

**Module 3**  
**CHY1009 – Engineering Chemistry**

**PART 5**

**Electrochemistry  
and  
Chemical Sensors**

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**Corrosion**

# Corrosion

- The destruction of metals or alloys by surrounding environment through chemical or electrochemical changes.



- **Corrosion** is defined as the chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties.

## **Effects of Corrosion**



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graph LR; A[Effects of Corrosion] --- B[Loss of metal]; A --- C[Loss of time]; A --- D[Reduction of value of goods]; A --- E[Contamination of fluids due to chemical reaction]; A --- F[Changes in surface properties]; A --- G[Mechanical damage];
```

**Loss of metal**

**Loss of time**

**Reduction of value of goods**

**Contamination of fluids due to chemical reaction**

**Changes in surface properties**

**Mechanical damage**

# Conditions for Corrosion of Metals

- Metal (example: iron)
- Oxygen (usually from the atmosphere)
- An electrolyte (usually water)

# Corrosion of iron

- The most common and economically destructive form of corrosion is the **rusting** of iron.
- Rusting of iron arises through a complex electrochemical process.



# Some facts of iron corrosion

- Iron does not rust in dry air: **moisture** must be present.
- Iron does not rust in air-free water: **oxygen** must be present.
- The loss of iron and the depositing of rust often occur at *different* places on the *same* object.
- Iron rusts more quickly at **low pH** (high  $[H^+]$ ).
- Iron rusts more quickly in contact with ionic solutions.
- Iron rusts more quickly in contact with a less active metal (such as Cu) and more slowly in contact with a more active metal (such as Zn)

$\text{F}_2(\text{g}) + 2 \text{e}^-$	$\longrightarrow 2 \text{F}(\text{aq})$	2.87
$\text{H}_2\text{O}_2(\text{aq}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^-$	$\longrightarrow 2 \text{H}_2\text{O}(\text{l})$	1.78
