IGCSE Chemistry CIE

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4. Electrochemistry

CONTENTS

4.1 Electrolysis

4.1.1 Electrolysis Principles

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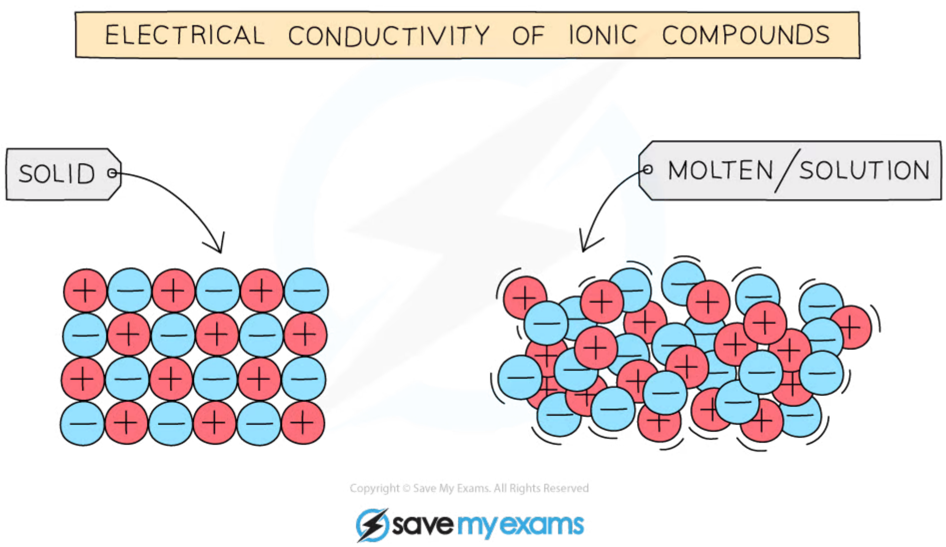
Electrolysis: General Principles

- When an electric current is passed through a **molten ionic compound** the compound decomposes or breaks down
- The process also occurs for **aqueous solutions** of ionic compounds
- Covalent compounds cannot conduct electricity hence they do not undergo electrolysis
- Ionic compounds in the solid state cannot conduct electricity either since they have **no free ions** that can move and carry the charge



Particles in ionic compounds are in fixed position in the solid state but can move around when molten or in solution

Key terms used in a simple electrolytic cell

- **Electrode** is a rod of metal or graphite through which an electric current flows into or out of an electrolyte
- **Electrolyte** is the ionic compound in a molten or dissolved solution that conducts the electricity
- **Anode** is the positive electrode of an electrolysis cell
- **Anion** is a negatively charged ion which is attracted to the anode
- **Cathode** is the negative electrode of an electrolysis cell
- **Cation** is a positively charged ion which is attracted to the cathode

