# Effect of electricity on substances

### Electricity

Electricity is a form of energy. An electric current is a flow of electrons in a material.

## Conductors and non-conductors

Those substances that allow electricity to pass through them are called conductors while those that do not allow the passage of electricity through them are called non-conductors or insulators. Sugar, sodium chloride, plastic, cloth, sulphur, wood are some examples of non-conductors.

All metals, whether in solid state or molten state, are good conductors of electricity because they have free and mobile electrons. Carbon in the form of graphite is the only non-metal that is a good conductor of electricity. In non-conductors, electrons are locked up in covalent bonds and are not free to move.

## Electrolysis

Electrolysis is the decomposition of an electrolyte in aqueous solution or molten state by passing an electric current through it.

### Electrolytes and non-electrolytes

An **electrolyte** is a compound in aqueous solution or in molten state which conducts an electric current and it is decomposed as it does so. Electrolytes are composed of ions. In the solid state, the ions are rigidly held in regular positions and are not able to move freely. Melting the solid breaks the forces between the ions and therefore the ions are free to move in a molten electrolyte. Dissolving a solid in water or any other polar solvent, causes the breakdown of the lattice setting the ions free in aqueous state.

A **non-electrolyte** is a solution or a molten compound which does not conduct electricity and therefore cannot be decomposed by an electric current e.g. paraffin, sugar solution, ethanol etc. Non-electrolytes exist only in the form of molecules and are incapable of ionization. The molecules have no charge and are therefore not able to carry an electric current.

### Strong and weak electrolytes

Strong electrolytes are completely ionised in aqueous solution. They have many free and mobile ions. Therefore strong electrolytes have a high electrical conductivity. Examples of strong electrolytes include dilute hydrochloric acid, sodium hydroxide solution and calcium chloride solution.

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

$$NaOH_{(aq)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

$$CaCl_{2(aq)} \rightarrow Ca^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

Weak electrolytes slightly ionise in aqueous solution. They have very few free and mobile ions and therefore they have a low electrical conductivity. Examples of weak electrolytes include ethanoic acid and ammonia solution.

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$

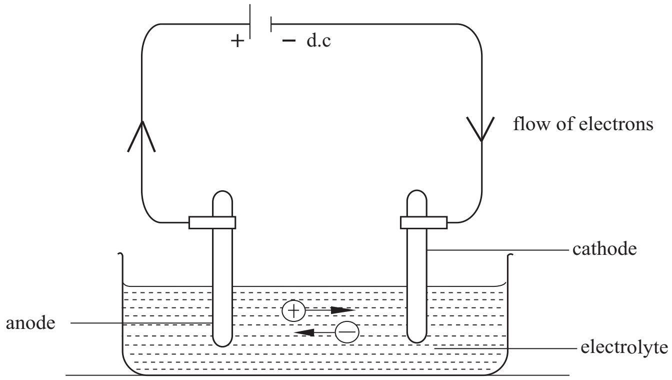
$$NH_4OH_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$$

Other examples of weak electrolytes are carbonic acid, water and most organic acids such as citric acid.

***Refer to exercise 17.2 (Understanding Chemistry by Kaweesi Livingstone)***

## Theory of electrolysis (ionic theory)

When an electrolyte is dissolved in water, the oppositely charged ions are released and start moving freely within the solution. When an electric current is applied to the electrolyte, the negatively charged ions called **anions** move to the positively charged electrode called the **anode.**



Once there, they lose electrons to become atoms and are said to be **discharged**. The positively charged ions called **cations** move to the negatively charged electrode called **cathode** where they gain electrons and become atoms which are then said to be discharged. The electrodes bring the electric current (flow of electrons) into and out of the solution.

**Note:** Anode is the positive electrode at which the electrons enter the external circuit.
Cathode is the negative electrode at which the electrons leave the external circuit.
An electrode must be a good conductor of electricity and should not react with the electrolyte.

