Introduction to electrolysis - electrolytes and non-electrolytes

Electrolysis is the process of electrically inducing chemical changes in a conducting melt or solution e.g. splitting an ionic compound into the metal and non-metal.

SUMMARY OF COMMON ELECTRICAL CONDUCTORS

These materials carry an electric current via freely moving electrically charged particles, when a potential difference (voltage!) is applied across them, and they include:

All metals (molten or solid) and the non-metal carbon (graphite).

This conduction involves the movement of free or delocalised electrons (e- charged particles) and does not involve any chemical change.

Any molten or dissolved material in which the liquid contains free moving ions is called the electrolyte and can conduct an electrical current. Ions are charged particles e.g. Na+ sodium ion, or Cl- chloride ion, and their movement or flow constitutes an electric current, in other words the electrolyte consists of a stream of moving charged particles.

What does the complete electrical circuit for electrolysis consist of?

There are two ion currents in the electrolyte flowing in opposite directions positive cations e.g. sodium Na+ are attracted to the negative cathode electrode, and negative anions e.g. chloride Cl- are attracted to the positive anode electrode.

Remember no electrons flow in the solution, but they do flow in metal wires or carbon (graphite) electrodes of the external circuit.

sub-note:

(i) The greater the concentration of the electrolyte ions, the lower the electrical resistance of the solution. This is because there are more ions present to carry the current e.g. if the voltage (V, volts) is kept constant, the current flowing (I, amps) will steadily increase as the concentration of the electrolyte is increased.

The molten or dissolved materials are usually acids, alkalis or salts and their electrical conduction is usually accompanied by chemical changes e.g. decomposition.

The chemical changes occur at the electrodes which connect the electrolyte liquid containing ions with the external d.c. electrical supply.

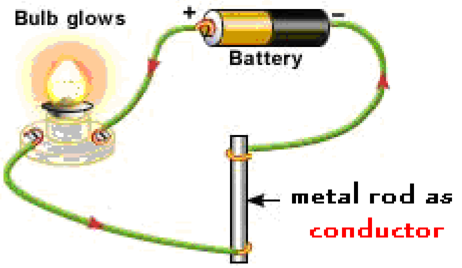
Liquids that conduct must contain freely moving ions to carry the current and complete the circuit. In solid ionic compounds the ions are too tightly held by chemical bonds and can't flow from their ordered situation! When an ionically bonded substances are melted or dissolved in water the ions are free to move about.

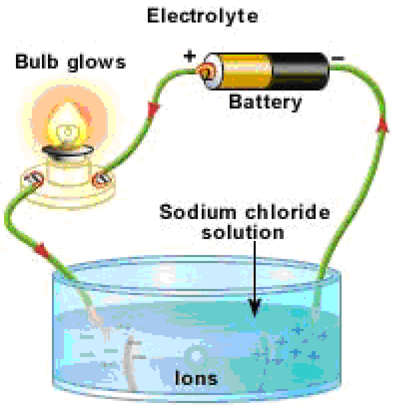
However some covalent substances dissolve in water and form ions. e.g. hydrogen chloride HCl, dissolves in water to form 'ionic' hydrochloric acid H+Cl-(aq)

The solution or melt of ions is called the electrolyte which forms part of the circuit. The circuit is completed by e.g. the external copper wiring and the (usually) inert electrodes like graphite (form of carbon) or platinum AND electrolysis can only happen when the current is switched on and the circuit complete.

Conductor versus electrolyte

An electrolyte is a solution that can conduct electricity due to ions present in it.
What is the difference between a conductor and an electrolyte?





The figure below shows two circuits : one for a conductor and one for an electrolyte. The differences between the two are as follows:

a) In a conductor, electrical current is flowing through the material in its solid form. Conductors are generally metals. On the other hand, an electrolyte can carry current in its molten state or in a solution form. Electrolytes are generally made from ionic compounds and not covalent compounds (HCl and NH_3 are a few of the exceptions). When a current passes through a conductor, it may get heated up because of its inherent resistance. Other than this physical change, there is **no other change in the conductor**. Once, the current stops flowing, the conductor returns to its original state. On the other hand, in an electrolyte, the cations and anions go in opposite directions and get neutralized at the positive and negative electrodes respectively. **The chemical change thus produced is irreversible**.

b) The current through a conductor is due to free electrons that flow and complete the circuit. The current through an electrolytic cell is because of the flow of ions.

c) For a given conductor and a cell, the current flowing through the circuit is constant. In an electrolytic cell, the current depends on the strength of the electrolyte, which may change over time.