$\text{MnO}_4^-(\text{aq}) + 8 \text{H}^+(\text{aq}) + 5 \text{e}^-$	$\longrightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l})$	1.51
$\text{Cl}_2(\text{g}) + 2 \text{e}^-$	$\longrightarrow 2 \text{Cl}^-(\text{aq})$	1.36
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^+(\text{aq}) + 6 \text{e}^-$	$\longrightarrow 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O}(\text{l})$	1.33
$\text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 4 \text{e}^-$	$\longrightarrow 2 \text{H}_2\text{O}(\text{l})$	1.23
$\text{Br}_2(\text{l}) + 2 \text{e}^-$	$\longrightarrow 2 \text{Br}^-(\text{aq})$	1.09
$\text{Ag}^+(\text{aq}) + \text{e}^-$	$\longrightarrow \text{Ag}(\text{s})$	0.80
$\text{Fe}^{3+}(\text{aq}) + \text{e}^-$	$\longrightarrow \text{Fe}^{2+}(\text{aq})$	0.77
$\text{O}_2(\text{g}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^-$	$\longrightarrow \text{H}_2\text{O}_2(\text{aq})$	0.70
$\text{I}_2(\text{s}) + 2 \text{e}^-$	$\longrightarrow 2 \text{I}^-(\text{aq})$	0.54
$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^-$	$\longrightarrow 4 \text{OH}^-(\text{aq})$	0.40
$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^-$	$\longrightarrow \text{Cu}(\text{s})$	0.34
$\text{Sn}^{4+}(\text{aq}) + 2 \text{e}^-$	$\longrightarrow \text{Sn}^{2+}(\text{aq})$	0.15
$2 \text{H}^+(\text{aq}) + 2 \text{e}^-$	$\longrightarrow \text{H}_2(\text{g})$	0
$\text{Pb}^{2+}(\text{aq}) + 2 \text{e}^-$	$\longrightarrow \text{Pb}(\text{s})$	-0.13
$\text{Ni}^{2+}(\text{aq}) + 2 \text{e}^-$	$\longrightarrow \text{Ni}(\text{s})$	-0.26
$\text{Cd}^{2+}(\text{aq}) + 2 \text{e}^-$	$\longrightarrow \text{Cd}(\text{s})$	-0.40
$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^-$	$\longrightarrow \text{Fe}(\text{s})$	-0.45
$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^-$	$\longrightarrow \text{Zn}(\text{s})$	-0.76
$2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^-$	$\longrightarrow \text{H}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$	-0.83
$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^-$	$\longrightarrow \text{Al}(\text{s})$	-1.66