### Electrolysis of molten lead(II) bromide

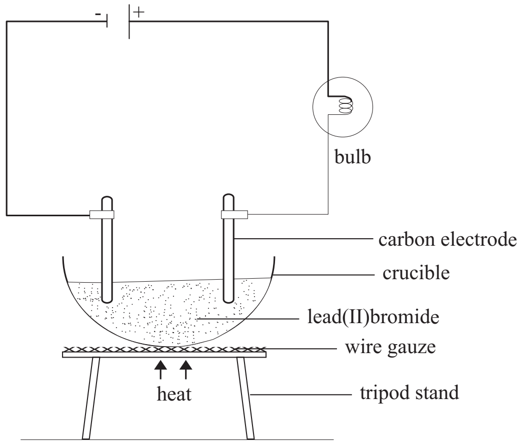
The bulb does not give out light while the lead(II) bromide is solid showing that no electric current passes through the solid lead(II) bromide. As soon as the lead(II) bromide melts, the bulb gives out light. After a while, bubbles of a brown gas are observed at the anode and a shiny grey solid is deposited at the cathode.

*Reaction at the anode:*

$2Br^{-}_{(l)} \rightarrow Br_{2(g)} + 2e^{-}$

*Reaction at the cathode:*

$Pb^{2+}_{(l)} + 2e^{-} \rightarrow Pb_{(s)}$



***Refer to exercise 17.3 (Understanding Chemistry by Kaweesi Livingstone)***

## Selective discharge of ions

When two or more ions of similar charges are present under similar conditions in a solution e.g. $K^+$ and $H^+$ or $SO_4^{2-}$ and $OH^-$, one is selected for discharge. The selective discharge depends on the following factors.

**(a) Position of the metal or group in the electrochemical (activity) series**

If there are two ions with the same charge in the solution, the least reactive ion is discharged first. For example, in electrolysis of sodium chloride solution, both $Na^+$ and $H^+$ (from water) are present and migrate to the cathode. The $H^+$ being less reactive than the $Na^+$, is discharged first.

Reactivity decreasing

| *Cations* | *Anions* |
|---|---|
| $K^+$ | $SO_4^{2-}$ |
| $Na^+$ | $NO_3^-$ |
| $Ca^{2+}$ | $Cl^-$ |
| $Mg^{2+}$ | $Br^-$ |
| $Al^{3+}$ | $I^-$ |
| $Zn^{2+}$ | $OH^-$ |
| $Fe^{2+}$ | |
| $Pb^{2+}$ | |
| $H^+$ | |
| $Cu^{2+}$ | |
| $Ag^+$ | |

Reactivity decreasing

**(b) The nature of electrodes**

This factor may sometimes influence the choice of ion for discharge depending on whether the electrode is active or inert or amount of energy required to discharge the ion at a given electrode.

The most important contrast is the electrolysis of a solution of sodium chloride with mercury as a cathode and with platinum as cathode. With platinum, the hydrogen ion is discharged in accordance with the order of the activity series, sodium ion being higher in the series. The cathode product is hydrogen gas. If the mercury cathode is used, there is a possibility of discharging sodium ion to form sodium amalgam with mercury. This requires less energy than the discharge of hydrogen ions to form hydrogen gas and so occurs in preference.

An example where active or inert electrodes are used, is the electrolysis of copper(II) sulphate solution.

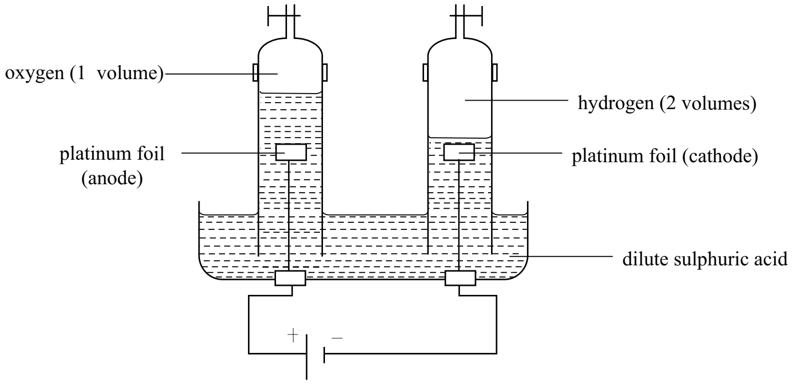
**(c) Concentration of the ions**

Increase of concentration of an ion tends to promote its discharge. For example, in concentrated sodium chloride solution, there are hydroxide ions and chloride ions but the concentration of the chloride ions exceeds that of the hydroxide ions and therefore chloride ions are discharged. The more concentrated ions are discharged in preference to ones which are less concentrated.