Some definitions regarding electrolysis

1.**Electrolysis** : It is a chemical process where a substance in its molten state or in an aqueous solution is decomposed by the passage of electric current.

2.**Electrolyte** : A compound that allows electric current to pass through itself, when either in a molten state or in an aqueous solution, is called an electrolyte. Solutions of sodium chloride, copper sulphate, dilute sulphuric acid are examples of strong electrolytes. Weak electrolytes are those compounds which are poor conductors of electricity when they are in a molten state or in an aqueous solution.

3. **Non-electrolyte** : A compound which does not allow electric current to pass through itself in any state, molten or aqueous, is called a non-electrolyte.

4.**Electrodes** : The strips of metals inserted in the electrolytes for conduction of electricity are called electrodes. The metal electrode connected to the positive terminal of the battery is called the **anode** (+). The metal electrode connected to the negative terminal of the battery is called the **cathode** (-).

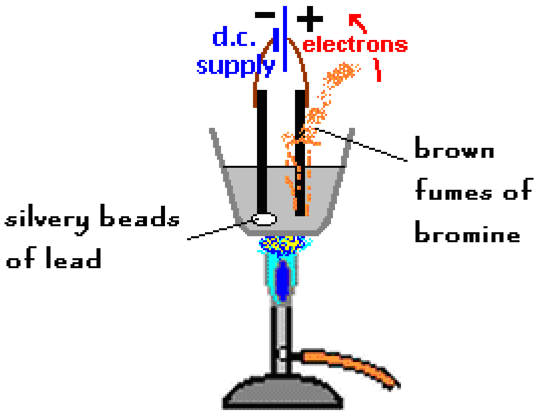
5.**Electrolytic cell** : The complete set-up for electrolysis is called the electrolytic cell. This consists of the vessel containing the electrolyte, anode, cathode, battery and wires. Electrolytic cell is also known as a **voltameter**, since it generates voltage (or current) at its two terminals.

To summarize the process of electrolysis, we can say the following

- Electrolytes dissociate to form negatively charged anions and positively charged cations.
- The ions conduct electricity through the electrolyte.
- Cations are attracted towards the negative electrode. They take the excess electrons from the electrode and neutralize themselves.
- Anions are attracted towards the positive electrode. They give up the excess electrons from the electrode and neutralize themselves. The electrolyte dissociates and the constituent elements of the salt are liberated at the electrodes.

Electrolysis of Molten Lead(II) bromide with carbon electrodes

Carbon (graphite) electrodes dipped into molten salt which has been strongly heated in a crucible. It is difficult to collect the gases at the electrodes! The salts may be very high melting, so sometimes a small amount of another salt impurity is added to lower the melting point.



Reaction at anode: (Oxidation of Bromide ions to bromine gas)

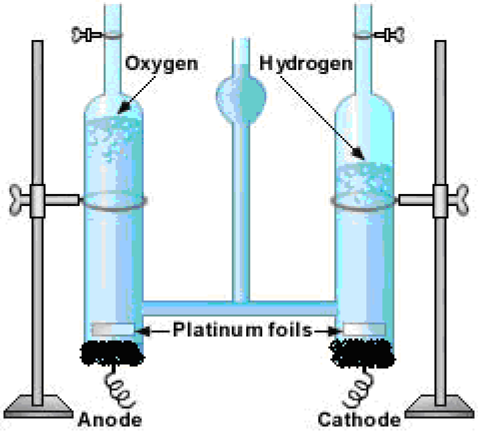
$2Br^- \rightarrow Br_2 + 2e^-$

Reaction at cathode: (Reduction of lead(II) ions to lead atoms)

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

Electrolysis of water (Electrolysis of dilute sulphuric acid)

The apparatus or the electrolytic cell, required for performing electrolysis of water is shown in the figure below. The cell is called Hoffman's voltameter.



Since water is a covalent compound, pure or distilled water is a very weak electrolyte. A few drops of ionic compound like dilute sulphuric acid are enough to make the water become an electrolyte. The anode collects oxygen and the cathode arm collects hydrogen gas.

The overall reaction that takes place is:

$H_2SO_4 \rightarrow 2H^+ \quad + \quad SO_4^{2-}$

Water also is capable of dissociation.

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

Reaction at the cathode

$2H^+ + 2e^- \rightarrow H_2$

Reaction at the anode

$4OH^- \rightarrow H_2O + O_2 + 4e^-$

At the anode OH^- ions are released in preference to SO_4^{2-} ions. This is because it is easier for an OH^- ion to give up an electron quickly than for the SO_4^{2-} ion to do so.

