IGCSE CHEMISTRY 0620 · CHAPTER 4 NOTES · ~15 MIN READ

Electrochemistry

How electricity splits compounds, how to predict what appears at each electrode in seconds, how electroplating works — and how a fuel cell turns hydrogen into electricity.

Electrolysis | Products at electrodes | Electroplating | Ionic half-equations | Fuel cells

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No tag = **Core** (everyone) EXTENDED Extended only highlight = comes up again and again

Test yourself at the end

IN 30 SECONDS

- **Electrolysis** = using electricity to break down an ionic compound that is **molten or dissolved**.
- **Cathode (–)** attracts **positive ions** (cations). **Anode (+)** attracts **negative ions** (anions). Remember **PANIC**: Positive Anode, Negative Is Cathode.
- At the cathode you get a **metal or hydrogen**. At the anode you get a **non-metal** (never hydrogen).
- A **hydrogen–oxygen fuel cell** makes electricity from H_2 + O_2 and its only product is **water**.

BY THE END YOU CAN

- Define electrolysis, electrolyte, anode and cathode, and say why the compound must be molten or dissolved.
- Predict the products of electrolysis of molten compounds, concentrated sodium chloride and dilute sulfuric acid.
- Describe electroplating: purpose, set-up and why the object is the cathode.
- Predict products for copper(II) sulfate and halide solutions, and write half-equations. EXT
- Describe a hydrogen–oxygen fuel cell and compare it with a petrol engine. EXT

1 What happens in electrolysis

The key words

Electrolysis — the breakdown of an ionic compound, molten or in aqueous solution, by the passage of electricity.

Electrolyte — the molten or dissolved ionic compound that conducts electricity and is broken down.

Electrode — a rod (usually graphite or platinum) that carries current into or out of the electrolyte. **Inert** electrodes do not take part in the reaction.

Anode — the **positive** electrode. Anions (negative ions) move to it.

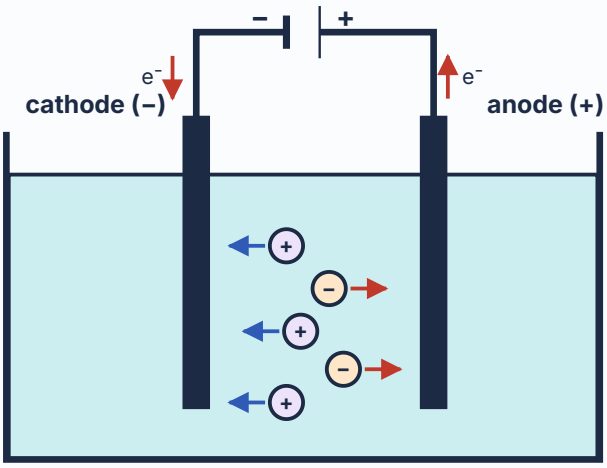
Cathode — the **negative** electrode. Cations (positive ions) move to it.

MEMORY TRICK

PANIC — Positive Anode, Negative Is Cathode.

Why must the electrolyte be molten or dissolved?

- Current in a **wire** is carried by moving **electrons**. Current in an **electrolyte** is carried by moving **ions**.
- In a solid ionic compound the ions are locked in the lattice, so a solid does **not** conduct. When it is **molten** or **dissolved**, the ions are free to move.
- Opposite charges attract: **cations → cathode (–)**, **anions → anode (+)**.



cation

anion

cathode: cations gain electrons = reduction (metal or H_2 forms)

anode: anions lose electrons = oxidation (non-metal forms)

OIL RIG

electrolyte: molten or dissolved ionic compound
carbon (graphite) electrodes are inert

The electrolysis cell. Cations are attracted to the cathode and gain electrons (reduction). Anions go to the anode and lose electrons (oxidation).

What happens at the electrodes?

- At the cathode, a positive ion **gains electrons** and becomes neutral. This is **reduction**.
- At the anode, a negative ion **loses electrons** and becomes neutral. This is **oxidation**.
- This is called **discharging** the ion: it loses its charge.
- EXT Electrons are pushed round the circuit by the power supply. They leave the **negative terminal** and enter the **cathode**; they are taken from the **anode** and return to the **positive terminal**.
- Remember **OIL RIG**: Oxidation Is Loss (of electrons), Reduction Is Gain.

