Electrochemistry

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Electrochemistry links electrical energy to chemical change. The same principles that explain how batteries work also explain how aluminium is extracted from its ore, how jewellery is silver-plated, and why iron rusts faster when in contact with a less reactive metal.

Conductors and Non-Conductors

Substances that allow electric current to pass through them are **conductors**; those that do not are **non-conductors** (insulators).

Conductors	Non-conductors
All metals (copper, aluminium, iron)	Plastics, rubber, glass
Graphite	Dry ionic solids
Molten ionic compounds	Covalent molecular substances (sugar, distilled water)
Aqueous ionic solutions	

Metallic and Electrolytic Conduction

There are two fundamentally different ways a substance can conduct electricity:

Feature	Metallic conduction	Electrolytic conduction
Charge carriers	Delocalised electrons	Mobile ions
Occurs in	Metals and graphite	Molten or aqueous ionic substances
Chemical change?	No	Yes — new substances form at electrodes
Effect of increasing temperature	Conductivity decreases (lattice vibrations impede electrons)	Conductivity increases (ions move faster)

Strong and Weak Electrolytes

An **electrolyte** is a molten or aqueous substance containing mobile ions that can carry electrical charge.

A **strong electrolyte** ionises completely, producing a high concentration of ions and conducting electricity well. Examples: NaCl, HCl, H_2SO_4, NaOH.

A **weak electrolyte** ionises only partially, so the ion concentration is low and conductivity is poor. Examples: ethanoic acid (CH_3COOH), ammonia solution ($NH_3(aq)$), carbonic acid.

A **non-electrolyte** produces no ions at all and does not conduct. Examples: sugar solution, distilled water, ethanol.

Definitions Related to Electrolysis

Electrolysis is the decomposition of an electrolyte by the passage of electricity.

Cathode is the negative electrode. Reduction occurs here — positively charged cations are attracted to it and gain electrons.

Anode is the positive electrode. Oxidation occurs here — negatively charged anions are attracted to it and lose electrons.

Memory aid: **AN OX** (Anode = Oxidation) and **RED CAT** (Reduction at Cathode).

Cations (positive ions) move toward the cathode.

Anions (negative ions) move toward the anode.

Ion Drift During Electrolysis

When a potential difference is applied across an electrolyte:

- Cations drift toward the negative cathode, where they gain electrons and are discharged (reduced).
- Anions drift toward the positive anode, where they lose electrons and are discharged (oxidised).

Which ion is discharged when more than one is present depends on position in the electrochemical series and concentration.

The Electrochemical Series

The electrochemical series ranks elements by their tendency to lose electrons (be oxidised). It is closely related to the reactivity series. Metals high in the series lose electrons readily; metals low in the series hold electrons more tightly.

At the cathode, the ion that is most easily reduced (lowest in the series, closest to the noble metals) is preferentially discharged. At the anode, the ion most easily oxidised is discharged first — generally, halide ions (Cl^-, Br^-) are discharged before OH^- when present in high concentration.

Electrolysis of Selected Substances

Molten Lead(II) Bromide

Electrolyte: molten $PbBr_2$ (contains Pb^{2+} and Br^- ions)

Electrode	Reaction	Observation
Cathode (−)	$Pb^{2+} + 2e^- \rightarrow Pb$	Silvery-grey molten lead forms
Anode (+)	$2Br^- \rightarrow Br_2 + 2e^-$	Brown bromine vapour produced

Acidified Water (Dilute Sulfuric Acid)

Electrolyte: dilute H_2SO_4 (contains H^+ and OH^- ions; SO_4^{2-} is not discharged)

Electrode	Reaction	Observation
Cathode (−)	$2H^+ + 2e^- \rightarrow H_2$	Colourless gas; squeaky pop with a lit splint
Anode (+)	$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$	Colourless gas; relights a glowing splint

The volume of hydrogen collected is twice the volume of oxygen (reflecting the 2 : 1 molar ratio in the reactions).

Concentrated Brine (Saturated NaCl Solution)

Electrolyte: concentrated NaCl(aq) (contains Na^+, H^+, Cl^-, OH^-)

At high chloride concentration, Cl^- is preferentially discharged at the anode rather than OH^-

Electrode	Reaction	Observation
Cathode (−)	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	Hydrogen gas
Anode (+)	$2Cl^- \rightarrow Cl_2 + 2e^-$	Chlorine gas (yellow-green, pungent)
Solution remaining	—	Sodium hydroxide solution

The three products — hydrogen, chlorine, and sodium hydroxide — are all industrially important.

Copper(II) Sulfate Solution

The outcome depends on the electrode material.

With inert (carbon or platinum) electrodes:

Electrode	Reaction	Observation
Cathode (−)	$Cu^{2+} + 2e^- \rightarrow Cu$	Pink-brown copper deposited
Anode (+)	$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$	Oxygen gas produced; solution becomes more acidic

With copper electrodes (used in copper purification and electroplating):

Electrode	Reaction	Observation
Cathode (−)	$Cu^{2+} + 2e^- \rightarrow Cu$	Copper deposited; cathode grows
Anode (+)	$Cu \rightarrow Cu^{2+} + 2e^-$	Anode dissolves; concentration of Cu^{2+} stays constant

📝 **Exam Tip**

When copper electrodes are used in $CuSO_4$ electrolysis, the anode dissolves as copper passes into solution, and the same amount of copper deposits at the cathode. The solution concentration remains constant. This is the basis of copper refining (purification).