Example: Electrolysis of sodium chloride solution

The ions present in the solution are:

sodium ions	chloride ions	hydrogen ions	hydroxide ions
Na+	Cl-	H+	OH-

At the cathode

The positive ions are attracted to the negative cathode. There is competition between the sodium ions and the hydrogen ions. As the hydrogen ion | hydrogen redox equilibrium appears lower in the electrochemical series than the sodium ion | sodium equilibrium, then the hydrogen ions are preferentially reduced and hydrogen gas is produced at the electrode (bubbles are seen)

$$\mathbf{2H^+ + 2e \rightarrow H_2}$$

At the anode

There is competition between the negative ions at the positive anode. The chloride ions compete with the hydroxide ions to release their electrons to the anode. When the solution is **fairly concentrated** the chloride ions preferentially lose electrons to become chlorine atoms (and then molecules)

$$\mathbf{2Cl^- - 2e \rightarrow Cl_2}$$

Ions remaining in solution

The ions that are removed from the solution, then, are the hydrogen ions and the chloride ions. This means that the sodium ions and the hydroxide ions remain in the solution - i.e sodium hydroxide is also produced.

Note: When the solution of chloride ions is dilute then OH. ions are preferentially released at the anode.

Example: Electrolysis of copper (II) sulphate solution

The ions present in the solution are:

copper ions	sulphate ions	hydrogen ions	hydroxide ions
Cu^{2+}	SO_4^{2-}	$H+$	$OH-$

At the cathode

The positive ions are attracted to the negative cathode. There is competition between the copper ions and the hydrogen ions. As the hydrogen ion | hydrogen redox equilibrium appears higher in the electrochemical series than the copper ion | copper equilibrium, then the copper ions are preferentially reduced and copper metal is deposited at the electrode (a pink layer is observed)

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

At the anode

There is competition between the negative ions at the positive anode. The sulphate ions compete with the hydroxide ions to release their electrons to the anode. The hydroxide ions are much better reducing agents and are preferentially released AS OXYGEN GAS and water

$$\mathbf{4OH^{-} - 4e \rightarrow 2H_2O + O_2}$$

Ions remaining in solution

The ions that are removed from the solution, then, are the copper ions and the hydroxide ions. This means that the hydrogen ions and the sulphate ions remain in the solution - i.e sulphuric acid is also produced.

Example: Electrolysis of copper II sulphate solution using copper electrodes (participating electrodes)

The ions present in the solution are:

copper ions	chloride ions	hydrogen ions	hydroxide ions
Cu^{2+}	SO_4^{2-}	H+	OH-

At the cathode

The positive ions are attracted to the negative cathode. There is competition between the copper ions and the hydrogen ions. As the hydrogen ion | hydrogen redox equilibrium appears higher in the electrochemical series than the copper ion | copper equilibnrium, then the copper ions are preferentially reduced and copper metal is deposited at the electrode (a pink layer is observed)

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

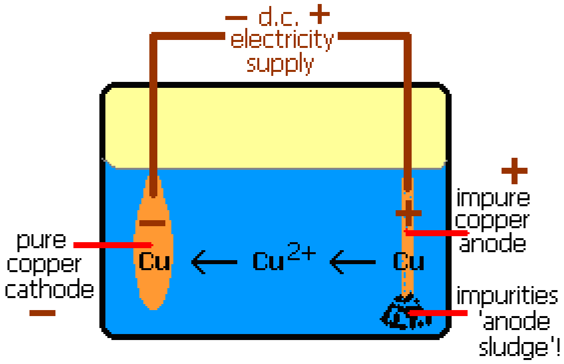
At the anode

In this case, the electrode is made of copper and it is easier for the copper to dissolve leaving its electrons behind on the anode than for any other ion to be released.

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

Ions remaining in solution

Copper is deposited at the cathode and is dissolved at the anode. Consequently the concentration of copper ions in solution remains constant. This can be used as a method of purification of copper as only pure copper is deposited at the cathode.



In this purification an anode made of impure copper is turned to pure copper at the cathode leaving the impurities behind (the sludge in the diagram).

Summary

Reactive metals (more reactive than hydrogen) are never deposited during electrolysis of aqueous solutions. If the metal ion comes from a metal more reactive than hydrogen then hyrogen gas is liberated at the cathode.