***Refer to exercise 17.4 (Understanding Chemistry by Kaweesi Livingstone)***

## Electrolysis of dilute sulphuric acid *(commonly called electrolysis of water)*

Acidified water can be electrolysed using the figure as shown below.



Ions present in acidified water are $H^+$, $OH^-$ and $SO_4^{2-}$.

*Reaction at cathode:*
The hydrogen ions migrate to the cathode, gain electrons and become hydrogen gas.

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

*Reaction at anode:*
The hydroxide ions and sulphate ions migrate to the anode. The hydroxide ions being less reactive than sulphate ions are discharged and oxygen gas is formed.

$$4OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^-$$

*pH changes at anode and cathode:*
The acidity at the cathode decreases (pH increases) because the hydrogen ions are discharged as hydrogen gas and therefore the concentration of hydrogen ions in solution decreases. At the anode, the acidity increases (pH decreases). The discharge of hydroxide ions disturbs the ionic equilibrium of water and therefore more water ionizes to restore it.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

Therefore the excess hydrogen ions produced, with incoming sulphate ions, is equivalent to increased concentration of sulphuric acid.

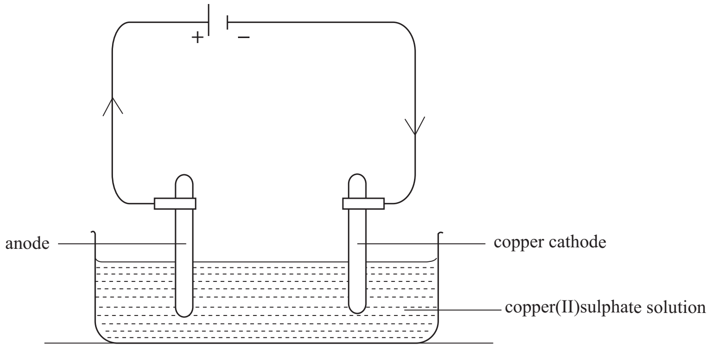
## Electrolysis of copper(II) sulphate solution

*(using copper electrodes - active electrodes)*

Ions present: $Cu^{2+}$, $OH^-$, $H^+$ and $SO_4^{2-}$

*Reaction at cathode:*
Copper(II) ions and hydrogen ions migrate to cathode. Copper(II) ions are discharged because they are less reactive than hydrogen ions. A brown layer of copper is deposited at the cathode.

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$



*Reaction at anode:*

Both the sulphate and hydroxide ions migrate to the anode but none loses its electrons. Instead the copper anode itself loses electrons and as it does so, it becomes copper(II) ions which dissolve in solution. The anode electrode dissolves.

$$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$$

## Electrolysis of copper(II) sulphate solution

*(using copper cathode and platinum anode - inert electrode)*

Ions present are $H^+$, $OH^-$, $Cu^{2+}$ and $SO_4^{2-}$.

Copper(II) ions and hydrogen ions move to the cathode. Copper(II) ions being less reactive than hydrogen ions are discharged. Copper(II) ions gain electrons and copper is deposited.

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$$

Sulphate ions and hydroxide ions move to the anode. Hydroxide ions being less reactive than sulphate ions are discharged by giving up their electrons. Bubbles of a colourless gas (oxygen) are formed at the anode.

$$4OH^-_{(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)} + 4e^-$$

*Observations*

- Bubbles of a colourless gas at anode.
- A brown solid is deposited at cathode.
- The blue solution of the electrolyte fades (because copper(II) ions are removed from the solution).

## Electrolysis of concentrated sodium chloride solution

*(using carbon anode and carbon or platinum cathode)*

Sodium ions from sodium chloride and hydrogen ions from water migrate to the cathode. Hydrogen ions are discharged because they are less reactive than sodium ions.

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$$

Chloride ions from sodium chloride and hydroxide ions from water move to the anode but chloride ions are discharged because they are more concentrated than hydroxide ions, thus chlorine gas (greenish yellow gas) is liberated.

$$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-$$

However, if the sodium chloride solution is very dilute, some discharge of hydroxide ions will also occur. As the sodium chloride solution is diluted, there will not be a point at which chlorine ceases to be produced and oxygen replaces it. Instead, a mixture of the two gases will come off, with the proportion of oxygen gradually increasing.

The same case arises in the electrolysis of hydrochloric acid because the same anions are involved.

