

Electrochemistry

Introduction to Electrochemistry

Electrolyte

- Ionic compound in molten or aqueous state
- Conducts electricity due to free mobile ions
- Examples: mobile dilute H_2SO_4 , molten NaCl and CuSO_4 solution

Electrodes

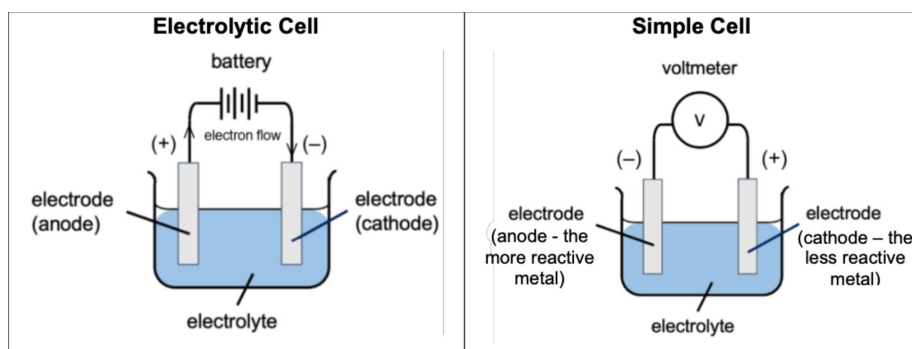
- A rod or plate which conducts electricity through the electrolyte
- **ANODE - OXIDATION** takes place at this electrode
- **CATHODE - REDUCTION** takes place at this electrode
- Types of Electrodes:
 - **Inert Electrode** - An electrode that does not take part in chemical reactions during electrolysis, e.g. graphite/carbon and platinum.
 - It does not react with the product of electrolysis or the electrolytes, and not oxidised in the process.
 - **Reactive Electrode** - An electrode that takes part in chemical reactions during electrolysis, e.g. metal plates such as copper.

Electrolytes

Electrolytes conduct electricity differently from electrodes such as metals and graphite.

	Electrolytes (ionic compound)	Metals	Graphite
Method of Conduction	Mobile ions	Flow of mobile electrons from one end to another	Flow of mobile valence electrons along the layers
Effect of Conduction	Decomposed to form new substances (chemical change)	Remains chemically unchanged.	Remains chemically unchanged

Electrolytic Cells vs Simple Cells



	Electrolytic Cell	Simple Cell
Source of Energy	Electrical energy is supplied by an external source (e.g. battery)	Electrical energy is produced through chemical reactions
Energy Conversion	Electrical -> Chemical	Chemical -> Electrical
Electron Movement	Electrons move from negative terminal of battery to cathode, through electrolyte into anode.	Electrons move from anode to external circuit (voltmeter/bulb e.t.c) into cathode.

Similarities

- Both have positive and negative electrodes
- Both have electrolyte
- Both form a closed circuit with the electrons flowing.
- Electrons flow from anode to cathode.

Differences

Electrolytic Cell

- Electrodes connected by battery (source of energy)
- Anode is positive, cathode is negative

Simple Cell

- Electrodes connected by voltmeter
- Electrodes are different metals (difference in reactivity as the source of chemical energy)
- Anode is negative, cathode is positive.

Why are there these similarities and differences?

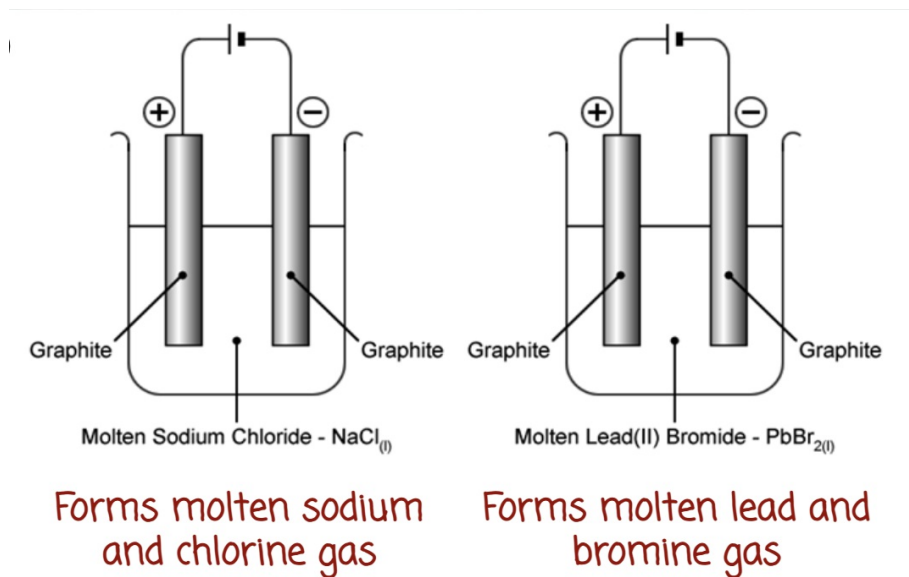
- Opposite polarity for anode and cathode due to difference in energy conversion
- Oxidation always occurs at anode, reduction always occurs at cathode.

