



UNIT 5 : Electrochemistry and Metal Corrosion, its Prevention

Electrochemistry and Metal Corrosion: Understanding and Prevention

Introduction

Electrochemistry delves into the relationship between electricity and chemical changes. One of the practical implications of electrochemical processes is metal corrosion, a ubiquitous phenomenon that affects industries, infrastructure, and daily life. Understanding its mechanisms is the first step towards its prevention.

1. Electrochemistry: An Overview

Electrochemistry studies the movement of electrons in redox reactions and the resultant conversion between electrical and chemical energy. Key components in electrochemical reactions include:

- **Electrodes:** Conductive materials where oxidation (anode) and reduction (cathode) reactions occur.
- **Electrolyte:** A medium allowing ion movement, completing the circuit.

Applications range from batteries and fuel cells to electrolysis and electroplating.

2. Metal Corrosion: The Electrochemical Perspective

Corrosion is an electrochemical process where metals deteriorate due to their environment. For metals like iron, the process can be simplified as:

Anode : $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$ - Anode: $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$ - Cathode: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$

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The result is the formation of iron oxides or what we commonly call rust.

3. Factors Influencing Corrosion:

- **Environmental:** Presence of electrolytes, humidity, temperature, and pH levels can accelerate corrosion.
- **Material Properties:** Impurities in the metal, grain size, and inherent electrochemical properties.
- **Physical Factors:** Mechanical stresses and strain can impact the rate of corrosion.

4. Prevention of Metal Corrosion:

- **Barrier Methods:**
 - **Painting:** A protective coat of paint prevents environmental factors from reaching the metal.
 - **Coating:** Metals can be coated with non-corrosive materials like zinc (in a process known as galvanization) or chromium.
- **Sacrificial Anodes:** A more reactive metal (like zinc) is attached to the metal structure. This "sacrificial" metal corrodes instead of the primary metal, offering protection.



- **Alloying:** Introducing other elements into the metal can enhance its resistance to corrosion. Stainless steel, an alloy of iron, chromium, and nickel, is an example.
- **Cathodic Protection:** A technique where an external voltage source is used to ensure that the metal structure becomes the cathode of the electrochemical cell, thus preventing its corrosion.
- **Environmental Control:** Reducing exposure to corrosive agents, using dehumidifiers, or regular cleaning can minimize corrosion.
- **Corrosion Inhibitors:** Chemicals that slow down or prevent corrosion when added to the environment or applied to the metal.

Conclusion:

Electrochemistry provides the foundational understanding behind the pervasive problem of metal corrosion. By comprehending the electrochemical processes driving corrosion and armed with an array of prevention techniques, we can significantly extend the life span of metal structures and devices, ensuring safety and sustainability in numerous applications.

1.1 Electrolyte- Types of electrolyte, ionization and dissociation ,Cathode, Anode, Electrode potential: oxidation and reduction, Mechanism of electrolysis: Electrolysis, Electrochemical series for cations and anions. Mechanism of electrolysis of CuSO₄ solution

Electrolytes and Electrolysis: Unraveling Electrochemical Processes

Introduction

Electrolytes and the process of electrolysis lie at the heart of electrochemistry, influencing everything from industrial processes to biological systems. Delving into their nature, types, and the underlying mechanisms can provide insights into their widespread significance.

1. Electrolyte:

Definition: Electrolytes are substances that, when dissolved in a solvent (usually water), produce ions, thus becoming capable of conducting electricity.

- **Types of Electrolyte:**
- **Strong Electrolytes:** Fully ionize or dissociate in a solution, giving a high concentration of ions. Example: Sodium chloride (NaCl).
- **Weak Electrolytes:** Partially ionize in solution, producing a relatively low concentration of ions. Example: Acetic acid (CH₃COOH).
- **Ionization and Dissociation:**
 - **Ionization:** Process in which neutral molecules produce ions when dissolved in a solvent. It often refers to the formation of ions from acids or bases.
- **Dissociation:** Refers to the breaking up of a compound into its constituent ions. It's typically used for salts.