$\text{Mg}^{2+}(\text{aq}) + 2 \text{e}^-$	$\longrightarrow \text{Mg}(\text{s})$	-2.37
$\text{Na}^+(\text{aq}) + \text{e}^-$	$\longrightarrow \text{Na}(\text{s})$	-2.71
$\text{Li}^+(\text{aq}) + \text{e}^-$	$\longrightarrow \text{Li}(\text{s})$	-3.04

Weaker  
reducing  
agent



Stronger  
reducing  
agent



# Mechanism of Corrosion

## Galvanic cell formation

The corrosion process resemble those of a voltaic cell/**Galvanic cell**

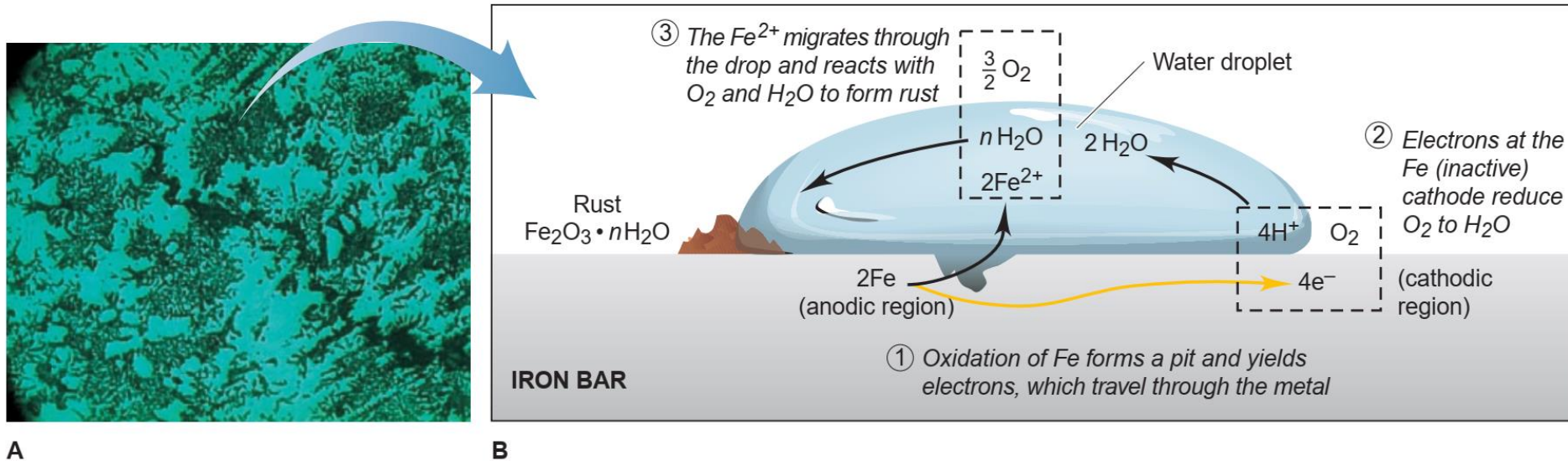


## Differential Aeration

Uneven **supply of oxygen** to areas of the same metal component



# Mechanism of iron corrosion: Galvanic cell formation



Strains, ridges, and dents in contact with water are typically the sites of iron loss (fact 1). These sites are called **anodic regions** because the following half-reaction occurs there:



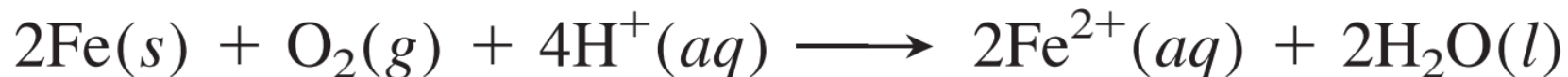
# Mechanism of iron corrosion

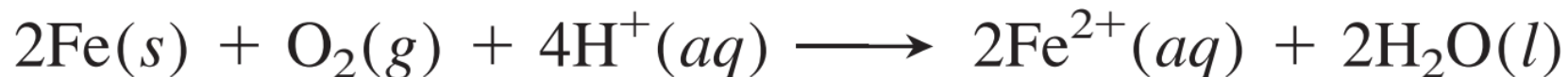


- The freed electrons move through the external circuit—the piece of iron itself—until they reach a region of relatively high  $\text{O}_2$  concentration (fact 2), near the surface of a surrounding water droplet, for instance. At this ***cathodic region***, the electrons released from the iron atoms reduce  $\text{O}_2$  molecules:

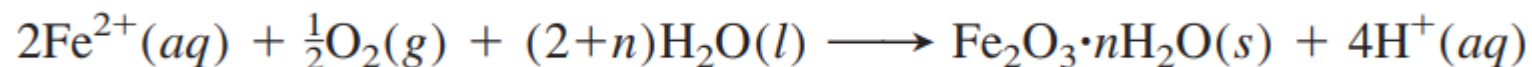


- Notice that this overall redox process is complete; thus, the iron loss has occurred without any rust forming:





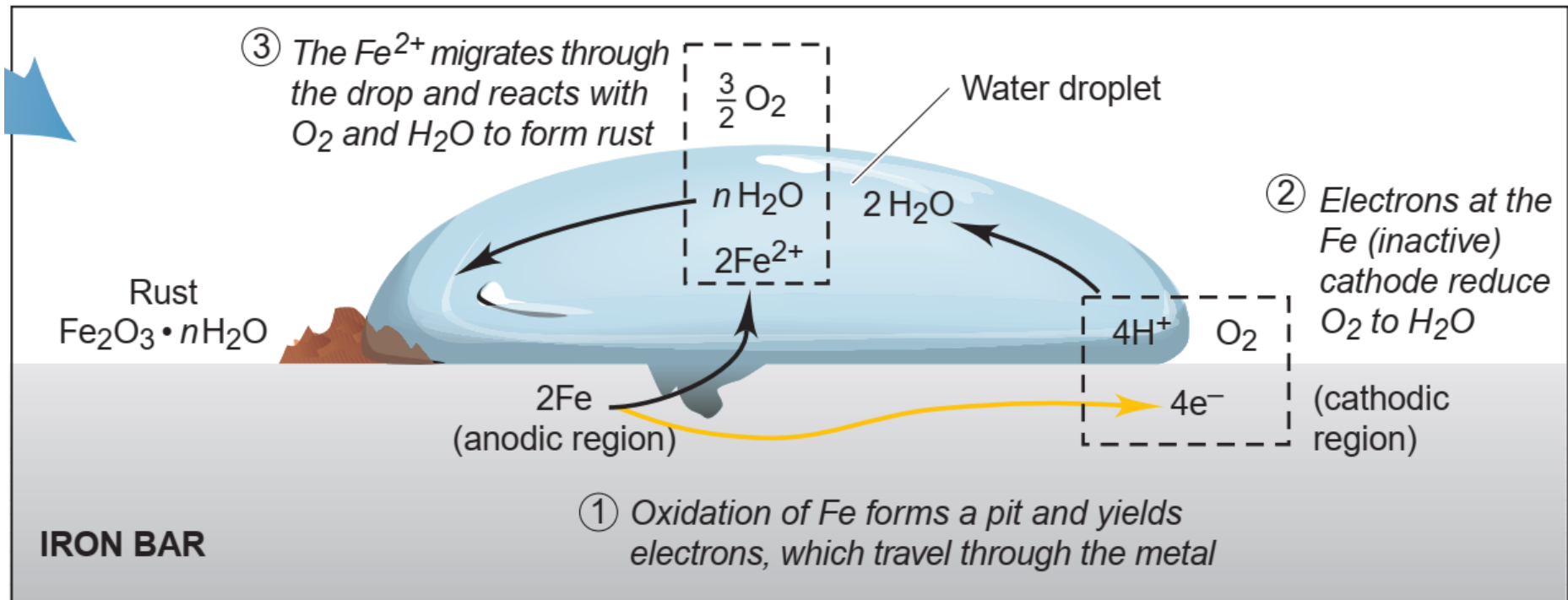
- Rust forms through another redox reaction in which the reactants make direct contact.
- The  $\text{Fe}^{2+}$  ions formed originally at the anodic region disperse through the surrounding water and **react with  $\text{O}_2$** , often at some distance from the pit. The overall reaction for this step is:



**overall equation for the rusting of iron:**



- The canceled  **$\text{H}^+$  ions** are shown to emphasize that they act as a **catalyst**; that is, they speed the process as they are used up in one step of the overall reaction and created in another.