Factors Affecting Products of Electrolysis

The polarity of a terminal in an electrolytic cell is **determined by the polarity of the battery it is connected to**.

Definition of Electrolysis

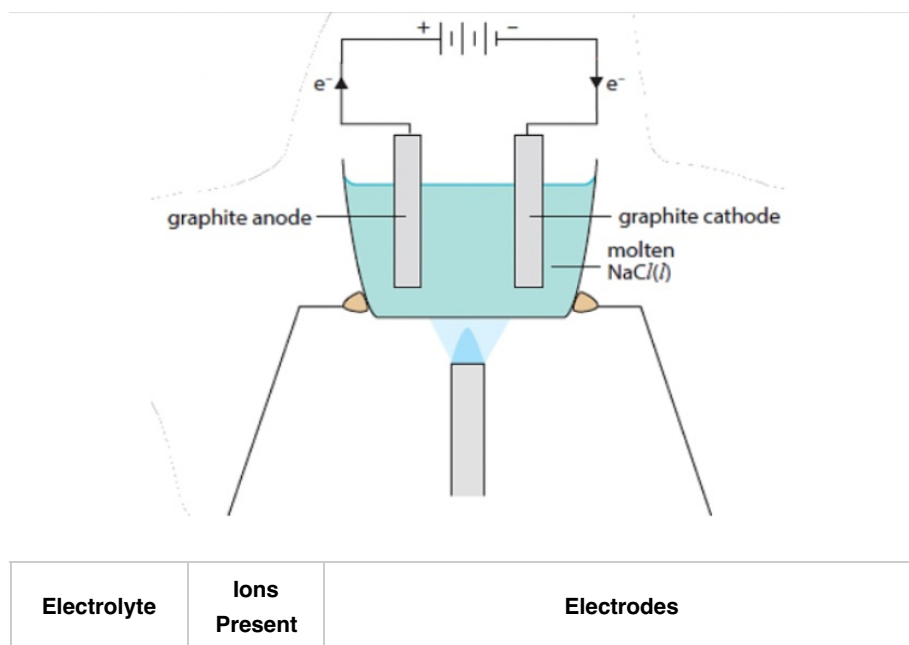
Electrolysis is the decomposition of a compound by electricity.



When the ionic compound is **molten** or when it is **dissolved in water**, the positive and negative **ions** become **mobile** and are free to move towards the electrode of opposite charge, thus **conducting electricity**.

Electrolysis of Molten Sodium Chloride

Set up



Electrolyte	Ions Present	Electrodes
molten sodium chloride, NaCl(l)	$\text{Na}^+(\text{l}), \text{Cl}^-(\text{l})$	Graphite electrode (inert) - may have to be replaced periodically due to graphite reacting with oxygen gas under high temperature.

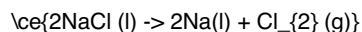
Anode (+) (Oxidation)

- Cl^- attracted to anode
- Cl^- lose electrons to form $\text{Cl}_2(\text{g})$, Cl^- is oxidised
- Cl^- discharged (*meaning ions leave the electrode*)
- Half equation: $2\text{Cl}^-(\text{l}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$

Cathode (-) (Reduction)

- Na^+ attracted to cathode
- Na^+ gain electrons form Na(l) , Na^+ is reduced
- Na^+ is discharged
- Half equation: $\text{Na}^+(\text{l}) + \text{e}^- \rightarrow \text{Na(l)}$ (reduction)

Overall Equation



Observations

- Effervescence of greenish-yellow gas appears around at the anode.
- Greyish (or silvery) liquid is formed at the cathode.

Selective Discharge of Cations and Anions (Aqueous Electrolytes)

- Consider the difference in ions present in molten sodium chloride and aqueous sodium chloride - molten sodium chloride contains only Na^+ and Cl^- ions, while aqueous sodium chloride contains Na^+ , Cl^- , H^+ , OH^- ions.
- In an aqueous solution, water undergoes partial ionisation to form H^+ and OH^- ions:

$$\text{H}_2\text{O(l)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$$
- In an aqueous electrolyte, there will always be more than one type of cation and anion present.
- However, only one type of cation and anion will be selectively (preferentially) discharged during electrolysis.