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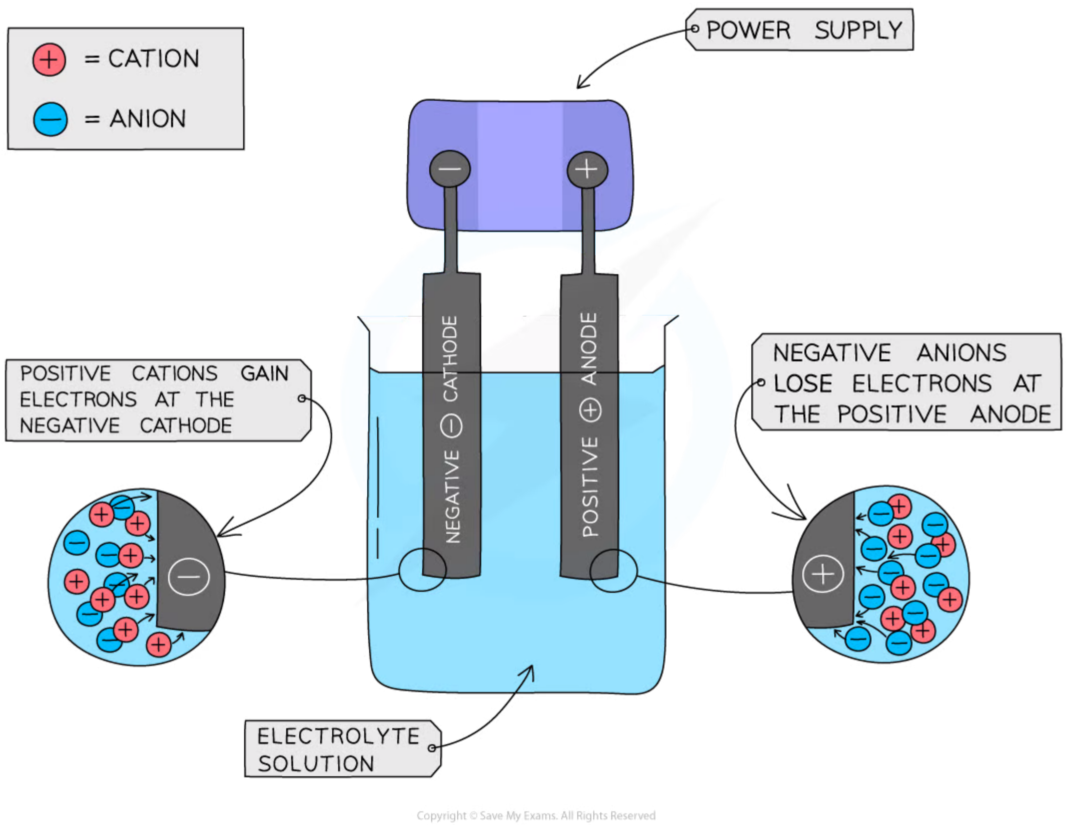

The basic set-up of an electrolytic cell

- Metals and hydrogen form positively charged ions and so either a **metal** or **hydrogen** gas is formed at the **cathode**
- Non-metals form negatively charged ions and so **non-metals (except hydrogen)** are formed at the **anode**

Exam Tip

Use the PANIC mnemonic to remember which electrode is the positive and which is the negative:

Positive (is) Anode Negative Is Cathode

Electrolysis: Charge Transfer

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- During electrolysis, current needs to flow around the circuit
- In order for this to occur, charge must be transferred around the circuit (current is a measure of the rate of flow of charge) by charge carriers
- The power supply provides the **cathode** with a supply of **electrons**, causing it to become negatively charged
- **Positive ions** (cations) in the electrolyte move towards the cathode where they **gain electrons**
- **Negative ions** (anions) in the electrolyte move towards the anode where they **lose electrons**
- The **electrons** move from the anode back towards the power supply
- So, in a complete circuit:
  - **Electrons** are the charge carriers in the **external circuit**
  - **Ions** are the charge carriers in the **electrolyte**

