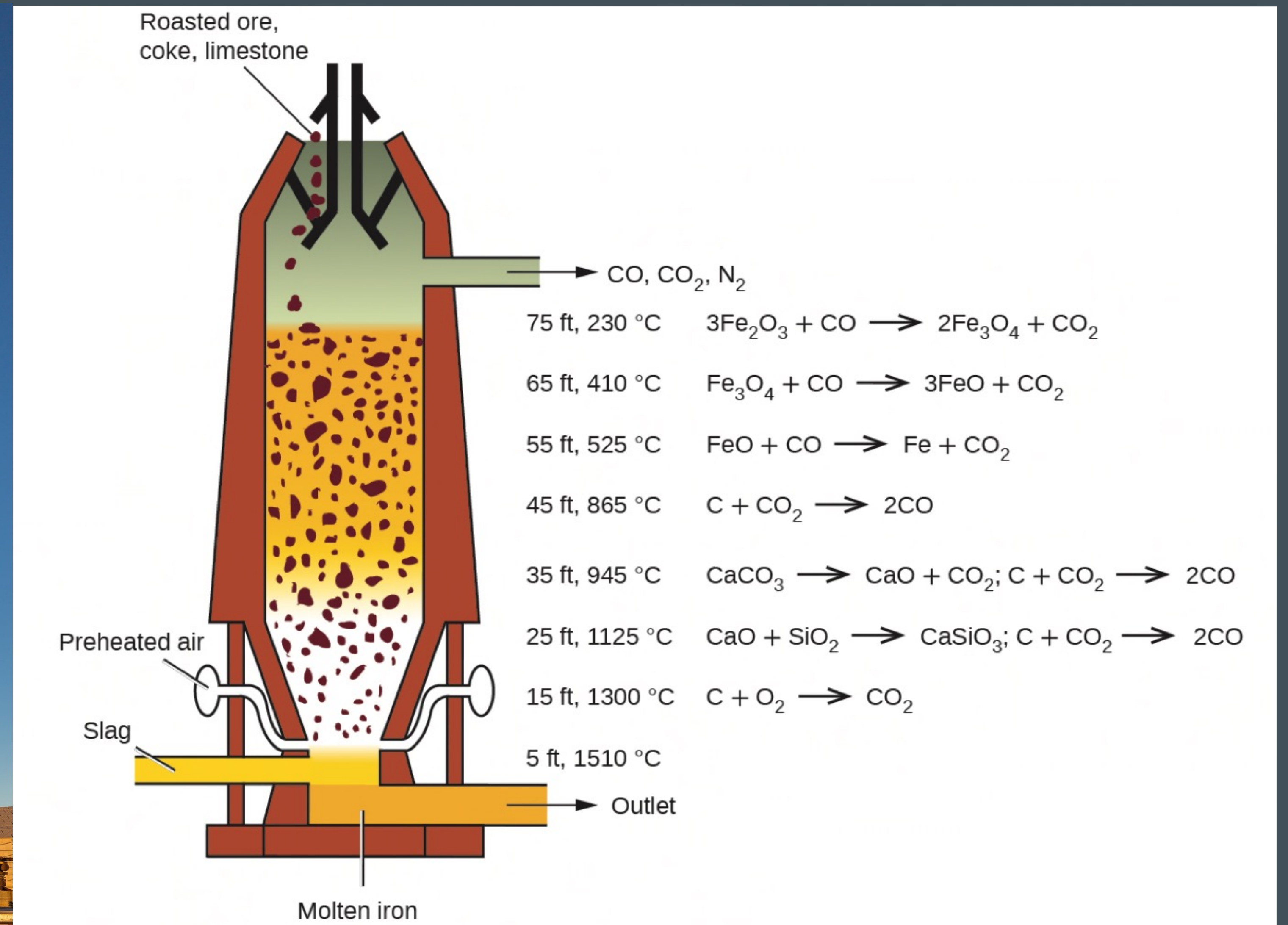
Inert anodes are hard to make.
 O_2 is not inert at $1000\text{ }^\circ\text{C}$.