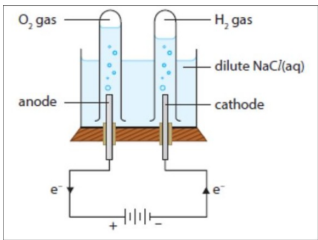
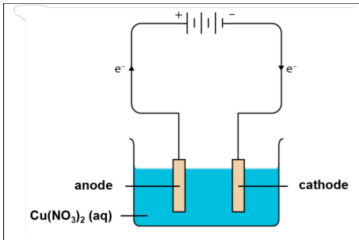
Selective discharge of cations (reactivity series)

Increasing reactivity			Increasing ease of discharge of cation
	potassium (K)	K^+	
	sodium (Na)	Na^+	
	calcium (Ca)	Ca^{2+}	
	magnesium (Mg)	Mg^{2+}	
	zinc (Zn)	Zn^{2+}	
	iron (Fe)	Fe^{2+}	
	lead (Pb)	Pb^{2+}	
	hydrogen (H)	H^+	
	copper (Cu)	Cu^{2+}	
	silver (Ag)	Ag^+	

Selective discharge of anions (electrochemical series)

sulfate	SO_4^{2-}	Increasing ease of discharge of anion
nitrate	NO_3^-	
chloride	Cl^-	
bromide	Br^-	
iodide	I^-	
hydroxide	OH^-	

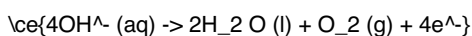
Comparing Dilute Sodium Chloride vs Dilute Copper(II) Nitrate

	Electrolysis of Dilute Sodium Chloride solution	Electrolysis of dilute Copper(II) nitrate solution
Set-Up		
Electrolyte	aqueous sodium chloride, NaCl(aq)	aqueous copper(II) nitrate, $\text{Cu(NO}_3)_2 \text{(aq)}$
Ions present	$\text{Na}^+ \text{(aq)}$, $\text{Cl}^- \text{(aq)}$, $\text{H}^+ \text{(aq)}$, $\text{OH}^- \text{(aq)}$	$\text{Cu}^{2+} \text{(aq)}$, $\text{NO}_3^- \text{(aq)}$, $\text{H}^+ \text{(aq)}$, $\text{OH}^- \text{(aq)}$
Electrodes	graphite electrode (inert)	graphite electrode (inert)

Anode (+) (Oxidation)

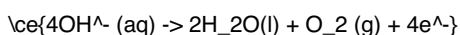
Dilute Sodium Chloride

- Cl^- and OH^- attracted to anode
- OH^- is lower than Cl^- in electrochemical series, hence OH^- is selectively discharged.
- Half equation:



Dilute Copper(II) Nitrate

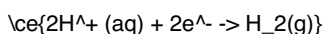
- NO_3^- and OH^- attracted to anode.
- OH^- is lower than NO_3^- in electrochemical series, hence OH^- is selectively discharged.
- Half equation:



Cathode (-) (Reduction)

Dilute Sodium Chloride

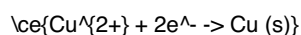
- Na^+ and H^+ attracted to cathode
- Hydrogen is less reactive than sodium, hence H^+ is selectively discharged
- Half equation:



Dilute Copper(II) Nitrate

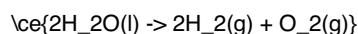
- Cu^{2+} and H^+ attracted to cathode
- Copper is less reactive than hydrogen, hence copper is selectively discharged.

- Half equation:

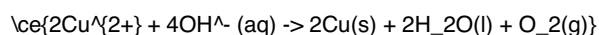


Overall Equation

Dilute Sodium Chloride



Dilute Copper(II) Nitrate



Observations

Dilute Sodium Chloride

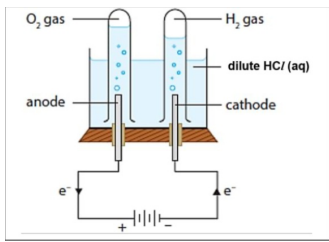
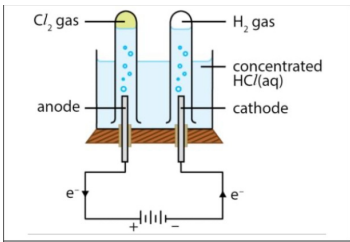
1. Solution remains neutral as both H^+ and OH^- ions are discharged.
2. Water levels drops
3. Effervescence of colourless gas at both electrodes. Volume of hydrogen gas collected at the cathode is twice the volume of oxygen gas collected at the anode. For every 4 moles of electrons transferred, 2 moles of hydrogen gas and 1 mole of oxygen is produced.