- As a result of this action, **rusting is faster at low pH** (high  $[\text{H}^+]$ )<sup>12</sup>



B

# How corrosion of iron resembles to **voltaic cells**

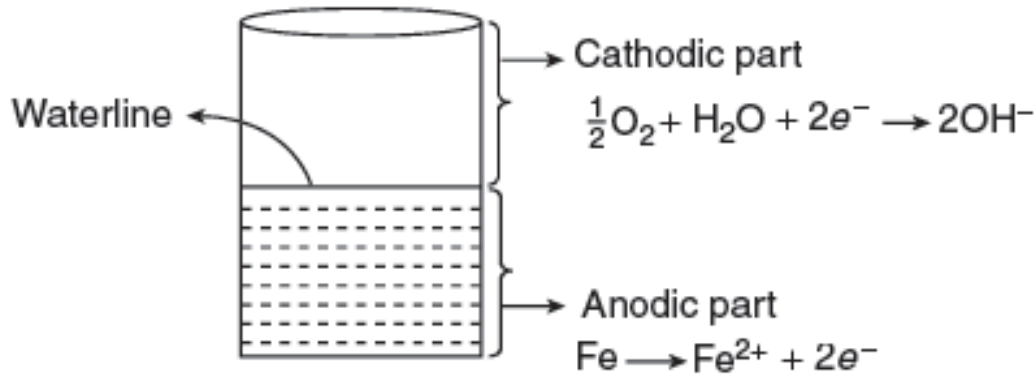
- In many ways, the components of the corrosion process resemble those of a voltaic cell:
- Anodic and cathodic regions are **separated** in space
- In the **anodic** region, **iron** behaves like an active electrode, whereas in the **cathodic** region, it is inactive
- The **moisture** surrounding the **pit** functions somewhat like a **salt bridge**, a means for ions to ferry back and forth and keep the solution neutral



# Mechanism of iron corrosion: **Differential Aeration**

- Differential Aeration Corrosion takes place when there is an uneven **supply of oxygen** to areas of the same metal component.
- Metals that are **submerged in water** are also subjected to this type of corrosion, because varying oxygen concentration in the water and atmosphere
- It is a type of electrochemical corrosion that affects metals such as **steel and iron**.
- When a poorly oxygenated area is adjacent to an area with a good supply of oxygen, an anodic/cathodic reaction occurs.





(a)



(b)

- In the **cathode**, oxygen from the air to is reduced to produce hydroxide ions.



- When the ions between the cathodic and **anodic** areas meet iron hydroxide forms, precipitates and oxidises to form the corrosive material or rust.



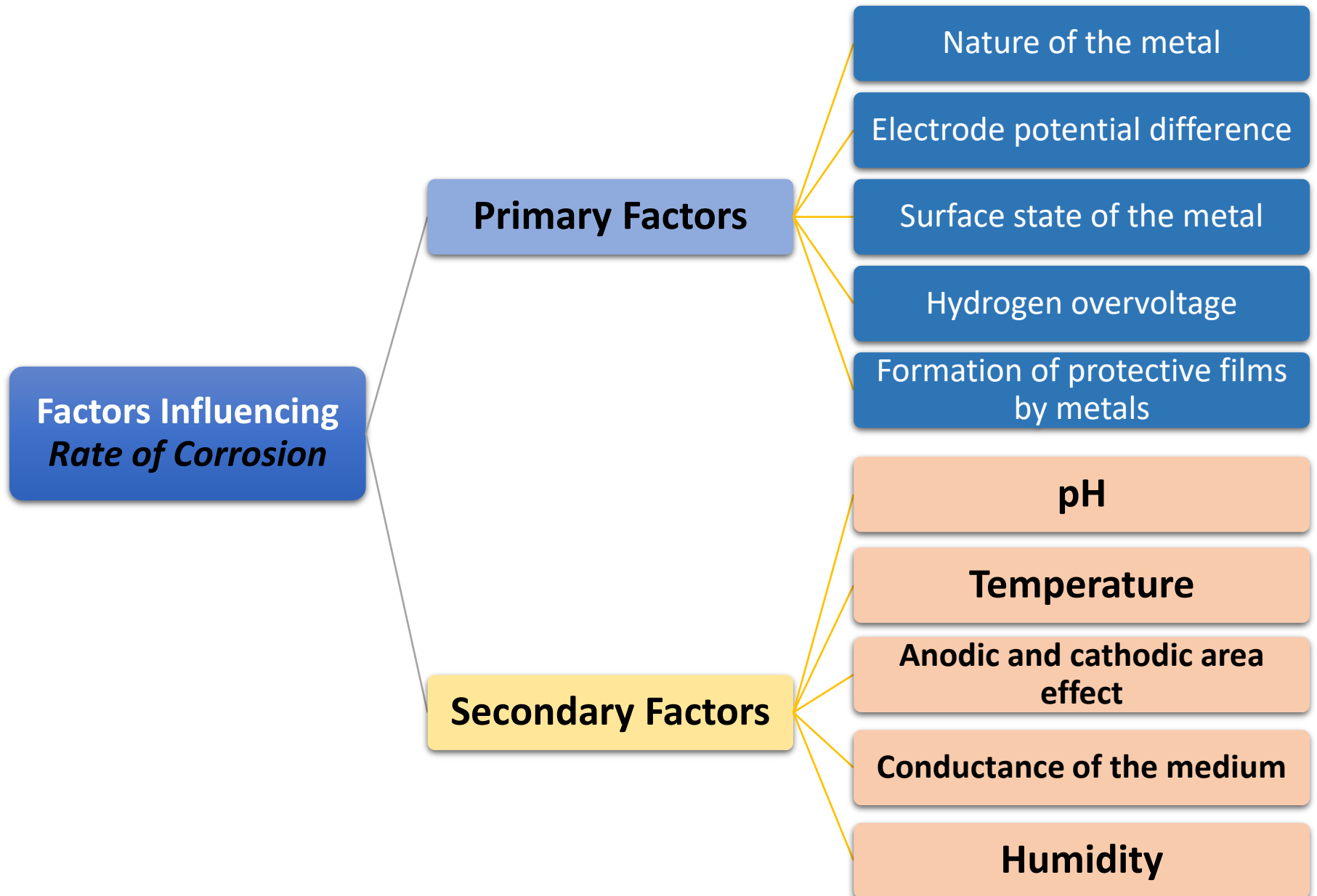


# Iron corrosion

**Anode Reaction:**  $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^{-}$

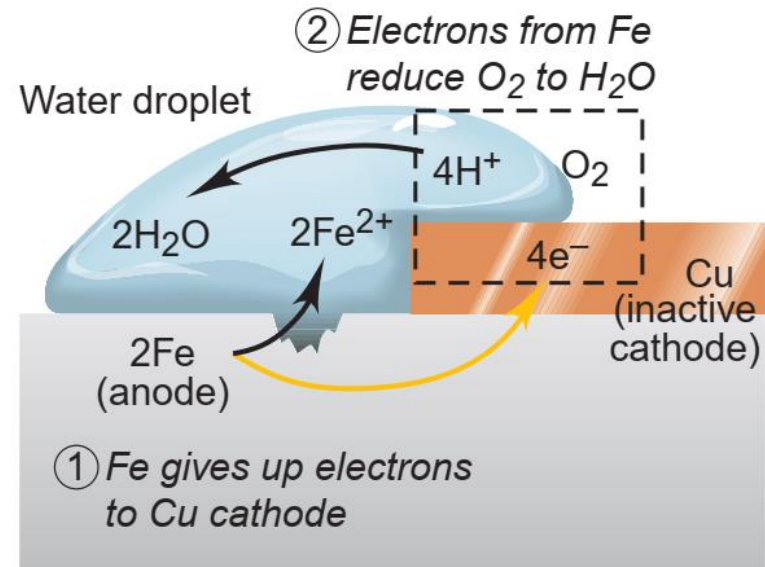