Halide ions (chloride, bromide, iodide) are released preferentially and if these are not present, the hydroxide ions from the water are released at the anode.

Unreactive metals, such as copper or nickel, may participate in reactions at the anode.

Electrolysis and the electrochemical series

The electrochemical series of half-cell reaction potentials, can be used to predict which ions are likely to be preferentially discharged to form electrolysis products on the cathode(+ pole in electrolysis) or anode (+ pole in electrolysis).

At the negative (-) cathode electrode (reduction half reaction)

- The more positive/less negative the half-cell potential, the more easily the cation is discharged by reduction, e.g. copper metal from copper(II) ions (+0.34V) will be discharged deposited on a cathode preferentially from iron from iron(II) ions (-0.44V) from a solution containing both ions.

i.e. $\mathbf{Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}}$ **+0.34 V**

$\mathbf{Fe^{2+}_{(aq)} + 2e^- \rightarrow Fe_{(s)}}$ **-0.04 V**

At the positive (+) anode electrode (oxidation half reaction)

- The less positive the half-cell potential, the more easily the anion is discharged by oxidation, e.g. in an aqueous mixture of bromide and chloride ions, bromide forms bromine (+1.09V) more readily than chloride ion forms chlorine (+1.36V). Since the process involves electron loss, the ion which is the most readily formed will be the ion which is least readily discharged.

$\mathbf{2Br^-_{(aq)} \rightarrow Br_{2(aq)} + 2e^-}$ **-0.54 V**

occurs more readily than $\mathbf{2Cl^-_{(aq)} \rightarrow Cl_{2(aq)} + 2e^-}$ **-1.36 V**

But sometimes other factors come into consideration e.g. Concentrated or dilute sodium chloride solution (brine)

In concentrated $NaCl_{(aq)}$ evolution of chlorine predominates from

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

but in very dilute $NaCl_{(aq)}$ evolution of oxygen predominates from

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

Theoretically oxygen should be discharged first, but the hydroxide ion concentration is so low compared to the chloride ion that little oxygen is produced on anode-ion collision probability. Also, oxygen has a high 'overpotential' (which you can equate to a high activation energy giving a very slow rate of reaction which also inhibits its formation.

There will be differences in electrolysis products between inert and non-inert electrodes, e.g. copper(II) sulphate solution gives oxygen gas at the (-) anode if it is inert platinum/carbon, but a copper anode dissolves giving the copper(II) ion. In both cases copper metal is deposited on the (-) cathode.

Application of electrolysis

The process of electrolysis has many applications.

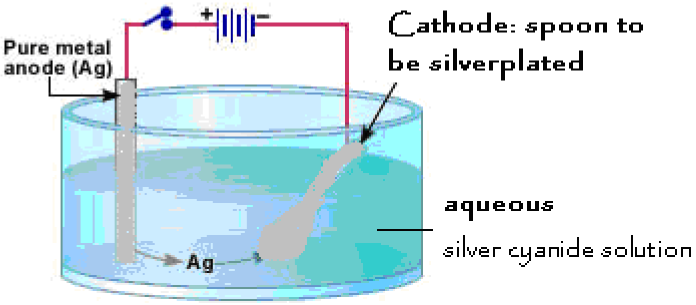
Electroplating of metals

Electroplating is a process whereby a thin coating of desired material is applied on a required material. This is mostly done on stainless steel to prevent rusting, or on some decorative items, so that they look attractive. On stainless steel, generally nickel-chromium plating is done. On decorative items, such as spoons, plates, jewelry items, silver, gold or other plating is done. Electroplating is cheap and cost effective. It enhances the life of the object and makes it look better in appearance.

The following method is adapted :

- First the item to be electroplated is smoothened and cleaned thoroughly. It should not have any oily or dirt marks on it.
- An electrolyte is selected whose ions are required to be deposited on the item.
- Direct current is preferred to alternating current, as alternating current may result in non-smooth deposit.
- The item to be electroplated forms the anode or cathode of the electrolytic cell. This is the drawback of the electroplating process. The item has to be electrically conducting, or has to be made electrically conducting.
- For a smooth coating, the electrolytic process has to be optimized for time, temperature and current in the cell.

Figure below is a conventionally used electrolytic cell for depositing silver. Let the item to be silver-plated be a spoon.



Electroplating with silver

Electrolyte used is sodium silver cyanide solution [Na{Ag(CN)2}]. The cathode is made out of the item on which the electro deposition is to be done, in this case it is a spoon. Anode is made of a block of silver.