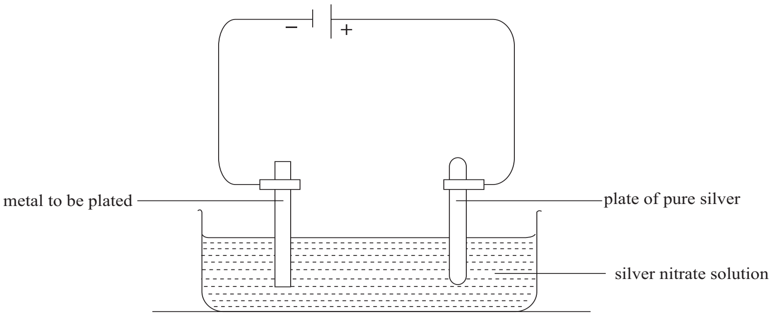
***Refer to exercise 17.5 (Understanding Chemistry by Kaweesi Livingstone)***

## Application of electrolysis

**(i)** ***Electroplating***

This is the process of coating a metal with another metal by the process of electrolysis. Electroplating is done to protect metals from corrosion and to improve their appearance.

The metal to be plated is made the cathode in a suitable electrolyte containing ions of the plating material. For example, during silver plating, the metal to be plated is made the cathode in a silver salt solution as an electrolyte and pure silver is made the anode.



The silver salt solution contains positively charged silver ions which are attracted to the cathode (metal to be plated). Once there, they gain electrons to form silver atoms.

$$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$$

The anode (plate of pure silver) loses its electrons and forms silver ions which dissolve in the solution to replace the ones moving to the cathode. The process continues until an adequate layer of silver has been deposited on the metal being plated.

**(ii)** ***Purification of metals***

Metals such as copper and zinc may be refined, that is, purified by electrolysis. The impure metal is made the anode and the pure metal the cathode. The electrolyte is a solution containing the metal ion.

***Refining of the impure copper***

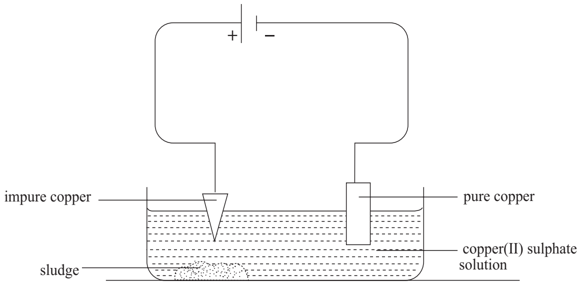
The impure copper is purified (refined) by electrolytic process using copper(II) sulphate solution as the electrolyte. The cathode is pure copper and the impure copper is made the anode. During electrolysis, the copper atoms of the anode lose electrons to form copper (II) ions which dissolve in the solution.

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$$

Then the copper(II) ions are attracted to the cathode where they gain electrons and become copper atoms.

$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$$

The overall effect is that copper gradually dissolves from the anode and is deposited on the cathode. Copper from the cathode is removed by stripping.



Impurities which are higher than copper in the activity series, such as iron, also dissolve from the anode but are not deposited on the cathode. They accumulate in solution in the electrolyte. Impurities which are lower than copper in the activity series do not dissolve at all. They fall to the bottom of the container as sludge.

**(iii)** ***Extraction of metals***

Reactive metals such as aluminium and sodium are extracted by electrolysis of the fused electrolytes.

*Extraction of sodium*

Sodium metal is extracted by electrolysis of fused sodium chloride (obtained from rock salt or seawater) to which calcium chloride has been added to lower its melting point from 800 °C to about 600 °C. This saves electrical energy and therefore makes the process more economical. An iron cathode and a carbon (graphite) anode are used. At 600 °C, sodium and chlorine would react violently together to reform sodium chloride. To prevent this reaction, the Down's cell contains steel gauze around the graphite anode to keep them apart.