Goal: 10% smelted Al by 2030

Iron smelting

- Chemical reduction
- Not electrochemical
- 8% global energy

Iron age 750-500 BC.
Some say we never left (Vaclav Smil)



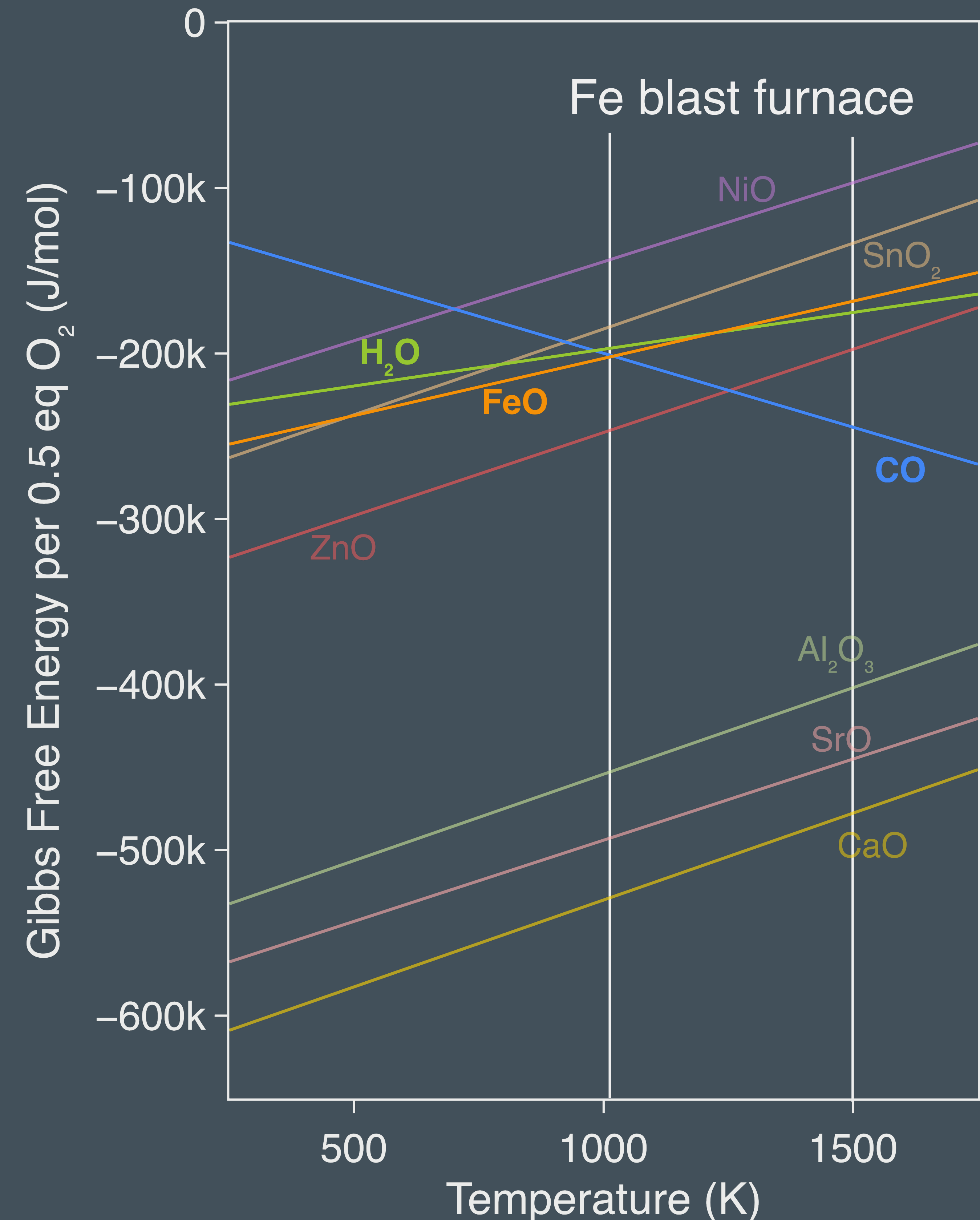


Temperature dependance: Ellingham diagram

Given the Ellingham diagram, how is it possible to direct reduce iron oxide with hydrogen gas.



- A. This reaction is highly exergonic at all temperatures and will proceed to completion on its own.
- B. A higher temperature is required compared to CO for direct reduction to become spontaneous.
- C. A secondary exothermic reaction of H₂O is required to make the net reaction exergonic.
- D. This reaction is not possible at any temperature or under any physical accessible conditions.