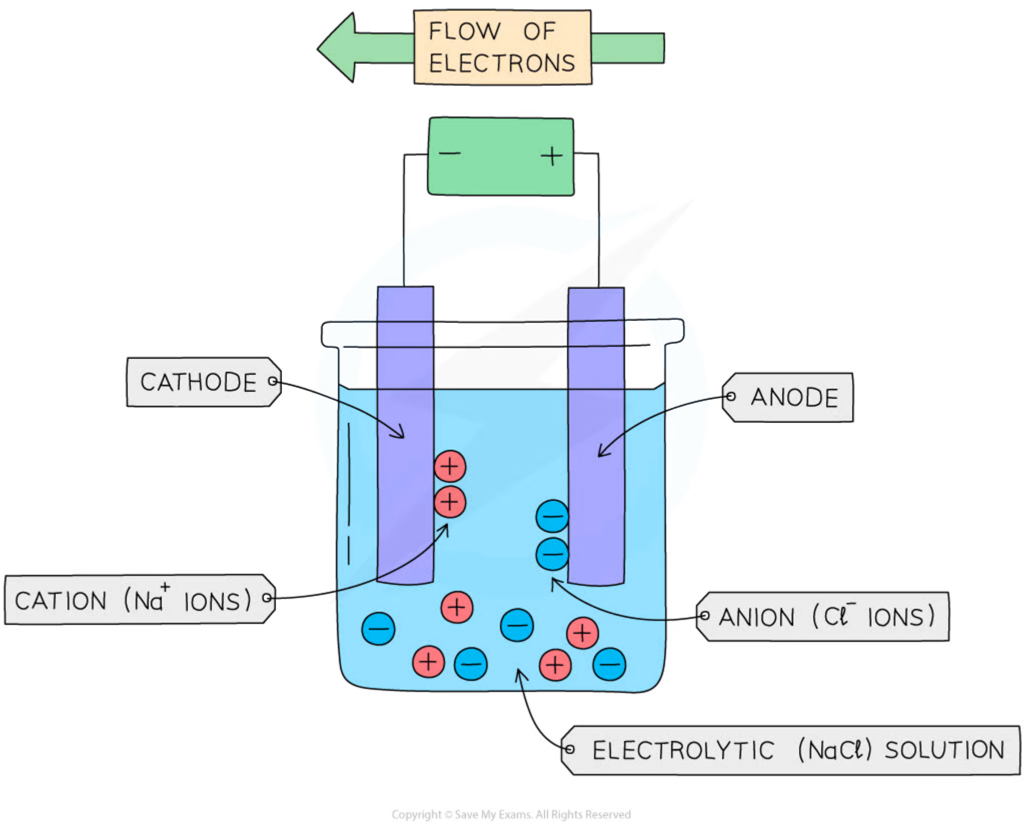

Diagram showing the direction of movement of electrons and ions in the electrolysis of NaCl

4.1.2 Electrolysis of Molten Compounds

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Electrolysis of Molten Compounds

- A binary ionic compound is one consisting of just two elements joined together by ionic bonding
- When these compounds undergo electrolysis they always produce their corresponding elements
- To predict the products made at each electrode, first identify the ions
- The **positive** ion will migrate towards the **cathode** and the **negative** ion will migrate towards the **anode**
- Therefore, the **cathode** product will always be the **metal,** and the product formed at the **anode** will always be the **non-metal**

Example: Electrolysis of molten lead(II) bromide

Method:

- Add lead(II) bromide into a beaker and heat it so it will turn molten, allowing ions to be free to move and conduct an electric charge
- Add two graphite rods as the electrodes and connect this to a power pack or battery
- Turn on the power pack or battery and allow electrolysis to take place
- Negative bromide ions move to the positive electrode (anode) and each loses one electron to form bromine molecules. There is bubbling at the anode as brown **bromine gas is given off**
- Positive lead ions move to the negative electrode (cathode) and gain electrons to form a **grey lead metal** which deposits on the surface of the electrode