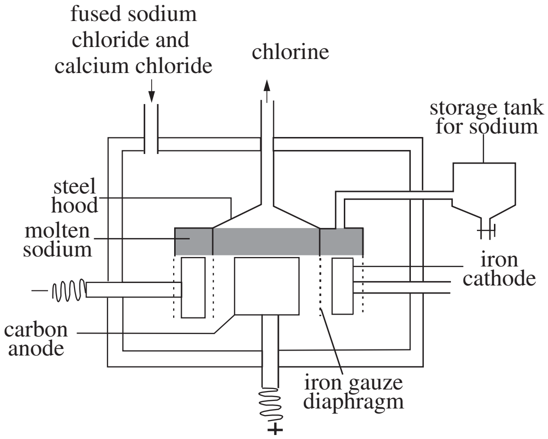
Chlorine gas produced as a by-product is collected in a cylinder. Molten sodium collects in the inverted trough, placed over the cathode, rises up the pipe, and is tapped off and collected under dry nitrogen. Nitrogen is inert under ordinary conditions and therefore hardly reacts with sodium. This process is called **Down's process**.

*Reaction at the cathode:*

$$Na^+_{(l)} + e^- \rightarrow Na_{(s)}$$

*Reaction at the anode:*

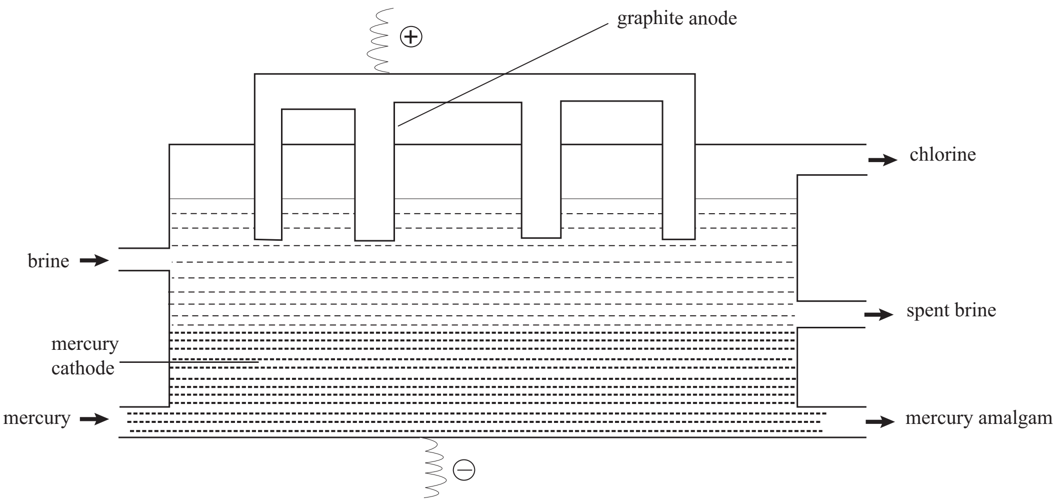
$$2Cl^-_{(l)} \rightarrow Cl_{2(g)} + 2e^-$$



**(v)** ***Manufacture of chemicals***

The most important example is the manufacture of sodium hydroxide, chlorine and hydrogen using the flowing mercury cathode cell. In the manufacture of sodium hydroxide, concentrated sodium chloride solution (brine) is electrolysed using a graphite (carbon) anode and a flowing mercury cathode. The mercury cathode enables sodium ions to discharge in preference to hydrogen ions. Sodium is deposited at the cathode and chlorine is liberated at the anode.

$$Na^+_{(aq)} + e^- \rightarrow Na_{(s)}$$
$$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-$$



The sodium formed dissolves in the mercury cathode to form a solution called sodium amalgam. Amalgams are solutions of metals in mercury. The amalgam is mixed with water producing sodium hydroxide solution, hydrogen and pure mercury.

$$2NaHg_{(l)} + 2H_2O_{(l)} \rightarrow 2NaOH_{(aq)} + H_{2(g)} + 2Hg_{(l)}$$

Mercury is then recycled by use of a pump. Hydrogen is collected as a by-product. Sodium hydroxide solution is evaporated to dryness.

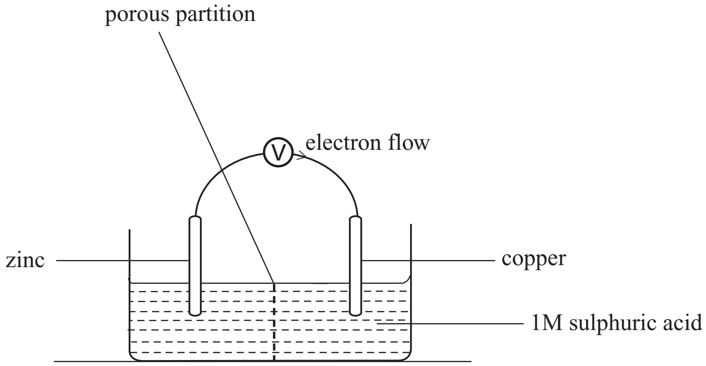
Sodium hydroxide is used in the manufacture of soap, rayon, paper and in the purification of bauxite for aluminium extraction.