Dilute Copper(II) Chloride

1. Solution becomes more acidic as OH^- ions are selective discharged while H^+ ions remain in solution.
2. Reddish-brown solid formed on cathode.
3. Effervescence of colourless gas at anode.
4. Blue solution fades/turns colourless

Concentration of Halide Ions (For aqueous electrolyte)

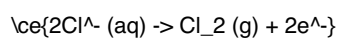
- In a concentrated solution, the ease of discharge of Cl^- , Br^- , or I^- anions increases.

	Electrolysis of dilute HCl(aq) acid	Electrolysis of concentrated HCl(aq)
Set Up		
Electrolyte	dilute hydrochloric acid, HCl(aq)	concentrated hydrochloric acid, HCl(aq)

	Electrolysis of dilute HCl(aq) acid	Electrolysis of concentrated HCl(aq)
Ions present	$\text{H}^+(\text{aq}), \text{OH}^-(\text{aq}), \text{Cl}^-(\text{aq})$	$\text{H}^+(\text{aq}), \text{OH}^-(\text{aq}), \text{Cl}^-(\text{aq})$
Electrodes	graphite electrode (inert)	graphite electrode (inert)

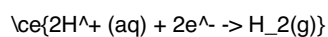
Anode (+) (Oxidation - Concentrated)

- Cl^- and OH^- are attracted to anode.
- Concentration effect applies since concentration of Cl^- is greater than OH^- , hence Cl^- is selectively discharged.
- Half equation:

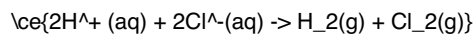


Cathode (-) (Reduction - Concentrated)

- H^+ attracted to cathode
- Since H^+ is the only cation, H^+ selectively discharged
- Half equation:



Overall Equation - Concentrated



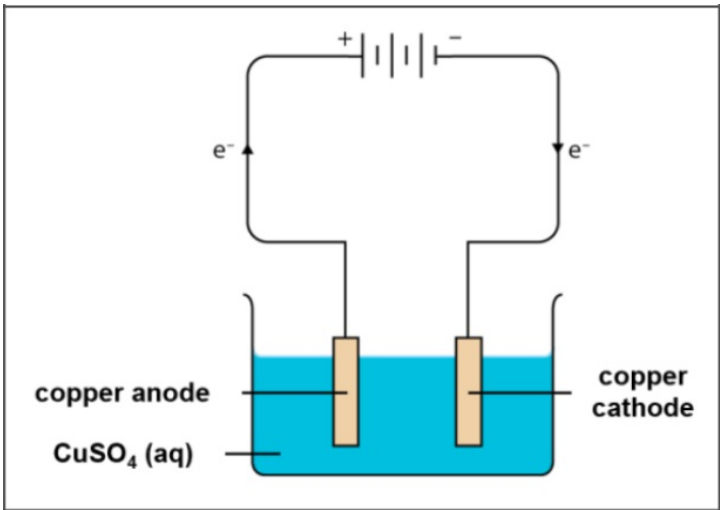
Observations - Concentrated

- Solution becomes less acidic as there is a net discharge of H^+ while OH^- ions remain in solution.
- Effervescence of colourless gas at cathode and greenish-yellow gas at anode. Volume of hydrogen gas collected at the cathode is same as the volume of chlorine gas collected at the anode. For every 2 mole of electrons transferred, 1 mole of hydrogen gas and 1 mole of chlorine is produced.

Types of Electrodes

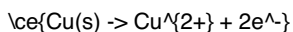
- If the electrode used is not graphite or platinum but another metal, the electrode is reactive and is oxidised as the anode during electrolysis.

	Electrolysis of dilute copper(II) sulfate solution with reactive electrode
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	Electrolysis of dilute copper(II) sulfate solution with reactive electrode
Set Up	
Electrolyte	dilute copper(II) sulfate solution
Ions present	$\text{Cu}^{2+}(\text{aq})$, $\text{SO}_4^{2-}(\text{aq})$, $\text{H}^+(\text{aq})$, $\text{OH}^-(\text{aq})$
Electrodes	copper electrode (inert)

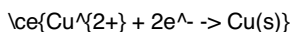
Anode (+) (Oxidation)

- SO_4^{2-} and OH^- attracted to anode
- However, copper electrode is a reactive electrode, copper electrode is oxidised instead of anions.
- Half equation:



Cathode (-) (Reduction)