The Faraday Constant

The **Faraday constant**(F) is the quantity of electric charge carried by one mole of electrons:

$$F = 96\,500 \text{ C mol}^{-1}$$

The quantity of electricity (charge) passed during electrolysis depends on the current and the time:

$$Q = It$$

where Q is charge in coulombs (C), I is current in amperes (A), and t is time in seconds (s).

Calculations Involving Electrolysis

The number of moles of electrons transferred is found from:

$$n(\text{electrons}) = \frac{Q}{F} = \frac{It}{F}$$

Then the mole ratio from the electrode equation gives moles of product, and mass or volume follows.

📋 **Example**

A current of 2.0 A flows through molten PbBr,for 10 minutes. Calculate the mass of lead deposited at the cathode. (Ar: Pb = 207)

Cathode reaction: Pb^{2}z+ 2e{'Pb (2 electrons per Pb atom)

Charge: Q = It = 2.0 × (10 × 60) = 1200 C

Moles of electrons = 1200 / 96500 = 0.01244 mol

Moles of Pb = 0.01244 / 2 = 0.00622 mol

Mass of Pb = 0.00622 × 207 = **1.29 g**

📋 **Example**

How long must a current of 3.0 A flow through acidified water to produce 240 cm^3 of hydrogen at RTP?

Cathode: $2H^+ + 2e^- \rightarrow H_2$ (2 electrons per H_2 molecule)

Moles of H_2 = 0.240 / 24 = 0.010 mol

Moles of electrons = 0.010 × 2 = 0.020 mol

Charge = 0.020 × 96500 = 1930 C

Time = Q / I = 1930 / 3.0 = **643 s** (about 10.7 minutes)

Industrial Applications of Electrolysis

Extraction of Aluminium

Aluminium is too reactive to be reduced by carbon, so electrolysis is used instead. The ore is bauxite (impure aluminium oxide, Al_2O_3).

Process:

- 1. Bauxite is purified to give aluminium oxide.
- 2. The Al_2O_3 is dissolved in molten cryolite (Na_3AlF_6). Cryolite lowers the melting point from ~2050 °C to ~950 °C, reducing energy costs significantly and also improving conductivity.
- 3. Electrolysis of the molten mixture is carried out in large steel tanks lined with carbon (cathode), with carbon anodes suspended in the melt.

Electrode	Reaction
Cathode (steel lining)	$Al^{3+} + 3e^- \rightarrow Al$ (molten aluminium collects at the bottom and is tapped off)
Anode (carbon)	$2O^{2-} \rightarrow O_2 + 4e^-$ (oxygen produced)

The carbon anodes gradually burn away as the oxygen produced reacts with them:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

Anodes must be replaced periodically.

Electroplating

Electroplating coats an object with a thin layer of another metal using electrolysis. Purposes include improving appearance, preventing corrosion, and reducing cost (using a cheaper base metal).

Setup for silver plating an object:

- Object to be plated = **cathode**
- Silver metal = **anode**
- Electrolyte = silver nitrate solution ($AgNO_3$)

Electrode	Reaction
Cathode (object)	$Ag^+ + e^- \rightarrow Ag$ (silver deposited on object)
Anode (silver)	$Ag \rightarrow Ag^+ + e^-$ (silver dissolves to replenish solution)

The silver concentration in the solution stays constant as the anode dissolves at the same rate as silver deposits on the cathode.

Anodising

Anodising increases the thickness of the protective oxide layer on aluminium. The aluminium object is made the anode in dilute sulfuric acid. Oxygen produced at the anode reacts with the aluminium surface to build up a thicker, harder Al_2O_3 layer. This layer can be dyed to produce coloured finishes.

Purification of Copper

Impure copper (from smelting) is refined using electrolysis in copper sulfate solution. Impure copper is the anode, pure copper is the cathode. Copper dissolves from the anode and deposits as pure copper at the cathode. Insoluble impurities fall to the bottom as anode sludge.

Rusting and Corrosion

Corrosion is the gradual destruction of a metal by chemical reaction with its environment. **Rusting** is specifically the corrosion of iron, forming hydrated iron(III) oxide:

$$4\mathrm{Fe} + 3\mathrm{O}_2 + x\mathrm{H}_2\mathrm{O} \rightarrow 2\mathrm{Fe}_2\mathrm{O}_3 \cdot x\mathrm{H}_2\mathrm{O}$$

Both oxygen and water are required — neither alone causes rusting. Salt water accelerates rusting because it improves conductivity and speeds up the electrochemical process involved.

Methods of preventing rusting:

Method	How it works
Painting	Barrier — excludes air and water
Oiling or greasing	Barrier — especially for moving parts
Galvanising (zinc coating)	Barrier and sacrificial protection
Electroplating (tin or chromium)	Barrier — protects appearance and surface
Alloying (stainless steel)	Chromium in steel forms its own protective oxide layer
Sacrificial protection	A more reactive metal (e.g. magnesium blocks on ships) corrodes preferentially, protecting the iron

In **sacrificial protection**, the more reactive metal is oxidised in preference to iron because it loses electrons more readily. As long as the sacrificial metal is present and in electrical contact with the iron, the iron is protected — even if its surface is scratched.