PICTURE IT

Think of the power supply as a pump. It pumps electrons into the cathode, which stuffs them into positive ions. At the anode negative ions give their spare electrons back to the pump.

COMMON MISTAKE

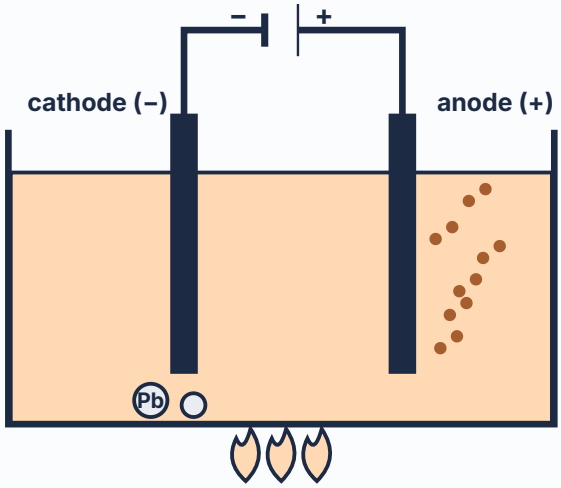
"Electrons travel through the electrolyte." They do not. **Ions** carry the current through the liquid. Electrons only travel in the wires and electrodes.

COMMON MISTAKE

Mixing up the electrodes: the **anode is positive** in electrolysis. Check using PANIC.

2 Electrolysis of molten compounds

Molten lead(II) bromide, $PbBr_2$



cathode (reduction)
$Pb^{2+} + 2e^- \rightarrow Pb$
molten lead sinks

anode (oxidation)
$2Br^- \rightarrow Br_2 + 2e^-$
brown bromine gas

solid $PbBr_2$ does not conduct: the ions are fixed. It must be molten

Molten lead(II) bromide. Lead forms at the cathode; brown bromine gas forms at the anode.

- The compound is heated until it melts, so the ions can move. Ions present: **Pb^{2+}** and **Br^-**.
- **Cathode (–):** Pb^{2+} is attracted here and gains electrons. **Lead** forms as a molten silver-grey metal, which sinks to the bottom.
- **Anode (+):** Br^- is attracted here and loses electrons. **Bromine** is made — orange-brown fumes.
- EXT Cathode (reduction): **$Pb^{2+} + 2e^- \rightarrow Pb$**
- EXT Anode (oxidation): **$2Br^- \rightarrow Br_2 + 2e^-$**

EXAM TIP

A molten **binary** ionic compound (two elements) always gives the **metal at the cathode** and the **non-metal at the anode**. Molten sodium chloride gives sodium and chlorine; molten aluminium oxide gives aluminium and oxygen.

COMMON MISTAKE

Using brine instead of molten NaCl. They give different products — molten NaCl has no water, so it gives sodium, not hydrogen.

- Do it in a **fume cupboard** — bromine is toxic.

Half-equations

EXTENDED

Half-equation — an equation showing what happens at one electrode. Balance the **atoms** and the **charge**. Electrons (e^-) are shown.

- **Cathode:** metal ion + electrons → metal atom (electrons on the **left**).
- **Anode:** non-metal ion → molecule + electrons (electrons on the **right**).

WORKED EXAMPLE

EXT **Write the half-equations for the electrolysis of molten aluminium oxide, Al_2O_3 (ions Al^{3+} and O^{2-}).**

1. Cathode: Al^{3+} gains 3 electrons: **$Al^{3+} + 3e^- \rightarrow Al$**
2. Anode: O^{2-} loses 2 electrons. Oxygen forms as O_2 molecules, so use 2 ions: **$2O^{2-} \rightarrow O_2 + 4e^-$**
3. **Check the charge on the left of the anode equation: 2 × (−2) = −4, and on the right: 4 × (−1) = −4 ✓**