**Cathode Reaction:**  $\text{O}_2(\text{g}) + 4\text{H}^{+}(\text{aq}) + 4\text{e}^{-} \longrightarrow 2\text{H}_2\text{O}(\text{l})$

- **moisture** must be present.
- Iron does not rust in air-free water: **oxygen** must be present.
- Iron rusts more quickly at **low pH** (high  $[\text{H}^{+}]$ )



# Enhancing Corrosion

- Relative activity of other metals in contact with iron (fact 6), which leads to the most effective way to prevent corrosion.
- The essential idea is that *iron functions as both anode and cathode in the rusting process, but it is lost only at the anode*
- Therefore, anything that makes **iron behave more like the anode increases corrosion.**
- When **iron is in contact with a less active metal** (weaker reducing agent), such as **copper**, its anodic function is enhanced.
- As a result, when iron plumbing is connected directly to copper plumbing, the **iron pipe corrodes rapidly.**



A Enhanced corrosion

# Corrosion Prevention

- A common approach to preventing or limiting corrosion is to **eliminate contact** with the corrosive factors.
- **Protective coating**: paint coating is a cost-effective way of preventing corrosion. Iron objects are frequently **painted** to keep out  $O_2$  and moisture, but if the paint layer chips, rusting proceeds.
- **Environmental Measurement**: Corrosion is caused by a chemical reaction between the metal and gases in the surrounding environment. By taking measures to control the environment, these unwanted reactions can be minimized. The simple act of washing off road **salt** removes the ionic solution from auto bodies.
- More **permanent coatings** include **chromium plated** on plumbing fixtures.