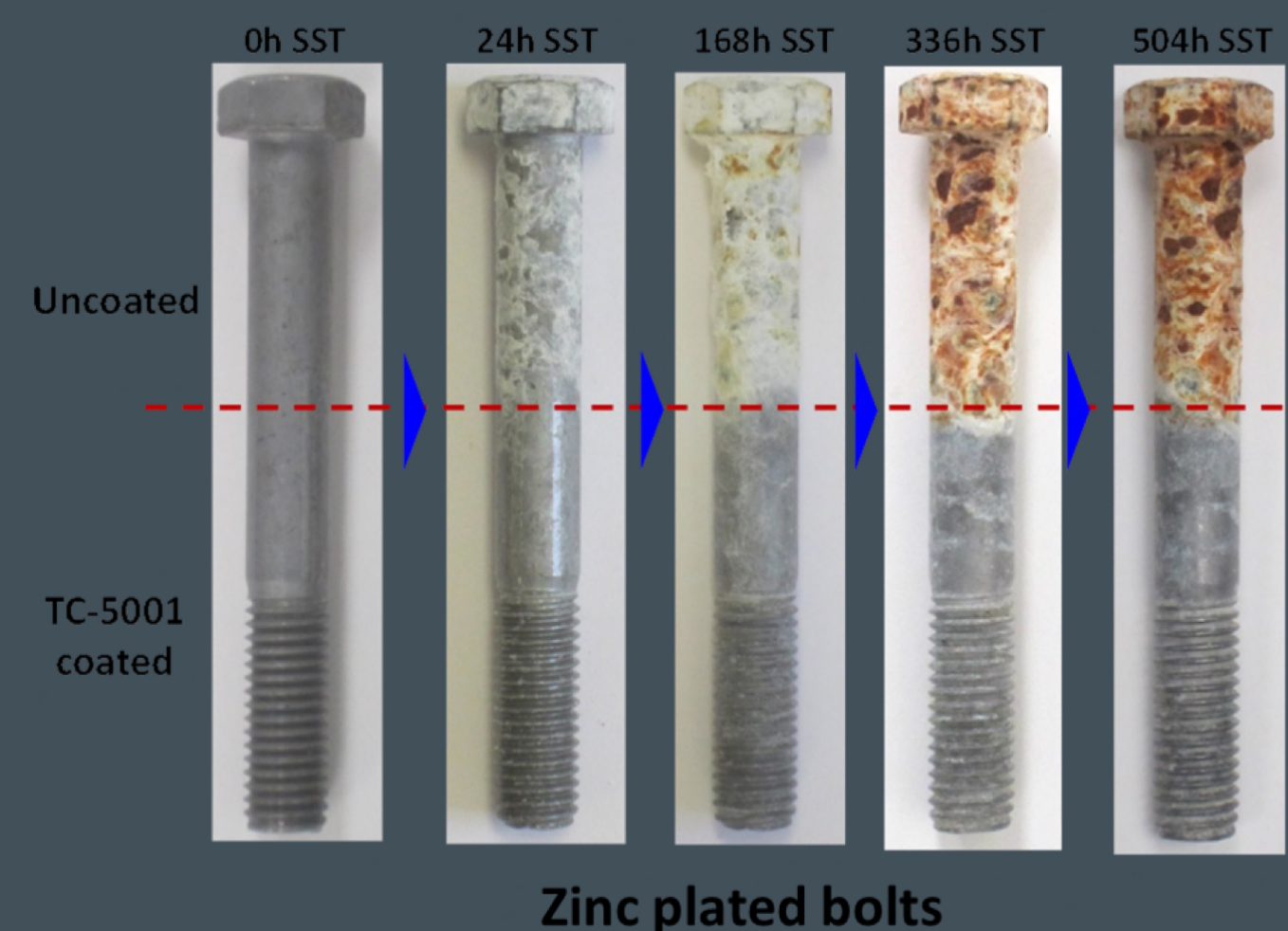
Free energy of formation at a function of temperature. Here we see $2 \text{C} + \frac{1}{2} \text{O}_2 \rightarrow 2 \text{CO}$