3 Electrolysis of aqueous solutions

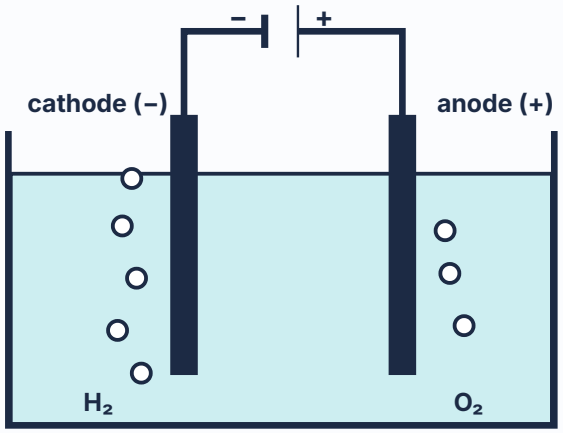
Water adds two extra ions

- In a **solution** there are two sources of ions: the dissolved compound **and** water. Water splits very slightly into **H^+** and **OH^-**.
- So at each electrode there are **two** ions competing to be discharged.

Electrode	Rule
cathode (−)	the metal is formed if it is **less reactive than hydrogen** (for example copper, silver). If the metal is more reactive than hydrogen (sodium, potassium, calcium, magnesium …) then **hydrogen** is formed instead
anode (+)	a **halogen** (Cl_2, Br_2, I_2) forms if a halide ion is present in **concentrated** solution. Otherwise **oxygen** forms from OH^- (this is the case for sulfate, nitrate and dilute halide solutions)

- Never at the anode: hydrogen. Never at the cathode: a non-metal other than hydrogen.

Dilute sulfuric acid



ions: H^+ OH^- SO_4^{2-}

cathode: H^+ discharged
$2H^+ + 2e^- \rightarrow H_2$

anode: OH^- discharged
$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

overall: water is split
$2H_2O \rightarrow 2H_2 + O_2$

dilute sulfuric acid, $H_2SO_4(aq)$

Dilute sulfuric acid is really the electrolysis of water. Hydrogen forms at the cathode and oxygen at the anode, in a 2 : 1 volume ratio.

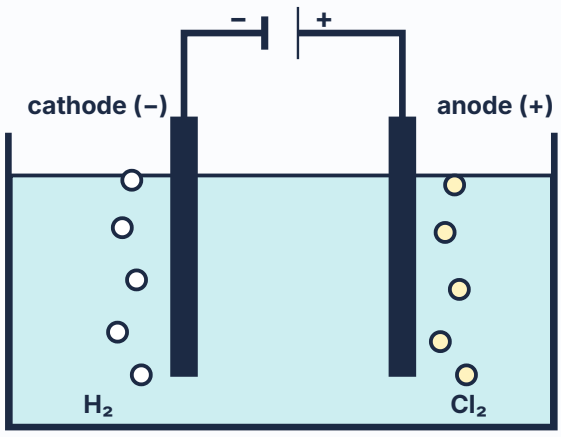
- Ions present: H^+, OH^- (from water) and SO_4^{2-} (from the acid).
- **Cathode:** H^+ is discharged → **hydrogen gas** (test: lit splint → "squeaky pop").
- **Anode:** OH^- is discharged (sulfate is not) → **oxygen gas** (test: glowing splint relights).
- EXT Cathode: **$2H^+ + 2e^- \rightarrow H_2$**. Anode: **$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$**.
- Overall, water is split: $2H_2O \rightarrow 2H_2 + O_2$. Twice as much hydrogen as oxygen by volume, because $2H_2O$ gives $2H_2$ and only 1 O_2. The acid is not used up — it just makes the water conduct, and it gets more concentrated.

WORKED EXAMPLE

In the electrolysis of dilute sulfuric acid, 18 cm^3 of oxygen is collected. What volume of hydrogen is collected?

1. The volume ratio is $H_2 : O_2 = 2 : 1$
2. **volume of $H_2 = 2 \times 18 = 36\ cm^3$**

Concentrated sodium chloride solution (brine)



concentrated sodium chloride solution

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

cathode: H^+ discharged
$2H^+ + 2e^- \rightarrow H_2$

anode: Cl^- discharged
$2Cl^- \rightarrow Cl_2 + 2e^-$

left behind: $Na^+ + OH^-$ = NaOH(aq)

Electrolysis of concentrated sodium chloride solution. Hydrogen forms at the cathode, chlorine at the anode, and sodium hydroxide solution is left behind.