2. Electrodes in Electrolysis:

- **Cathode:** The electrode where reduction (gain of electrons) occurs.
- **Anode:** The electrode where oxidation (loss of electrons) occurs.

3. Electrode Potential:

It represents the tendency of an electrode to lose or gain electrons.

- **Oxidation Potential:** The tendency of an electrode to get oxidized (lose electrons).
- **Reduction Potential:** The tendency of an electrode to get reduced (gain electrons). It is the negative of oxidation potential.

4. Mechanism of Electrolysis:

- **Electrolysis:** The process by which electrical energy is used to drive a non-spontaneous chemical reaction.
- **Electrochemical Series:** A list of elements arranged in order of their standard reduction potentials. It can be split into two:
 - **For Cations:** Elements at the top have the least tendency to get reduced, while those at the bottom have the highest.
 - **For Anions:** Elements at the bottom have the least tendency to get oxidized, while those at the top have the highest.

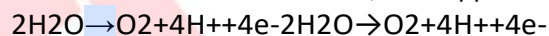
5. Electrolysis of CuSO₄ Solution:

When an electric current is passed through a CuSO₄ solution:

- **At the Cathode:** Reduction occurs. Copper ions (Cu²⁺) gain two electrons to form copper metal.



- **At the Anode:** Oxidation happens. Water molecules are oxidized to produce oxygen gas and H⁺ ions. In some cases, the copper of the anode can dissolve to form Cu²⁺ ions.



Over time, the anode (Made of copper) diminishes in size, while copper gets deposited on the cathode.

Conclusion

Electrolytes and the process of electrolysis encompasses a vast arena in electrochemistry. From purifying metals to understanding cellular processes, the principles and underpinning of these concepts shape myriad applications and phenomena in the natural and industrial world.



1.2 Faraday's laws of electrolysis: Faraday's first and second law, relation between electrochemical equivalent and chemical equivalent, Numerical. Applications of electrolysis: Electro-refining of copper and Electroplating.

Faraday's Laws of Electrolysis: Insights into Electrochemical Transformations

Introduction

Faraday's laws of electrolysis, formulated by the eminent scientist Michael Faraday, provide a quantitative understanding of the relationship between the amount of substance involved in an electrolytic reaction and the electrical current passing through the electrolyte. These laws have profound implications in various applications, from refining metals to electroplating.

1. Faraday's First Law:

Statement: The amount of any substance deposited or liberated during electrolysis is directly proportional to the quantity of electricity passed through it.

Mathematically: $m = zIt$, where m is the mass of the substance, z is the electrochemical equivalent (grams of substance deposited per coulomb of charge), I is the current, and t is the time.

2. Faraday's Second Law:

Statement: When the same quantity of electricity is passed through different electrolytes, the masses of the substances deposited or liberated at the electrodes are proportional to their equivalent weights.

Mathematically: $z_1m_1 = z_2m_2 = z_3m_3$, where m_1, m_2, m_3 are the masses of different substances and z_1, z_2, z_3 are their respective electrochemical equivalents.

3. Relation between Electrochemical Equivalent and Chemical Equivalent:

Chemical Equivalent: The amount of a substance that liberates or combines with 11 gram-equivalent of hydrogen or 88 grams of O_2 .

For any substance, the relation between its electrochemical equivalent z and chemical equivalent E is: $z = nE$, where n is the number of electrons involved in the reaction.

4. Applications of Electrolysis:

- **Electro-Refining of Copper:**
 - Impure copper is made the anode and pure copper is the cathode in a copper sulfate solution.
 - During electrolysis, impurities from the anode dissolve into the solution, while pure copper is deposited on the cathode.
 - This process is used to obtain high-purity copper for electrical applications.
- **Electroplating:**
 - Involves depositing a layer of metal onto another object through electrolysis.



