

Applications of electrolysis

Production of sodium—the Downs Cell

Sodium is made commercially by the electrolysis of molten sodium chloride. Sodium chloride normally melts at temperatures around 800°C but this can be lowered to around 600°C by adding calcium chloride to the mixture. This saves energy in the commercial production and any small amount calcium formed can be readily separated from the sodium.

Figure 1 shows a commercial Downs Cell used for the production of sodium.

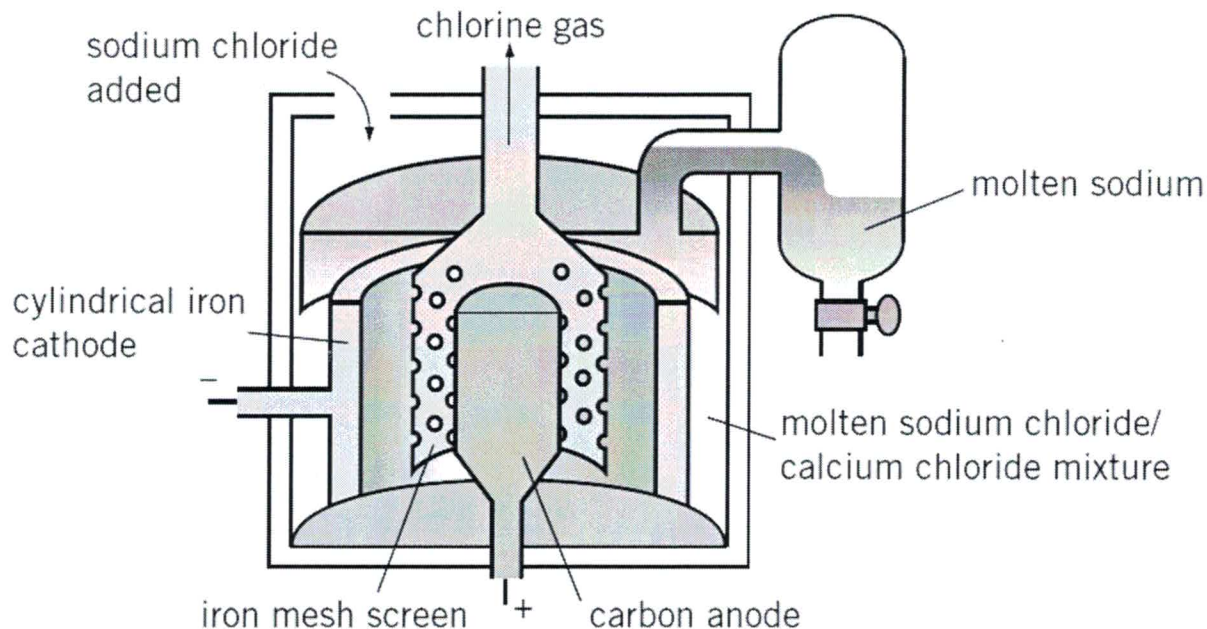
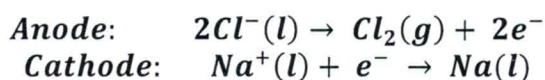


Figure 1 Downs Cell

The anode is made of graphite while the cathode is iron. At the anode, the only reaction is the oxidation of chloride ions to form chlorine. The key reaction at the cathode is the reduction of sodium ions to form sodium.



As sodium and chlorine are so reactive, care must be taken to keep the products separated. The chlorine gas is piped out at the top of the cell and there is a porous screen between the central anode and the cathode to ensure that the sodium and chlorine do not come into contact in the cell. The sodium is a liquid at the temperature of the molten mixture and would float on the molten sodium chloride. By encasing the cathode in a metal compartment the liquid sodium can be tapped off and collected in the absence of air that would immediately oxidise the reactive, molten metal.

Approximately 70 000 tonnes of sodium is made by electrolysis annually, although demand for the metal has decreased in recent years. Some of the sodium is used as a heat transfer agent in certain nuclear reactors where the use of water would reduce the efficiency of the reactor. Sodium melts at around 100°C and is an excellent conductor of heat. As a result, it can be used to transfer the heat energy produced in the core of the nuclear reactor to water that circulates in pipes positioned in the molten sodium. The water in the pipes is converted to steam which is then used to run turbines in the same way as in a fossil-fuel power station.