## Electrochemical cells

A **cell** is a device that converts chemical energy into electrical energy. The reactions that take place in electrochemical cells are redox reactions. Any cell that generates an electric current by the oxidation-reduction is called a galvanic or voltaic cell.

### Galvanic or voltaic cell

The common simple galvanic cell is that of zinc and copper strips dipped into 1M sulphuric acid.



The zinc strip dissolves to form zinc ions by losing electrons.

$$Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2e^-$$

The electrons lost by zinc accumulate around the zinc electrode making it negatively charged. Then the copper strip becomes positively charged. Since the copper strip is positively charged, it attracts the electrons from the zinc electrode. When these electrons move through the wire to the copper strip, they are gained by positively charged ions around the copper strip, that is, hydrogen ions thus forming hydrogen gas.

$$2H^+{}_{(aq)} + 2e^- \rightarrow H_{2(g)}$$

Overall equation: $Zn_{(s)} + 2H^+{}_{(aq)} \rightarrow Zn^{2+}{}_{(aq)} + H_{2(g)}$

This overall reaction is called the **cell reaction** which gives the electric current.

Although, the zinc electrode is negatively charged, it is the **anode** since oxidation occurs at the anode. Zinc electrode is oxidised to zinc ions by losing electrons. Copper is the **cathode,** although it is positively charged, because reduction occurs at the cathode. Hydrogen ions around the copper electrode are reduced to hydrogen gas by gaining electrones.

The current flows in the wire from copper to zinc. Daniell cells, dry cells and lead storage batteries are examples of voltaic cells.

### Daniell cell

It consists of zinc half-cell and copper half-cell separated by a porous partition. The two half-cells are connected by a wire. The more electropositive metal, zinc, loses its electrons and goes into the solution as zinc ions, that is, zinc is oxidised to zinc ions.

$$Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2e^-$$

The zinc half-cell can be represented as: $Zn(s) / Zn^{2+}{}_{(aq)}$

The electrons move to the copper electrode through the external wire. In other words, electrons are attracted to the positively charged electrode. At the copper electrode, the copper(II) ions already in solution gain the incoming electrons to form copper, that is, copper(II) ions are reduced to copper.

$$Cu^{2+}{}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$$

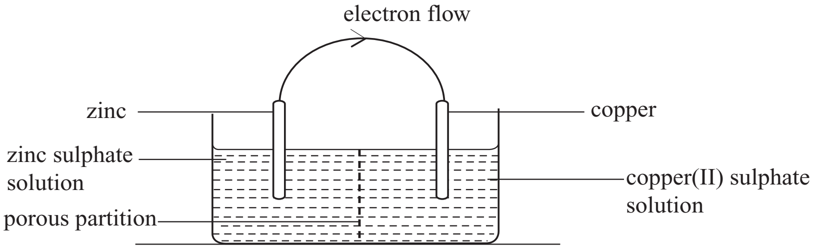
The copper half-cell can be represented as: $Cu^{2+}{}_{(aq)}/Cu_{(s)}$

Overall equation: $Zn_{(s)} + Cu^{2+}{}_{(aq)} \rightarrow Zn^{2+}{}_{(aq)} + Cu_{(s)}$

The cell convention for the complete cell is given by:

$$Zn_{(s)} \ / \ Zn^{2+}{}_{(aq)} \ / \ / \ Cu^{2+}{}_{(aq)} \ / \ Cu_{(s)}$$

The symbol // indicates a porous partition. Zinc electrode is the **anode** because it is where oxidation takes place whereby zinc is oxidised to zinc ions by losing electrons. Reduction of copper(II) ions to copper by gaining of electrons occurs at the copper electrode implying copper eletrode is the **cathode**.



## Practical uses of electrochemical cells

(i) They are used in making **dry cell batteries.** The ordinary torch battery is a simple cell.

(ii) They are used in making **rechargeable cells** such as *lead-acid storage batteries* used in cars.