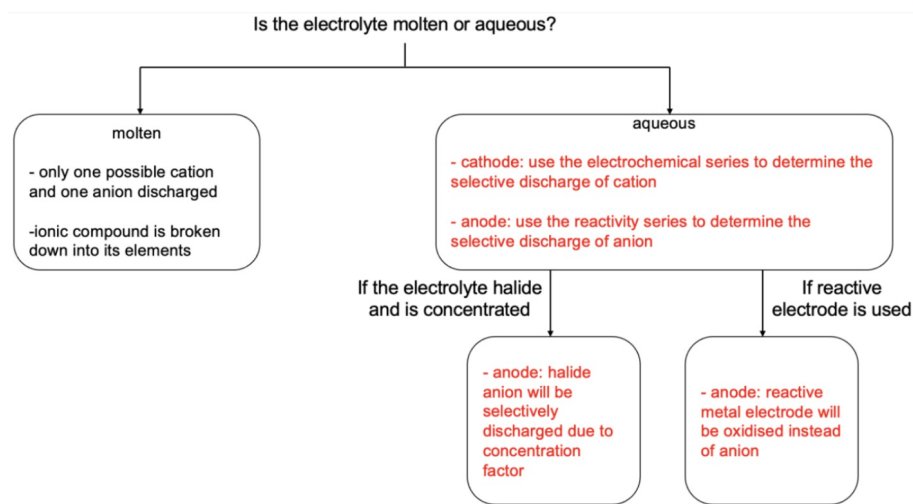
- Cu^{2+} and H^+ attracted to cathode
- Copper is less reactive than hydrogen, hence Cu^{2+} is selectively discharged.
- Half equation:



Observations

- Solution remains neutral as no H^+ and OH^- ions are discharged.
- Intensity of blue solution remains as concentration of Cu^{2+} remains unchanged.
- Size of anode decreases, size of cathode increases.

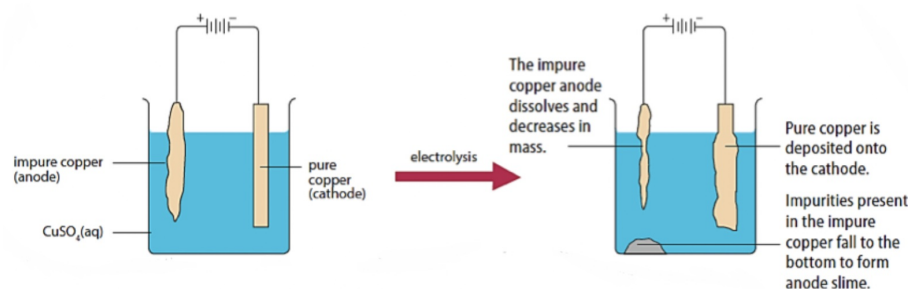
Summary



Applications of Electrolysis

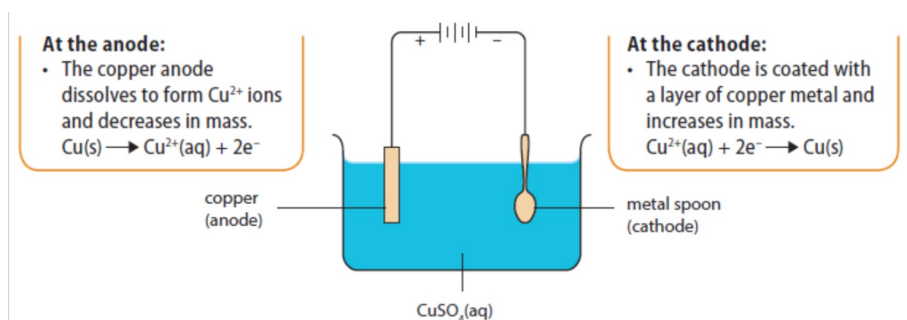
Metal Purification

- Impure copper can be purified using electrolysis
- The piece of impure copper is made the anode (+) and the piece of pure copper is made the cathode(-).
- Electrolyte is an aqueous solution of copper(II) ions.



Electroplating

- Electroplating is coating a thin layer of metal onto an object.
- This is done to protect the object from corrosion and give the object a more attractive appearance.
- The plating metal is made the anode (+), and the object to be plated is made the cathode (-)
- **Electrolyte is an aqueous solution of a salt of the plating metal.**



Hydrogen Fuel Cells

Suggest why scientists want to make hydrogen from sea water.

To reduce the usage of methane (a fossil fuel) to produce hydrogen from steam reforming.
To use non-potable sea water which is present in large quantities, to produce hydrogen instead of more precious fresh water.

Explain why electrolysis of water has high energy costs.

Electrical energy is constantly supplied to split water to form hydrogen and oxygen gas.

Write a half equation to show how chlorine is produced from chloride ions.