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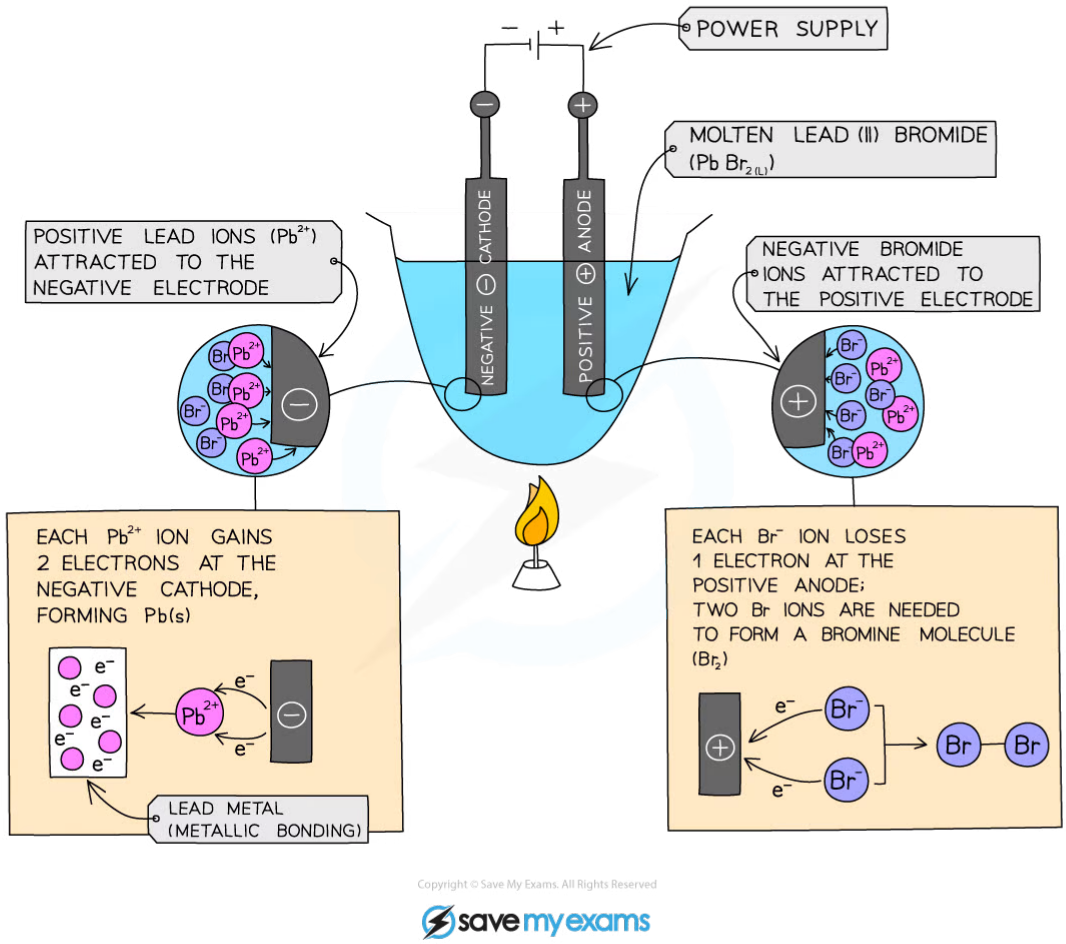

Diagram showing the electrolysis of lead(II) bromide

Worked Example

Identify the product formed at the anode and cathode during the electrolysis of molten potassium chloride.

Answer:

- The ions present are potassium (K^+) and chloride (Cl^-)
- The chloride ions are attracted to the anode and form chlorine gas
- The potassium ions are attracted to the cathode and form potassium metal

Exam Tip

Remember electrodes need to be inert such as graphite or platinum so that they don't participate in a side reaction with the electrolyte.

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Electrolysis of Aqueous Sodium Chloride & Dilute Sulfuric Acid

Aqueous sodium chloride

- **Brine** is a concentrated solution of aqueous sodium chloride
- It can be electrolysed using inert electrodes made from platinum or carbon/graphite
- When electrolysed, it produces bubbles of gas at both electrodes as chlorine and hydrogen are produced, leaving behind sodium hydroxide solution
- These substances all have important industrial uses:
  - Chlorine is used to make bleach
  - Hydrogen is used to make margarine
  - Sodium hydroxide is used to make soap and detergents

Product at the Negative Electrode:

- The H^+ ions are discharged at the **cathode** as they are less reactive than sodium ions
- The H^+ ions gain electrons to form hydrogen gas

Product at the Positive Electrode:

- The Cl^- ions are discharged at the **anode**
- They lose electrons and **chlorine gas forms**
- The Na^+ and OH^- ions remain behind and form the NaOH solution

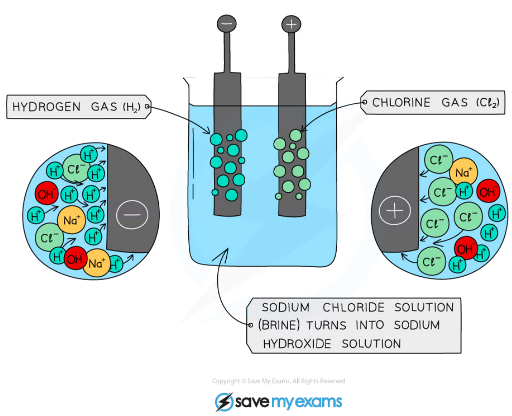

Diagram showing the products of the electrolysis of aqueous sodium chloride

Dilute sulfuric acid

- Dilute sulfuric acid can be electrolysed using inert electrodes made from platinum or carbon/graphite
- Bubbles of gas are seen at both electrodes

Product at the Negative Electrode

- H^+ ions are attracted to the **cathode,** gain electrons and form **hydrogen gas**