- **Corrosion Inhibition**: Inhibitors can be applied as a solution or as a protective coating using dispersion techniques. Corrosion inhibitors are commonly applied via a process known as passivation
- **Sacrificial coating: Cathodic Protection**: coating the metal with an additional metal type that is more likely to oxidize

# Sacrificial coating/ Cathodic Protection

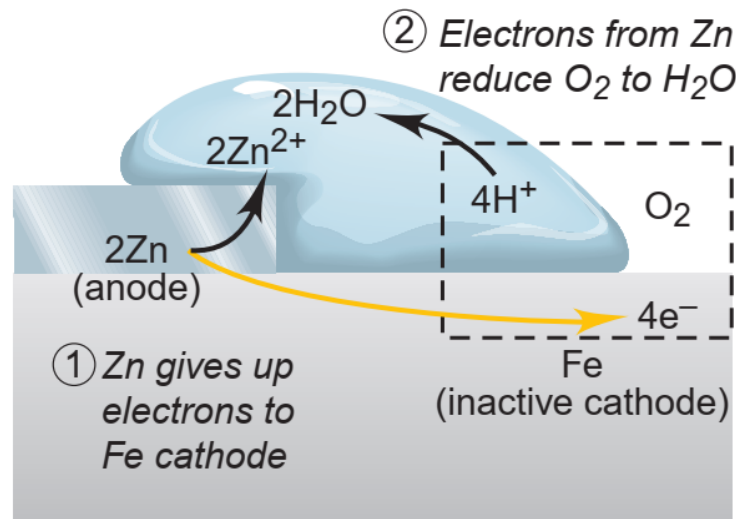
Cathodic protection (CP) is a means to prevent corrosion by applying a flow of electrical current **from** an external source (**anode**) through the environment and on **to the metallic structure** that is being protected

**Galvanic method**

**Impressed  
Current**

# 1. Cathodic Protection: Galvanic (sacrificial) methods

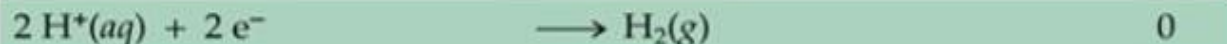
- Anything that makes iron behave more like the cathode prevents corrosion.
- In *cathodic protection*, iron makes contact with a **more active metal** (stronger reducing agent), such as **zinc** (ref. Electrochemical series)
- The iron becomes cathodic and remains intact, while the zinc acts as the anode and loses electrons



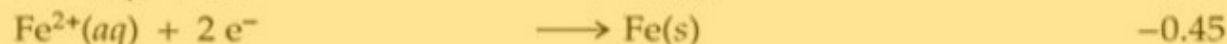
B Cathodic protection

## Cathode

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$\text{I}_2(\text{s}) + 2 \text{e}^-$	$\longrightarrow 2 \text{I}^-(\text{aq})$	0.54
$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^-$	$\longrightarrow 4 \text{OH}^-(\text{aq})$	0.40
$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^-$	$\longrightarrow \text{Cu}(\text{s})$	0.34
$\text{Sn}^{4+}(\text{aq}) + 2 \text{e}^-$	$\longrightarrow \text{Sn}^{2+}(\text{aq})$	0.15



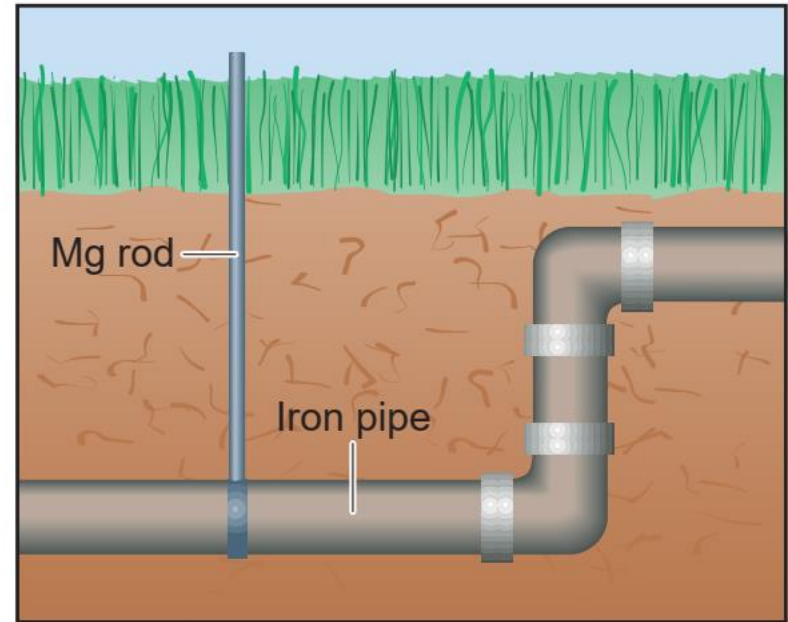
$\text{Pb}^{2+}(\text{aq}) + 2 \text{e}^-$	$\longrightarrow \text{Pb}(\text{s})$	-0.13
$\text{Ni}^{2+}(\text{aq}) + 2 \text{e}^-$	$\longrightarrow \text{Ni}(\text{s})$	-0.26
$\text{Cd}^{2+}(\text{aq}) + 2 \text{e}^-$	$\longrightarrow \text{Cd}(\text{s})$	-0.40



## Anode

$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^-$	$\longrightarrow \text{Zn}(\text{s})$	-0.76
$2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^-$	$\longrightarrow \text{H}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$	-0.83
$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^-$	$\longrightarrow \text{Al}(\text{s})$	-1.66
$\text{Mg}^{2+}(\text{aq}) + 2 \text{e}^-$	$\longrightarrow \text{Mg}(\text{s})$	-2.37
$\text{Na}^+(\text{aq}) + \text{e}^-$	$\longrightarrow \text{Na}(\text{s})$	-2.71
$\text{Li}^+(\text{aq}) + \text{e}^-$	$\longrightarrow \text{Li}(\text{s})$	-3.04

- Sacrificial anodes are employed to protect iron and steel structures (**pipes, tanks, oil rigs**, and so on) in marine and moist underground environments.