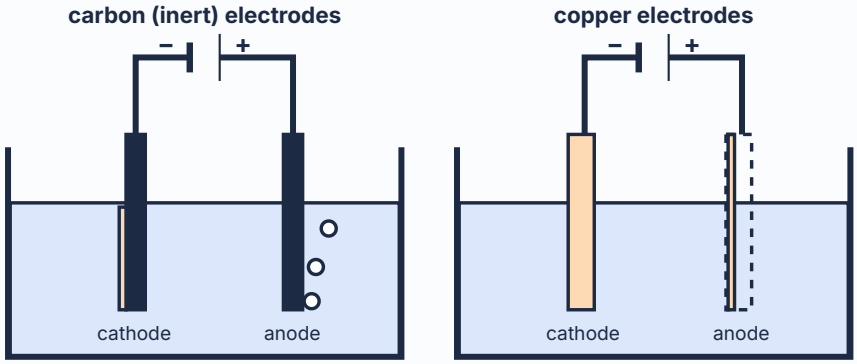
- Ions present: Na^+, H^+, Cl^- and OH^-.
- **Cathode:** sodium is more reactive than hydrogen, so **H^+ is discharged → hydrogen**. No sodium metal forms.
- **Anode:** the solution is concentrated, so **Cl^- is discharged → chlorine gas** (test: bleaches damp blue litmus paper).
- EXT Cathode: **$2H^+ + 2e^- \rightarrow H_2$**. Anode: **$2Cl^- \rightarrow Cl_2 + 2e^-$**.
- The ions left in solution are **Na^+** and **OH^-** — that is **sodium hydroxide solution**.
- **This is a big industry** (the chlor-alkali industry). Chlorine: water treatment, bleach, plastics (PVC). Sodium hydroxide: soap, paper, making aluminium oxide. Hydrogen: fuel and margarine.

COMMON MISTAKE

Saying sodium forms at the cathode in brine. It cannot — sodium is more reactive than hydrogen, so H_2 is formed.

Copper(II) sulfate solution

EXTENDED



cathode: $Cu^{2+} + 2e^- \rightarrow Cu$
(brown copper deposited)
anode: $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$
(O_2 bubbles)
blue colour fades

cathode: $Cu^{2+} + 2e^- \rightarrow Cu$
(copper grows thicker)
anode: $Cu \rightarrow Cu^{2+} + 2e^-$
(copper dissolves)
blue colour stays the same

Copper(II) sulfate solution. Left: carbon electrodes. Right: copper electrodes.

- **Carbon (inert) electrodes:** cathode → **copper** is deposited (copper is less reactive than hydrogen). Anode → **oxygen** (sulfate is not discharged, so OH^- is). The blue colour **fades**, as Cu^{2+} ions are removed, and the solution becomes acidic.
- **Copper electrodes:** the cathode gains a layer of copper. The **anode dissolves**: $Cu \rightarrow Cu^{2+} + 2e^-$. For every Cu^{2+} made at the anode, one is used up at the cathode, so the blue colour **stays the same**. The mass of the anode goes down by the same amount that the cathode goes up.
- Cathode: $\mathbf{Cu^{2+} + 2e^- \rightarrow Cu}$. Anode (carbon): $\mathbf{4OH^- \rightarrow 2H_2O + O_2 + 4e^-}$. Anode (copper): $\mathbf{Cu \rightarrow Cu^{2+} + 2e^-}$.

EXAM TIP

"Active" electrodes (copper) take part in the reaction. "Inert" electrodes (carbon, platinum) do not. Always read the electrode material in the question!

Halide solutions: dilute or concentrated?

EXTENDED

- **Concentrated** halide solution (chloride, bromide, iodide): the **halogen** is formed at the anode.
- **Dilute** halide solution: there are many more water molecules than halide ions, so OH^- is discharged instead and **oxygen** is formed.
- The cathode product is decided in the same way as before (metal or hydrogen).