- The object to be plated becomes the cathode, and the metal to be deposited is the anode.
- Electroplating is used to provide decorative finishes, improve corrosion resistance, and modify surface properties of objects.

5. Numerical Example:

Let's say we want to calculate the mass of copper deposited when a current of 22 A is passed through a copper sulfate solution for 3030 minutes.

Given: $I=22$ A, $t=3030$ min (181800 s), $z_{Cu}=0.000328$ g/C.

Using Faraday's First Law: $m = z \cdot I \cdot t = 0.000328 \times 22 \times 181800 = 1.118$ g.

Conclusion:

Faraday's laws of electrolysis provide a quantitative framework for understanding the relationships between electrical current, time, and the amount of substance transformed during electrolytic processes. These laws have practical applications in various industries, helping us refine metals, coat surfaces, and manipulate matter on a molecular level for numerous purposes.

1.3 Difference between primary and secondary cell.

Primary and Secondary Cells: Understanding the Distinctions

Introduction

Primary and secondary cells are two distinct types of electrochemical cells used to store and release electrical energy. While they share the basic principle of converting chemical energy into electrical energy, they differ in terms of their construction, use, and reusability.

1. Primary Cells:

Definition: Primary cells, also known as non-rechargeable cells, are energy storage devices that cannot be recharged once their chemical reactants are consumed.

Operation: They generate electrical energy through a chemical reaction that cannot be reversed. As the reactants are used up, the cell's voltage decreases until it becomes ineffective.

Advantages:

- **Simplicity:** Primary cells are straightforward to use since they don't require external charging.
- **Shelf Life:** They have a longer shelf life compared to secondary cells, making them suitable for emergency use.

Disadvantages:

- **Single Use:** Once the chemical reaction is exhausted, the cell cannot be recharged and must be discarded.
- **Cost:** Replacing primary cells frequently can be more expensive than using rechargeable alternatives.

Examples: Alkaline batteries, zinc-carbon batteries, button cells.



2. Secondary Cells:

Definition: Secondary cells, also known as rechargeable cells, are energy storage devices that can be recharged multiple times by reversing the electrochemical reactions.

Operation: They generate electrical energy through chemical reactions, similar to primary cells. However, the reversible nature of these reactions allows the cell to be recharged by applying an external voltage, reversing the reaction and restoring the reactants.

Advantages:

- **Reusability:** Secondary cells can be recharged many times, making them cost-effective over the long term.
- **Environmental Impact:** Since they are reusable, secondary cells generate less waste compared to primary cells.

Disadvantages:

- **Initial Cost:** Secondary cells often have a higher upfront cost due to their rechargeable nature.
- **Self-Discharge:** They tend to self-discharge over time even when not in use.

Examples: Lithium-ion batteries, nickel-metal hydride (NiMH) batteries, lead-acid batteries.

Conclusion:

In summary, primary cells are one-time-use energy storage devices that cannot be recharged, while secondary cells are rechargeable devices that can be used multiple times after recharging. The choice between primary and secondary cells depends on factors such as usage frequency, cost considerations, and environmental impact.

1.4 Corrosion: Definition and Types of corrosion Dry corrosion: Mechanism, Types of oxide film, Wet corrosion :Mechanism hydrogen evolution in acidic medium, oxygen absorption in neutral or alkaline medium ,Galvanic cell action by Daniel cell

Corrosion: An In-depth Analysis of Material Degradation

Introduction

Corrosion is the gradual degradation of metals due to their reaction with environmental factors. This natural process can compromise the integrity and lifespan of metals, leading to significant economic and structural consequences.

1. Definition of Corrosion:

Corrosion is the spontaneous interaction of a metal with its environment, leading to a measurable change in its properties. This change can be detrimental, causing material loss, alterations in appearance, and degradation in functional properties.