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Product at the Positive Electrode

- OH^- ions are attracted to the **anode**, lose electrons and form **oxygen gas** and water

Determining what gas is produced

- If the gas produced at the **anode** relights a glowing splint dipped into a sample of the gas then the gas is **oxygen**

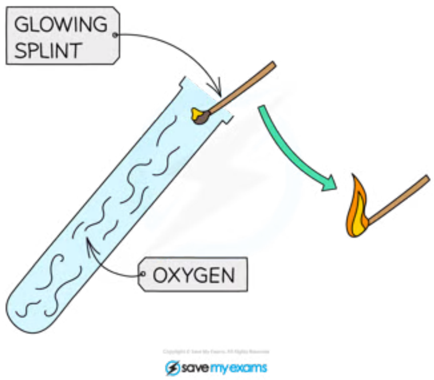

Diagram showing the test for oxygen gas

- If the gas produced at the **anode** bleaches damp litmus paper then the gas is **chlorine**

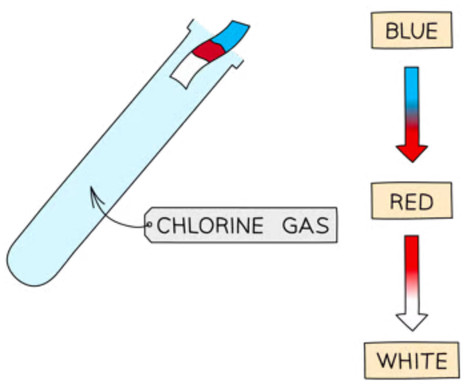

Diagram showing the test for chlorine gas

- If the gas produced at the **cathode** burns with a 'pop' when a sample is lit with a lighted splint then the gas is **hydrogen**

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Diagram showing the test for hydrogen gas

4.1.4 Electrolysis of Aqueous Solutions

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Electrolysis of Aqueous Solutions

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- Aqueous solutions will always have water present (H_2O)
- In the electrolysis of aqueous solutions, the water molecules dissociate producing H^+ and OH^- ions:

$$H_2O \rightleftharpoons H^+ + OH^-$$

- These ions are also involved in the process and their chemistry must be considered
- We now have an electrolyte that contains ions from the compound plus ions from the water
- Which ions get discharged and at which electrode depends on the **relative reactivity** of the elements involved
- Concentrated and dilute solutions of the **same** compound give **different** products
- For anions, the **more concentrated** ion will tend to get discharged over a more dilute ion

Positive Electrode (anode)

- Negatively charged OH^- ions and non-metal ions are attracted to the positive electrode
- If halide ions (Cl^-, Br^-, I^-) and OH^- are present then the halide ion is discharged at the anode, loses electrons and forms a halogen (chlorine, bromine or iodine)
- If no halide ions are present, then OH^- is discharged at the anode, loses electrons and forms oxygen gas
- In both cases the other negative ion remains in solution
- The concentration of the solution also affects which ion is discharged:
  - If a **concentrated** halide solution is being electrolysed, the **halogen** forms at the anode
  - If a **dilute** halide solution is being electrolysed, **oxygen** is formed
- For example:
  - For a concentrated solution of barium chloride, the Cl^- ions are discharged more readily than the OH^- ions, so chlorine gas is produced at the anode
  - If the solution is dilute however only the OH^- ion is discharged and so oxygen would be formed

Negative Electrode (cathode)

- Positively charged H^+ and metal ions are attracted to the negative electrode but only one will gain electrons
- Either hydrogen gas or metal will be produced
- If the metal is **above hydrogen** in the reactivity series, then hydrogen will be produced and bubbling will be seen at the cathode
- This is because the ions of the more reactive metal will remain in the solution, causing the ions of the least reactive metal to be discharged