WORKED EXAMPLE

EXT **Predict the products when concentrated aqueous potassium bromide is electrolysed using inert electrodes.**

1. Ions: K^+, H^+, Br^-, OH^-
2. Cathode: potassium is more reactive than hydrogen → **hydrogen** forms
3. Anode: bromide is concentrated → **bromine** forms (orange-brown)
4. **The solution left is potassium hydroxide**

Summary table

Electrolyte	Cathode (–)	Anode (+)	Left in the solution
molten $PbBr_2$	lead	bromine	–
concentrated NaCl(aq)	hydrogen	chlorine	NaOH(aq)
dilute H_2SO_4(aq)	hydrogen	oxygen	more concentrated acid
EXT $CuSO_4$(aq), carbon electrodes	copper	oxygen	paler blue, more acidic
EXT $CuSO_4$(aq), copper electrodes	copper (cathode gets heavier)	copper dissolves (anode gets lighter)	stays blue

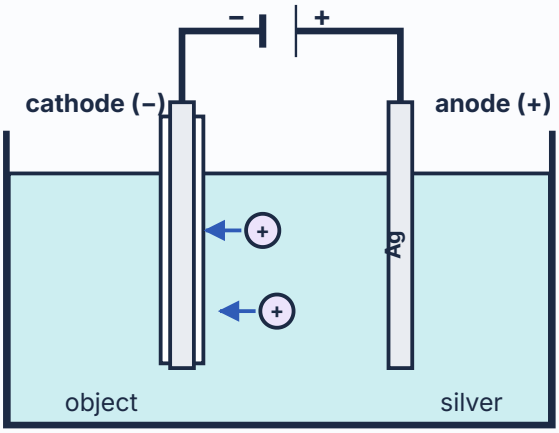
EXAM TIP

Method for any electrolysis: (1) list all the ions, including H^+ and OH^- for solutions; (2) cathode: metal or H_2?; (3) anode: halide (concentrated) or $OH^- \rightarrow O_2$?; (4) what stays in solution?

4 Electroplating

Coating one metal with another

Electroplating — using electrolysis to coat the surface of an object with a thin layer of a metal.



cathode (reduction)
$Ag^+ + e^- \rightarrow Ag$
a layer of silver grows

anode (oxidation)
$Ag \rightarrow Ag^+ + e^-$
the silver bar slowly dissolves

plating metal = anode
object = cathode
solution holds ions of the plating metal

Silver plating. The object to be plated is the cathode, the plating metal is the anode, and the electrolyte contains ions of the plating metal.

- **Object to be plated = cathode (–).**
- **Plating metal = anode (+).**
- **Electrolyte = a solution of a salt of the plating metal** (silver nitrate for silver; copper(II) sulfate for copper).
- Metal ions from the solution gain electrons at the cathode and form a **thin, even layer** on the object.
- EXT Cathode: **$Ag^+ + e^- \rightarrow Ag$**. Anode: **$Ag \rightarrow Ag^+ + e^-$**. The anode replaces the ions used, so the solution stays the same strength.
- **Why plate?** To protect from **corrosion** (chromium, zinc or tin plating on steel) or to improve **appearance** (silver or gold plating on cutlery and jewellery).

PICTURE IT

Imagine the silver bar slowly "posting" its atoms to the spoon: each silver atom dissolves from the bar as an ion and lands on the spoon as a new atom.

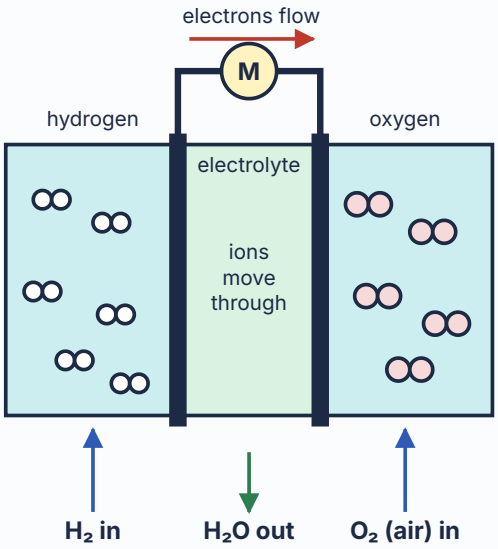
COMMON MISTAKE

Making the object the anode. If it were the anode, the object itself would dissolve!