- The metals that are most frequently used for this purpose are **magnesium and aluminum** because they are much more active than iron.
- As a result, they act as the anode while iron acts as the cathode



**Figure 21.24** The use of sacrificial anodes to prevent iron corrosion.

In cathodic protection, an active metal, such as magnesium or aluminum, is connected to underground iron pipes to prevent their corrosion. The active metal is sacrificed instead of the iron.

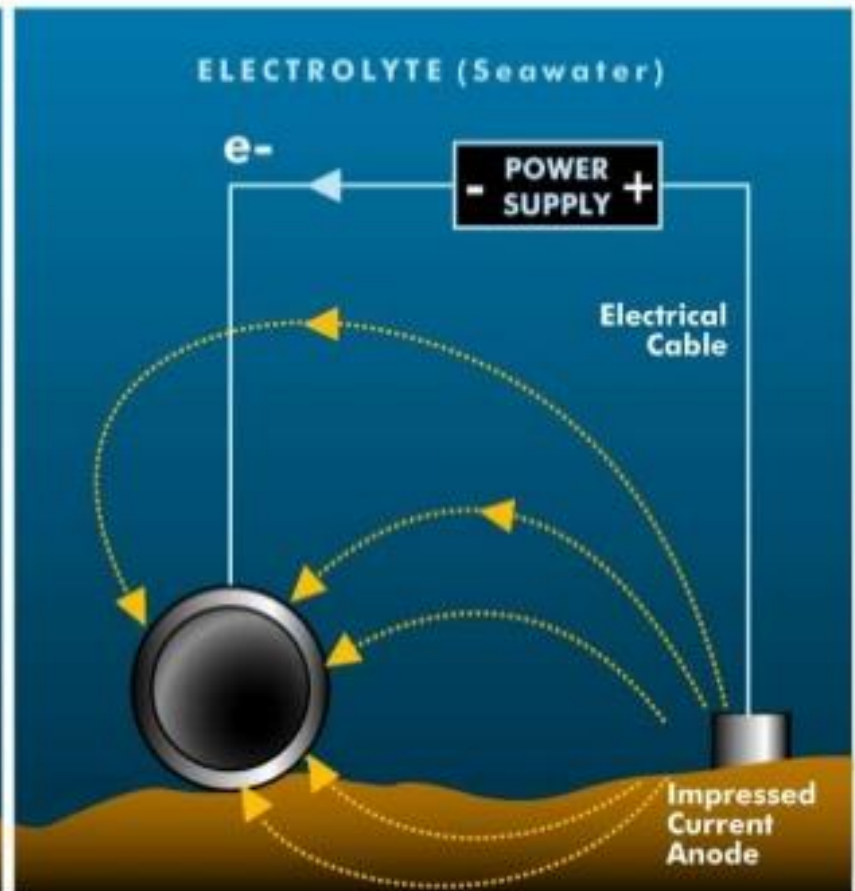
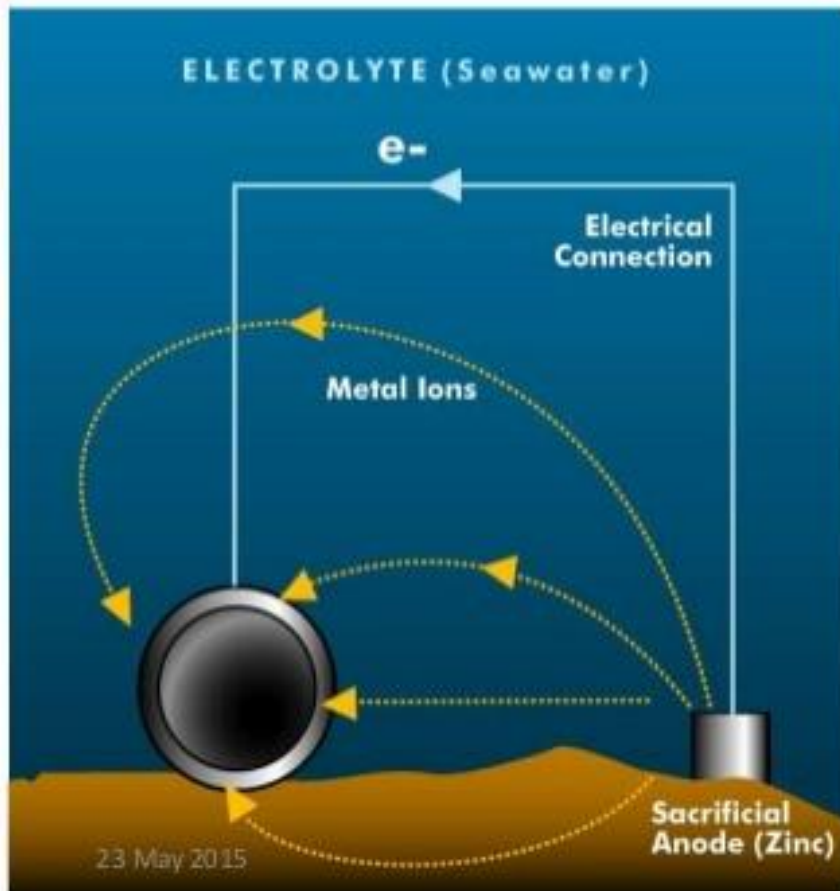


## 2. Impressed current protection methods

- Impressed current anode systems are different than galvanic (sacrificial) systems because they utilize an **external DC power** supply to create the electrical current flow.
- The use of an external power supply enables an impressed current system to generate significantly higher current output with fewer, longer lasting anodes than any sacrificial anode system.