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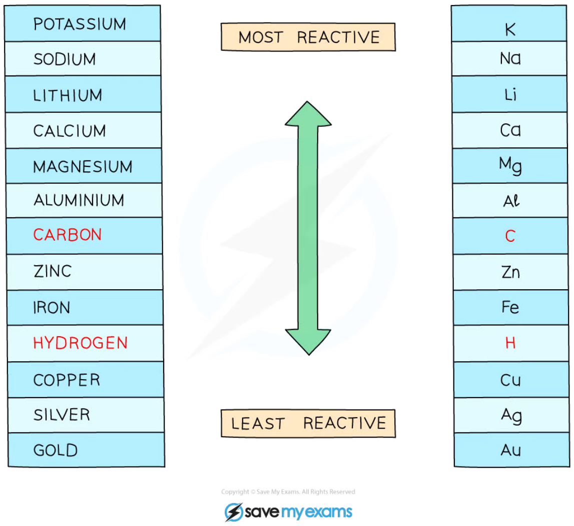
- Therefore, at the cathode, **hydrogen gas** will be produced unless the positive ions from the ionic compound are less reactive than hydrogen, in which case the **metal** is produced



The reactivity series of metals including hydrogen and carbon

Aqueous Copper Sulfate

- Aqueous copper sulfate contains the following ions:
  - Cu^{2+}, SO_4^{2-}, H^+ and OH^-

Product at the Cathode

- Cu^{2+} and H^+ will both be attracted to the cathode but the less reactive ion will be discharged
  - In this case, copper is less reactive than hydrogen
  - Copper ions are discharged at the cathode, gain electrons and are reduced to form copper metal
  - The half equation for the reaction at the electrode is:

$$Cu^{2+} + 2e^- \rightarrow Cu$$

Product at the Anode

- SO_4^{2-} and OH^- are both attracted to the anode
  - OH– ions lose electrons more readily than SO_4^{2-}
  - OH– lose electrons and are oxidised to form oxygen gas
  - The half equation for the reaction at the anode is

$$4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$$

Products formed for Common Aqueous Solutions

Aqueous Solution (Ions present)	Product at Anode	Product of Cathode
Concentrated Sodium Chloride (NaCl)	Chlorine gas released	Hydrogen gas released
Dilute Sodium Chloride (NaCl)	Oxygen produced	Hydrogen gas released
Concentrated aqueous Copper(II) Sulfate ($CuSO_4$)	Oxygen gas released	Copper is lower than hydrogen in the reactivity series so copper is preferentially discharged as a metal
Dilute Sulfuric Acid (H_2SO_4)	Oxygen gas released. H_2O more readily gives up electrons than SO_4^{2-}	Hydrogen gas released

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4.1.5 Ionic Half Equations

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Ionic Half Equations

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- In electrochemistry we are mostly concerned with the transfer of electrons, hence the definitions of oxidation and reduction are applied in terms of electron loss or gain rather than the addition or removal of oxygen
- **Oxidation** is when a substance **loses electrons** and **reduction** is when a substance **gains electrons**
- As the ions come into contact with the electrode, electrons are either lost or gained and they form **neutral s**ubstances
- These are then discharged as products at the electrodes
- At the **anode**, negatively charged ions **lose electrons** and are thus oxidised
- At the **cathode,** the positively charged ions **gain electrons** and are thus reduced
- **Ionic half equations** show the oxidation and reduction of the ions involved
- It is important to make sure the charges are balanced

Table of Reduction and Oxidation Reactions at the Electrodes

	Anode Reaction	Cathode Reaction
Molten Lead Bromide	$2Br^- \longrightarrow Br_2 + 2e^-$	$Pb^{2+} + 2e^- \longrightarrow Pb$
Concentrated Aqueous Sodium Chloride	$2Cl^- \longrightarrow Cl_2 + 2e^-$	$2H^+ + 2e^- \longrightarrow H_2$
Dilute Sulfuric Acid	$4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$	$2H^+ + 2e^- \longrightarrow H_2$

Exam Tip

To help you remember the definitions of oxidation and reduction use OIL RIG

Oxidation **I**s **L**oss (of electrons) **R**eduction **I**s **G**ain (of electrons)