5 Hydrogen–oxygen fuel cells

Electricity straight from a fuel

Fuel cell — a cell that is supplied continuously with a fuel and oxygen, and uses the reaction between them to generate electricity directly.



overall reaction:
$2H_2 + O_2 \rightarrow 2H_2O$

hydrogen is oxidised at one electrode, oxygen is reduced at the other; electrons flow through the wire and power the motor

only product: water (no CO_2 at the point of use)

A hydrogen–oxygen fuel cell. Hydrogen is oxidised at one electrode and oxygen is reduced at the other. The electrons go through the wire and power the motor.

- Overall reaction: **$2H_2 + O_2 \rightarrow 2H_2O$**.
- The only product is **water**. There is **no carbon dioxide** from the cell itself.
- It is **not** the same as burning hydrogen. In a fuel cell the energy comes out as **electricity**, not heat.

Fuel cell or petrol engine?

EXTENDED

	Hydrogen fuel cell	Petrol engine
product	water only	CO_2, CO, NO_x and soot
efficiency	higher	lower — much energy is wasted as heat
noise	quiet	noisy
fuel	H_2 is hard to store (needs high pressure or a big tank) and is flammable	liquid fuel is easy to store and refuel
fuel source	hydrogen must be made first (often from natural gas, which gives CO_2)	made from crude oil — non-renewable
cost and infrastructure	expensive cells, few filling stations	cheap, an established network

EXAM TIP

When a question says "evaluate" give both sides: advantages (clean, efficient, quiet) **and** disadvantages (storage, safety, hydrogen has to be made, expensive).

COMMON MISTAKE

"Fuel cells are carbon-free." They produce no CO_2 **at the point of use**, but making the hydrogen may produce CO_2.

Test yourself — cover the answers first

QUICK CHECK

1. What is electrolysis?
2. Why does solid sodium chloride not conduct, but molten sodium chloride does?
3. Which electrode is positive? Which ions go to it?
4. Name the products of electrolysis of molten lead(II) bromide.
5. What is the test for hydrogen, and for chlorine?
6. What is the only product of a hydrogen–oxygen fuel cell?
7. EXT Write the half-equation for the formation of chlorine at an anode.
8. EXT During electrolysis of copper(II) sulfate with copper electrodes, what happens to the blue colour?

EXAM-STYLE

9. Describe the electrolysis of concentrated sodium chloride solution. Name the product at each electrode and the substance left in solution. [4]
10. Explain how a steel spoon can be silver plated. [4]
11. EXT Write half-equations for electrolysis of dilute sulfuric acid and explain why hydrogen has twice the volume of oxygen. [4]
12. EXT Give one advantage and one disadvantage of a hydrogen fuel cell compared with a petrol engine. [2]

Show answers

1. breakdown of an ionic compound, molten or in solution, using electricity
2. in the solid the ions cannot move; when molten they are free to move and carry charge
3. anode; negative ions (anions)
4. lead at the cathode, bromine at the anode
5. hydrogen: lit splint gives a squeaky pop; chlorine: bleaches damp litmus paper
6. water
7. $2Cl^- \rightarrow Cl_2 + 2e^-$
8. it stays the same (copper dissolves at the anode and is deposited at the cathode)
9. cathode: hydrogen (H^+ discharged, sodium is more reactive than hydrogen)
   anode: chlorine (Cl^- discharged)
   sodium hydroxide solution is left
   because Na^+ and OH^- ions remain in solution
10. the spoon is the cathode (−)
    a bar of silver is the anode (+)
    electrolyte is silver nitrate solution
    silver ions gain electrons at the spoon and a layer of silver is deposited
11. cathode: $2H^+ + 2e^- \rightarrow H_2$
    anode: $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$
    4 electrons make 2 H_2 at the cathode but only 1 O_2 at the anode
    so the volume ratio is 2 : 1
12. advantage: only water is produced / no CO_2 at the point of use / more efficient
    disadvantage: hydrogen is difficult to store / flammable / expensive / must be made first

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Want regular help? Send this to your parent →