Other Electrochemical Applications

1. Electroplating
2. Electroforming
3. Electroless Deposition
4. Electrotyping
5. Electropolishing
6. EDM – Electric Discharge Machining
7. ECM – Electrochemical Machining

① Electroplating

Coat a metal work piece with another metal



② Electroforming

Electrodeposit metal onto a temporary mold

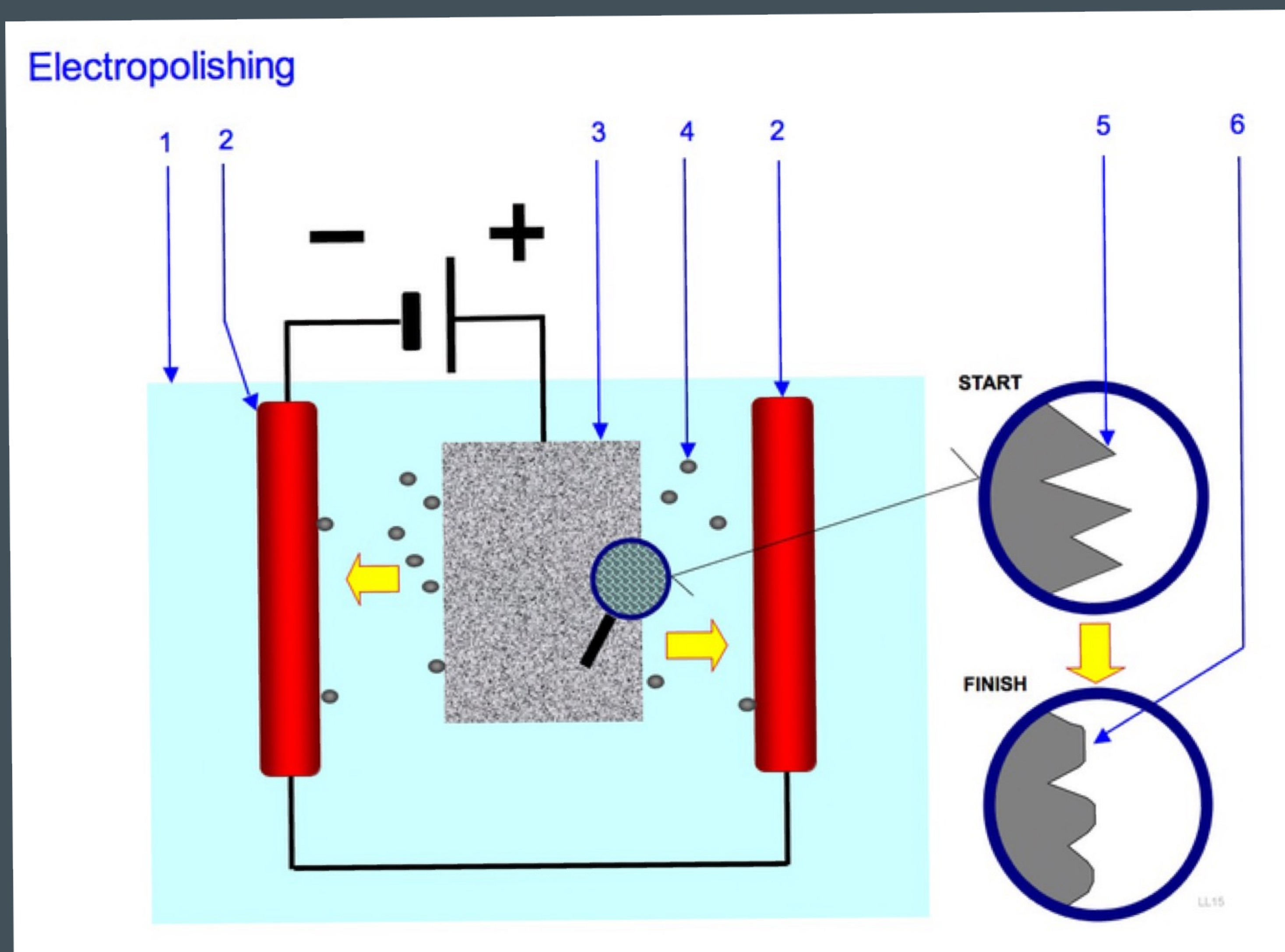


③ Electroless Deposition

Chemical reduction and precipitation of a metal



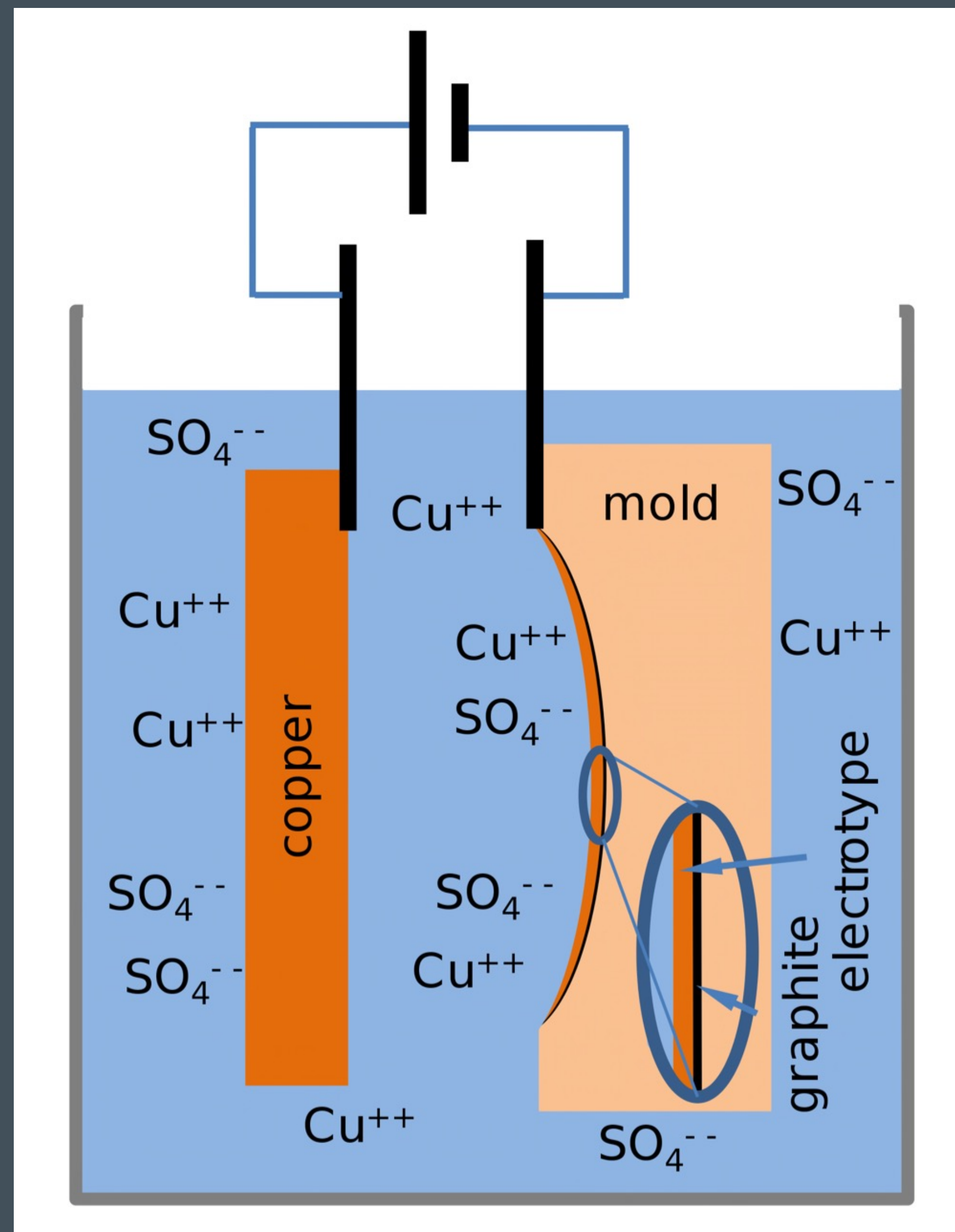
Electropolishing



Electropolish:
Reversibly deposit then redissolve surface metal to yield a smooth finish.