4.2 Applications of Electrolysis

4.2.1 Electroplating

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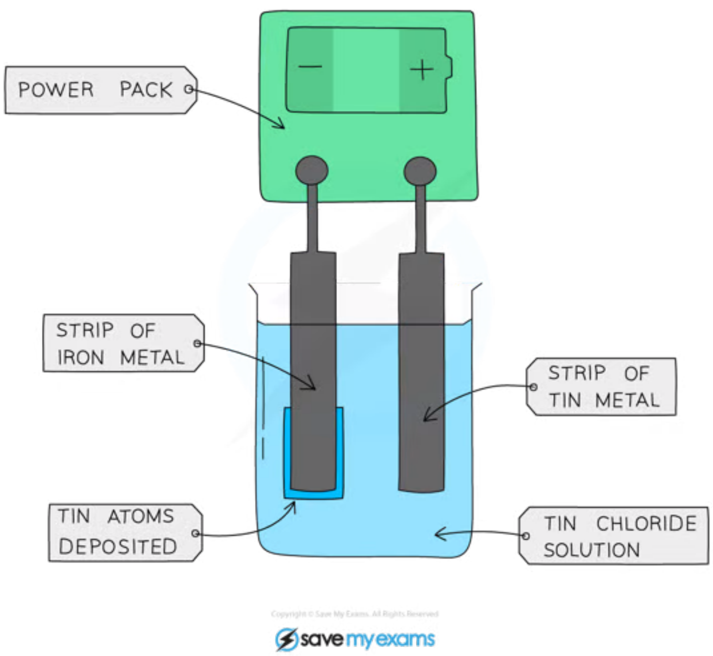
Electroplating

- Electroplating is a process where the surface of one metal is **coated** with a layer of a different metal
- The **anode** is made from the **pure** metal you want to coat your object with
- The **cathode** is the **object** to be electroplated
- The electrolyte is an aqueous solution of a soluble salt of the pure metal at the anode

- **Example:** coating a strip of iron metal with tin:



A piece of iron being electroplated with tin. The electrolyte is tin(II) chloride, a water-soluble salt of tin

- **At the anode:** Tin atoms lose electrons to form tin ions in solution
- **At the cathode:** Tin ions gain electrons to form tin atoms which deposit on the strip of iron metal, coating it with a layer of tin

Uses of electroplating

- Electroplating is done to make metals more **resistant** to corrosion or damage
  - e.g, chromium and nickel plating
- It is also done to **improve the appearance** of metals,
  - e.g. coating cutlery and jewellery with silver

Exam Tip

Extended students may be asked to write the ionic half equations for the reaction at each electrode. For the example above, these would be:

At the anode: $Sn\ (s) \rightarrow Sn^{2+}\ (aq) + 2e^-$

At the cathode: $Sn^{2+}\ (aq) + 2e^- \rightarrow Sn\ (s)$

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4.2.2 Hydrogen Fuel Cells

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Hydrogen Fuel Cells

- A fuel is a substance which releases energy when burned
- Hydrogen is used as a fuel in rocket engines and in fuel cells to power some cars
- A fuel cell is an electrochemical cell in which a fuel **donates** electrons at one electrode and oxygen **gains** electrons at the other electrode
- The **hydrogen-oxygen** fuel cell produces electricity by combining both elements, releasing energy and water
- The overall equation for the reaction within a hydrogen fuel cell is:

$$\text{hydrogen} + \text{oxygen} \rightarrow \text{water}$$

- The diagram below shows the setup of a hydrogen fuel cell
- The air entering provides the oxygen
- The fuel entering is hydrogen
- The only chemical product made is **water**