The $[Na\{Ag(CN)_2\}]$ dissociates as

$Na\{Ag(CN)_2\} \rightarrow Na^+ + Ag^+ + 2\,CN$

Reaction at the cathode

$Ag^+ + e^- \rightarrow Ag$

The positively charged Ag^+ ions are attracted to the cathode (-) and accept one electron and get deposited as a thin film over the cathode material, in this case the spoon.

Reaction at the anode

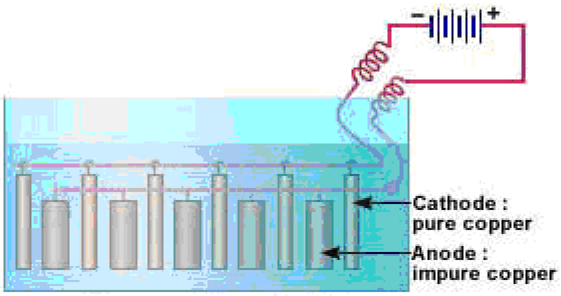
$Ag \rightarrow Ag^+ + e^-$

The silver atoms at anode loose electrons and enter into the electrolyte as an ion. This ensures that the concentration of the Ag in the solution remains constant. The electroplating is complete when a desired thickness of the silver film is deposited.

Electro-refining of metals

Similar to the process of electro-deposition, electrolysis can be used to purifying metals that are obtained from the ores. The process is known as electro-refining of metals. The metals that are generally refined by this process are Zn, Ag, Ni, Cu, Pb, Al, etc.

Figure below is a conventionally used electrolytic cell for purifying metal ores, in this case the metal is impure copper.



Electro-refining of metals

Let the cathode be made of pure copper sheets and the anode be made of impure copper block. The electrolytic solution is copper sulphate solution.

The electrolyte dissociated into

$CuSO_4 \rightarrow Cu^{2+} + SO_4^{2-}$

Reaction at the cathode

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

The positively charged Cu^{2+} ions are attracted to the cathode (-) and accept two electrons and get deposited as a thin film over the cathode material, in this case the pure copper sheets.

Reaction at the anode

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

The copper atoms at the anode loose electrons and enter into the electrolyte as an ion. This ensures that the concentration of the Cu in the solution remains constant. Besides the copper atoms, other atomic impurities such as Ag and Au also get into the electrolytic solution. Thus the impure block at the anode gets used up and pure copper is deposited at the cathode.

Extracting aluminium from bauxite

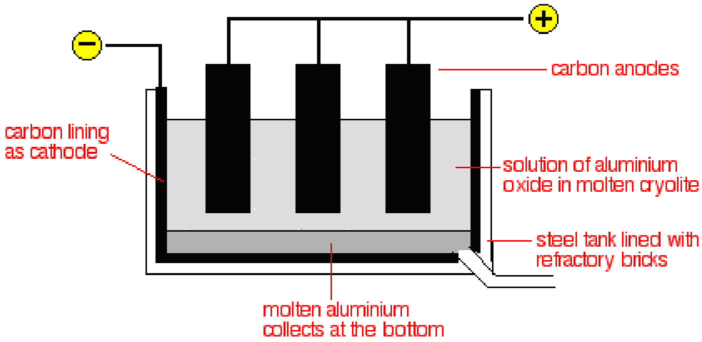
Aluminium is too high in the electrochemical series (reactivity series) to extract it from its ore using carbon reduction. The usual aluminium ore is ***bauxite***. Bauxite is essentially an impure aluminium oxide.

Conversion of the aluminium oxide into aluminium by electrolysis

The aluminium oxide is electrolysed in solution in molten ***cryolite***, Na_3AlF_6. Cryolite is another aluminium ore, but is rare and expensive, and most is now made chemically.

The electrolysis cell

The diagram shows a *very simplified* version of an electrolysis cell.



Although the carbon lining of the cell is labelled as the cathode, the effective cathode is mainly the molten aluminium that forms on the bottom of the cell. Molten aluminium is removed from the cell from time to time, and new aluminium oxide added at the top.

The cell operates at a low voltage of about 5 - 6 volts, but at huge currents of 100,000 amps or more. The heating effect of these large currents keeps the cell at a temperature of about 1000°C.

The electrode reactions

Aluminium is released at the cathode. Aluminium ions are reduced by gaining 3 electrons.

$$Al^{3+} + 3e^- \longrightarrow Al$$

Oxygen is produced initially at the anode.

$$2\,O^{2-} \longrightarrow O_2 + 4e^-$$

However, at the temperature of the cell, the carbon anodes burn in this oxygen to give carbon dioxide and carbon monoxide. Continual replacement of the anodes is a major expense.