- Impressed current cathodic protection systems have the benefit of using an external power supply to drive current. This makes it possible to protect virtually **any structure**, regardless of **size or current requirements using long life anodes** and enough appropriately sized power supplies.

# Cathodic Protection

# Impressed Cathodic Protection



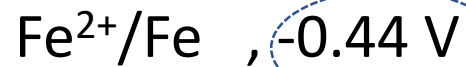
# **Impressed Current Cathodic Protection:**

## **Benefits**

- **Longer Life Anodes**
- **Higher Current Systems**
- **Greater System Control**
- **Ease of Monitoring and Control**

Which one of the following can be used as a sacrificial anode to protect the iron from corrosion? Explain why?

Standard Reduction Potentials



1. Sn



2. Pb



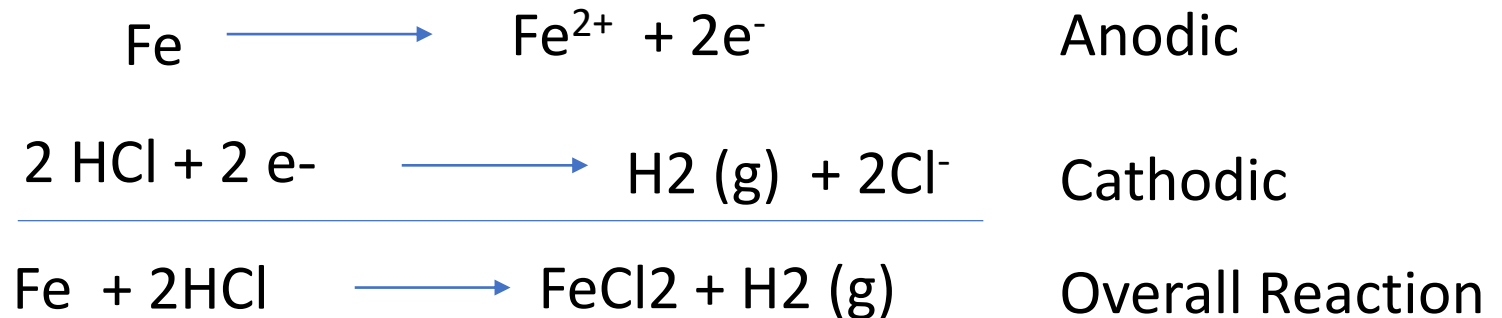
3. Al



4. Ni



# Corrosion of iron in deaerated acid solution



In deaerated acid solution,  $\text{H}^+$  is the electron sink. Hence, dipping of iron in acid solutions leads to corrosion of iron as well hydrogen ( $\text{H}_2$ ) evolution.