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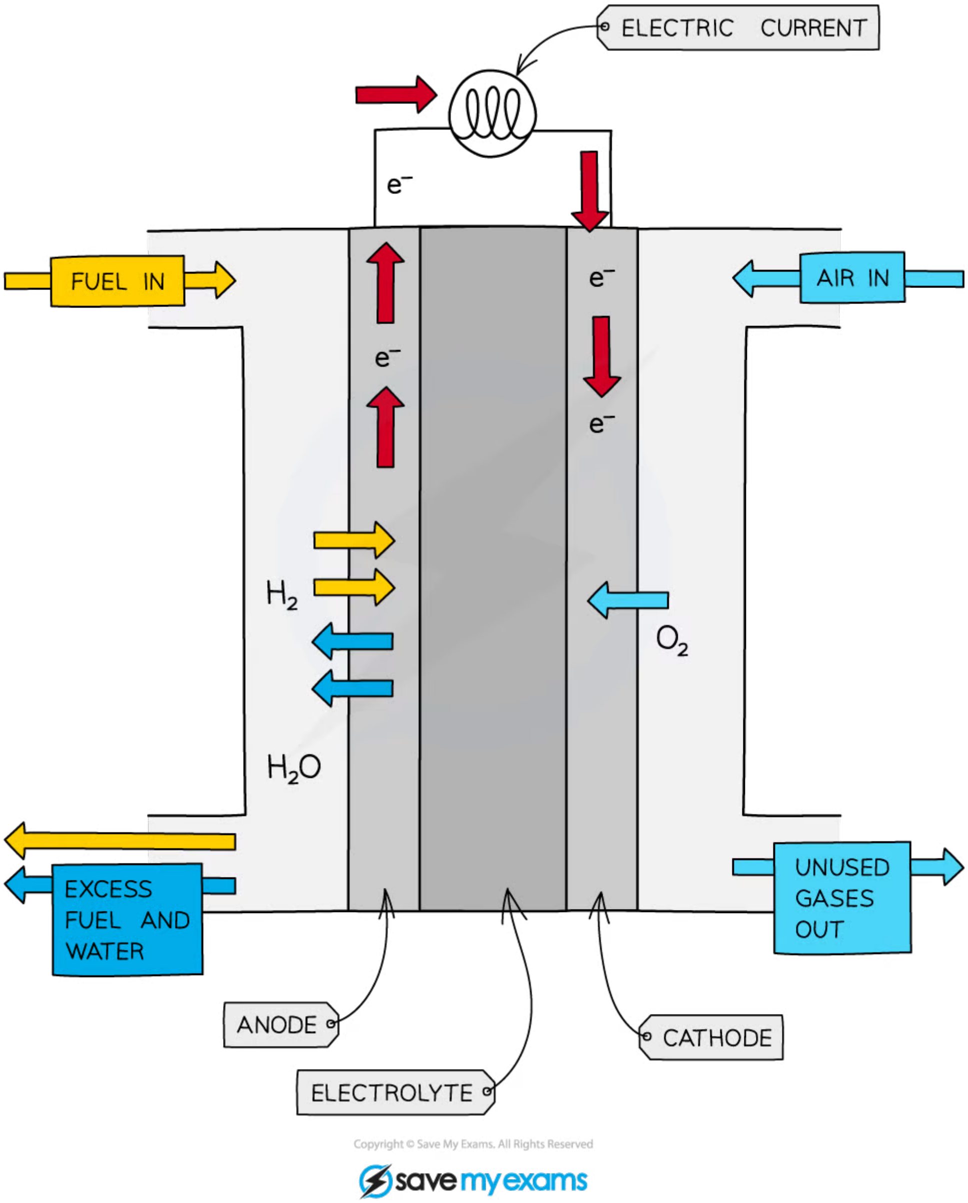

Diagram showing the movement of hydrogen, oxygen and electrons in a hydrogen-oxygen fuel cell

Advantages & Disadvantages of Hydrogen Fuel Cells

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EXTENDED

- Hydrogen-oxygen fuel cells are becoming more common in the automotive industry to replace petrol or diesel engines

Advantages

- They **do not produce any pollution**: the only product is water whereas petrol engines produce carbon dioxide, and oxides of nitrogen
- They release **more energy** per kilogram than either petrol or diesel
- No power is lost in transmission as there are no moving parts, unlike an internal combustion engine
- Quieter so less noise pollution compared to a petrol engine

Disadvantages

- Materials used in producing fuel cells are **expensive**
- Hydrogen is more difficult and expensive to store compared to petrol as it is very flammable and easily explodes when under pressure
- Fuel cells are affected by **low** temperatures, becoming less efficient
- There are only a small number of hydrogen filling stations across the country
- Hydrogen is often obtained by methods that involve the combustion of fossil fuels, therefore releasing carbon dioxide and other pollutants into the atmosphere

Exam Tip

You should be able to state advantages and disadvantages of the hydrogen-oxygen fuel cells in comparison to a petrol engine.