Electrotyping

Electrotyping:
Plate thin light metal forms.
Used on statuary and printing



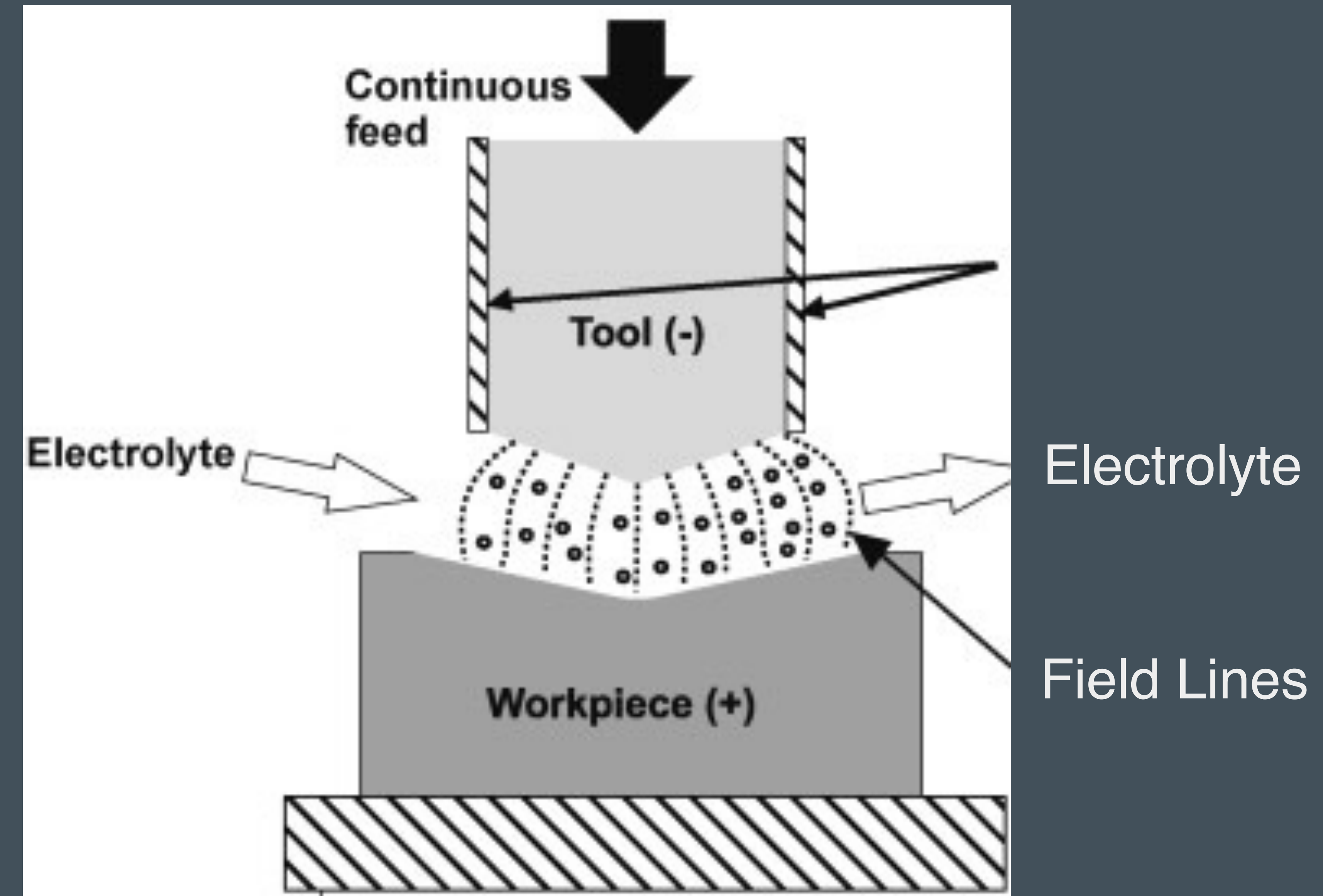
Electrochemical Machining

ECM:

A subtractive manufacturing process where work piece is the anode. Used to shape ultrahard materials

Shape hardened parts that cannot be machined:

- Tool steel
- Tungsten



Electrochemically dissolve workpiece into its final shape

Next Time

Electrochemical Energy Storage

- Primary vs. Secondary Batteries
- Supercapacitors
- Fuel Cells