2. Types of Corrosion:

There are various types of corrosion, but two principal categories are:

- **Dry Corrosion:** Occurs when metal reacts directly with gaseous oxygen without the presence of any liquid.
- **Wet Corrosion:** Involves the metal reacting with moisture in the environment, leading to the formation of corrosion products.

3. Dry Corrosion:

- **Mechanism:** Metal reacts directly with atmospheric oxygen, forming an oxide layer. This can be represented as:

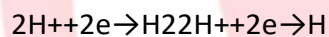


- **Types of Oxide Film:**

- **Passive Film:** A thin, stable, tightly adhering oxide layer that halts further corrosion. Examples include the oxide layer on aluminum or stainless steel.
- **Active Film:** A loose, porous oxide layer that does not protect the underlying metal and allows continued corrosion.

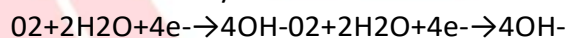
4. Wet Corrosion:

- **Mechanism:**
 - **Hydrogen Evolution in Acidic Medium:** Metal dissolves to form cations and releases electrons. These electrons reduce H^+ ions, resulting in the evolution of hydrogen gas.



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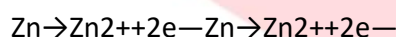
- **Oxygen Absorption in Neutral or Alkaline Medium:** Metal corrodes by releasing electrons, which are then consumed by oxygen in the presence of water, forming hydroxide ions.



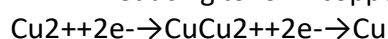
5. Galvanic Cell Action Using the Daniell Cell:

A Daniell cell is a fundamental example of galvanic cell corrosion. It consists of a copper electrode in a copper sulfate solution and a zinc electrode in a zinc sulfate solution, connected by a salt bridge.

- **At the Zinc Electrode:** Zinc oxidizes, losing electrons to become Zn^{2+} ions. This makes the zinc electrode the anode.



- **At the Copper Electrode:** Copper ions in the solution gain electrons from the external circuit, reducing to form copper metal. This makes the copper electrode the cathode.



The potential difference between the two electrodes drives the electron flow, resulting in the corrosion of the anode.



Conclusion:

Corrosion, both dry and wet, is a ubiquitous challenge faced in material science. It not only weakens structures but also incurs economic costs for mitigation and replacement. Understanding the underlying mechanisms and types of corrosion is pivotal for devising effective preventive measures.

1.5 Factors affecting the rate of corrosion.

Factors Affecting the Rate of Corrosion

Introduction

Corrosion, the detrimental reaction of metals with their environment, has significant implications for material durability and longevity. Various factors can influence the rate at which corrosion occurs. Recognizing and understanding these factors can aid in designing effective preventive measures.

1. Environmental Factors:

- **Moisture:** Water acts as a medium for the flow of ions, facilitating the electrochemical reactions responsible for corrosion.
- **Oxygen Concentration:** A higher concentration of oxygen can accelerate the corrosion process, especially in aqueous environments.
- **pH Level:** Extremely acidic or alkaline environments can speed up the corrosion rate. For instance, iron corrodes faster in acidic conditions.
- **Presence of Pollutants:** Salts, especially chlorides, can accelerate the corrosion process. Industrial pollutants like sulfur dioxide can lead to acid rain, which can hasten corrosion.

2. Material Properties:

- **Metal Type:** Some metals, like gold and platinum, are naturally resistant to corrosion, while metals like iron are more susceptible.
- **Purity of the Metal:** Impurities or inclusions in the metal can act as sites for accelerated corrosion, leading to pitting.
- **Protective Oxide Layer:** Metals like aluminum form a protective oxide layer that prevents further corrosion. If this layer is damaged or imperfect, corrosion can occur rapidly.

3. Physical Factors:

- **Temperature:** Increasing the temperature can enhance the rate of chemical reactions, accelerating corrosion. However, in some cases, elevated temperatures can promote the formation of protective oxide layers.
- **Flow Rate of the Fluid:** In environments with flowing liquids, a higher flow rate can remove protective layers on the metal, speeding up corrosion.
- **Stress:** Mechanical stresses in metals can lead to stress corrosion cracking, especially in specific environments.