Some economic and environmental considerations

Economic considerations

- The high cost of the process because of the huge amounts of electricity it uses. This is so high because to produce 1 mole of aluminium which only weighs 27 g you need 3 moles of electrons.
- Energy and material costs in constantly replacing the anodes.

- Energy and material costs in producing the cryolite, some of which gets lost during the electrolysis.

Environmental problems in mining and transporting the bauxite

- Loss of landscape due to mining, processing and transporting the bauxite.
- Noise and air pollution (greenhouse effect, acid rain) involved in these operations.

Extracting aluminium from the bauxite

- Loss of landscape due to the size of the chemical plant needed, and in the production and transport of the electricity.
- Noise.
- Atmospheric pollution from the various stages of extraction. For example: carbon dioxide from the burning of the anodes (greenhouse effect); carbon monoxide (poisonous); fluorine (and fluorine compounds) lost from the cryolite during the electrolysis process (poisonous).
- Pollution caused by power generation (varying depending on how the electricity is generated.)
- Disposal of red mud into unsightly lagoons.
- Transport of the finished aluminium.

Recycling

- Saving of raw materials and particularly electrical energy by not having to extract the aluminium from the bauxite. Recycling aluminium uses only about 5% of the energy used to extract it from bauxite.
- Avoiding the environmental problems in the extraction of aluminium from the bauxite.
- Not having to find space to dump the unwanted aluminium if it wasn't recycled.
- Energy and pollution costs in collecting and transporting the recycled aluminium.

Uses of aluminium

Aluminium is usually alloyed with other elements such as silicon, copper or magnesium. Pure aluminium isn't very strong, and alloying it adds to it strength.

Aluminium is especially useful because it

- has a low density;
- is strong when alloyed;
- is a good conductor of electricity;
- has a good appearance;
- resists corrosion because of the strong thin layer of aluminium oxide on its surface. This layer can be strengthened further by anodising the aluminium.

Anodising essentially involves etching the aluminium with sodium hydroxide solution to remove the existing oxide layer, and then making the aluminium article the anode in an electrolysis of dilute sulphuric acid. The oxygen given of at the anode reacts with the aluminium surface, to build up a film of oxide up to about 0.02 mm thick.

As well as increasing the corrosion resistance of the aluminium, this film is porous at this stage and will also take up dyes. (It is further treated to make it completely non-porous afterwards.) That means that you can make aluminium articles with the colour built into the surface.

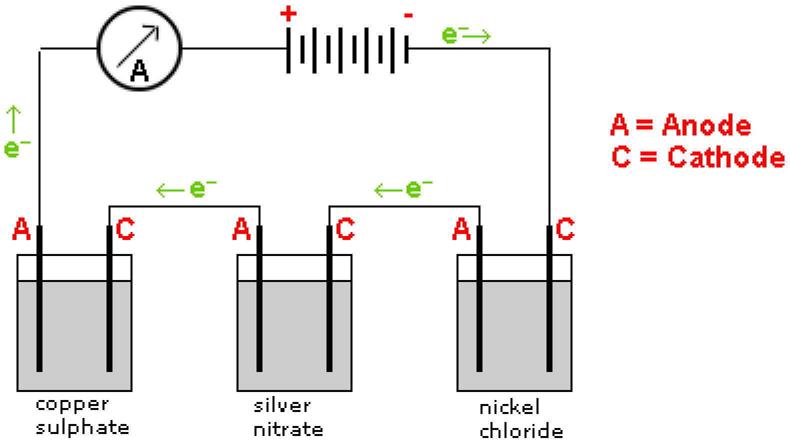
Some uses include:

aluminium is used for	**Because**
Aircraft	light, strong, resists corrosion
other transport such as ships' superstructures, container vehicle bodies, tube trains (metro trains)	light, strong, resists corrosion
overhead power cables (with a steel core to strengthen them)	light, resists corrosion, good conductor of electricity
Saucepans	light, resists corrosion, good appearance, good conductor of heat

Calculation:

Example

In the following diagram the number of moles of silver deposited will be twice the number of moles of copper deposited. The number of moles of copper deposited will be equal to the number of moles of nickel deposited.



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

$Ni^{2+}(aq) + 2e \rightarrow Ni_{(s)}$

$Ag^{+}(aq) + 1e \rightarrow Ag_{(s)}$