4. Electrochemical Factors:

- **Galvanic Coupling:** When two different metals are in contact in the presence of an electrolyte, the less noble (more anodic) metal corrodes faster than if it were alone.



- **Electrolyte Concentration:** A higher concentration of ions can enhance the conductivity of the solution, promoting corrosion.
- **Electrode Potential Difference:** A larger difference in electrode potential between two metals in contact can increase the corrosion rate.

5. Microbial Factors:

- **Microbial Activity:** Certain bacteria, like sulfate-reducing bacteria, can accelerate corrosion by altering the local environment or directly participating in electrochemical reactions.

Conclusion:

The rate of corrosion is influenced by a multitude of factors, ranging from environmental conditions to the inherent properties of the metal itself. Understanding these factors is essential for predicting corrosion behavior and devising strategies to mitigate its effects, ensuring the durability and reliability of metallic structures and devices.

1.6 Corrosion control: Modification of environment, Use of protective coatings, coating of less active metal like Tin (Tinning), coating of more active metal like Zinc (Galvanizing), Anodic and cathodic protection, Choice of material-using pure metal and using metal alloy

Corrosion Control: Methods and Techniques

Introduction

Corrosion, the insidious degradation of metals due to environmental interactions, has economic, structural, and safety implications. Given its potential for widespread damage, it's crucial to understand and employ various corrosion control methods.

1. Modification of Environment:

- **Control of pH:** Adjusting the pH of the environment can decrease the rate of corrosion. For example, neutralizing acidic effluents before disposal can minimize corrosion in containment structures.
- **Deaeration:** Removing dissolved oxygen from systems, especially in boilers, reduces oxidative corrosion.
- **Inhibitors:** Chemicals can be added to environments to slow down or prevent corrosion. These chemicals either form a protective layer on the metal or interfere with the corrosion mechanism.

2. Use of Protective Coatings:

- **Paints and Varnishes:** These act as barriers, preventing the metal from coming into contact with corrosive agents.
- **Organic Coatings:** Materials such as plastic or rubber can be used to coat and protect metals.
- **Metallic Coatings:** Applying a layer of metal over another metal can provide corrosion



resistance.

3. Coating with Less Active Metals (e.g., Tinning):

- **Tinning:** It involves coating a metal, usually iron or steel, with a layer of tin. This protects the base metal from corrosion while providing a surface that is resistant and solderable.

4. Coating with More Active Metals (e.g., Galvanizing):

- **Galvanizing:** This process involves coating steel or iron with zinc. The zinc corrodes preferentially, protecting the underlying metal.

5. Anodic and Cathodic Protection:

- **Anodic Protection:** A technique where a protective oxide layer is formed on a metal's surface by applying an external potential, making it act as an anode.
- **Cathodic Protection:** In this method, the metal to be protected is made the cathode of an electrochemical cell, often by connecting it to a more reactive metal. This prevents the metal from corroding.

6. Choice of Material:

- **Using Pure Metals:** Sometimes, using a pure metal can offer better corrosion resistance than an alloy, especially if the corrosion mechanism targets alloying elements.
- **Using Metal Alloys:** In many cases, alloys can provide superior corrosion resistance. For example, stainless steel, which contains chromium, forms a passive oxide layer that protects against corrosion.

7. Design Considerations:

- **Avoiding Crevices:** Designing structures to avoid small crevices and gaps can reduce localized corrosion.
- **Ensuring Proper Drainage:** Designing structures to prevent the pooling of water can prevent corrosion hotspots.

Conclusion:

Controlling corrosion is pivotal in ensuring the longevity, safety, and functionality of metal structures and devices. By understanding and implementing the various methods of corrosion control, industries can prevent material loss, extend equipment lifespan, and ensure structural integrity.