Other reactive metals like calcium and magnesium are also produced commercially by electrolysis of molten calcium chloride and magnesium chloride respectively. In addition, aluminium is commercially prepared in the electrolysis of a molten salt, aluminium oxide, obtained from the ore bauxite. **Electrowinning** is the general name given to these commercial electrolysis processes where metals are prepared from their molten salts using inert electrodes.

Anodised aluminium

Aluminium is a very versatile metal, second only to iron in terms of world production. It is widely used in the construction industry and is often alloyed with other metals. In addition to its use in cars, aircraft, bicycle frames, boats and house construction, aluminium is used in packaging, cooking utensils and electrical transmission lines. Despite aluminium being quite a reactive metal it is able to be used in situations where other, less reactive metals such as iron, might cause problems. Aluminium rapidly oxidises in air to form a thin, impervious oxide coating that protects the underlying metal from further reaction. However, in situations where even greater corrosion resistance is required, the aluminium may be anodised to give a thicker oxide coating.

Anodising aluminium involves making the aluminium the anode in an electrolytic cell containing sulfuric acid (Figure 2). At the anode, water is the strongest reductant and is oxidised to produce oxygen.



Figure 2 Anodised cups

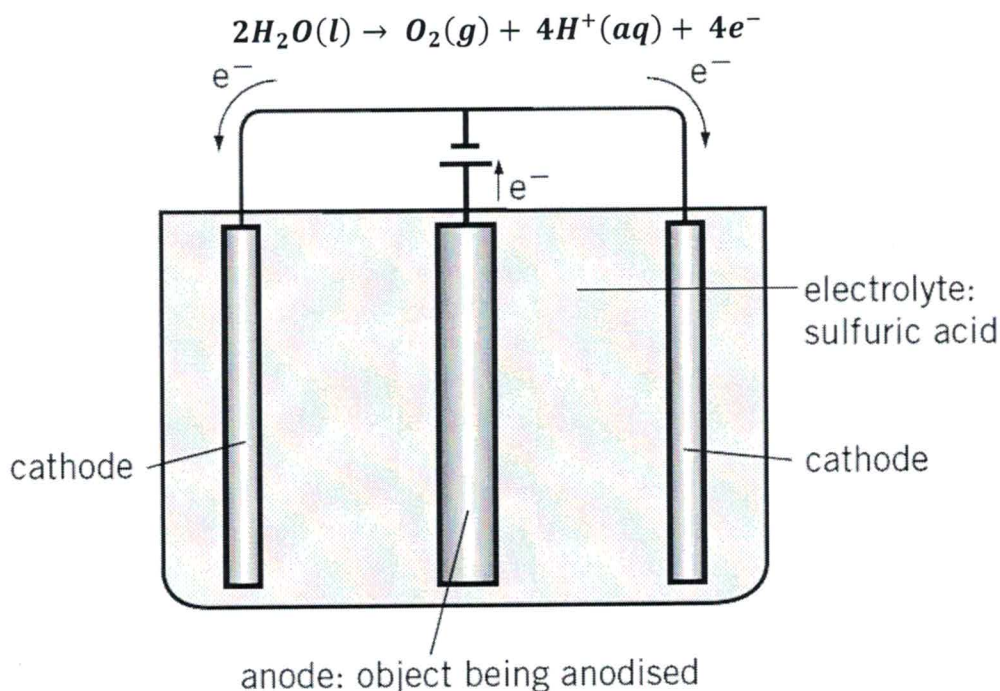


Figure 3 Anodising aluminium

The oxygen reacts with the aluminium to produce a uniform oxide coating that acts as a protective surface. Various dyes can be introduced into the anodising process to produce the coloured aluminium surfaces that can be seen in items such as iPods, digital cameras, cookware and sporting goods.

Electrolytic refining of copper

Copper that is made from the smelting or refining of various copper-containing ores is not pure. This impure copper may contain approximately 98% copper, with other metals such as silver, platinum, zinc, iron and nickel also present. For purposes such as electrical wiring the copper needs to be well in excess of 99% pure, so the final step in the production of pure copper is an electrolytic process known as electrorefining.

Electrorefining differs from electrowinning because the refining process involves the oxidation of the anode. That is the anode is not inert as it is in the electrowinning process. While the use of electrodes made of graphite or unreactive metals such as platinum ensures that only those species present in the electrolyte undergo oxidation or reduction, where a more reactive metal is used as the positive electrode it is possible for the electrode to be oxidised in preference to any other reductant in the cell.

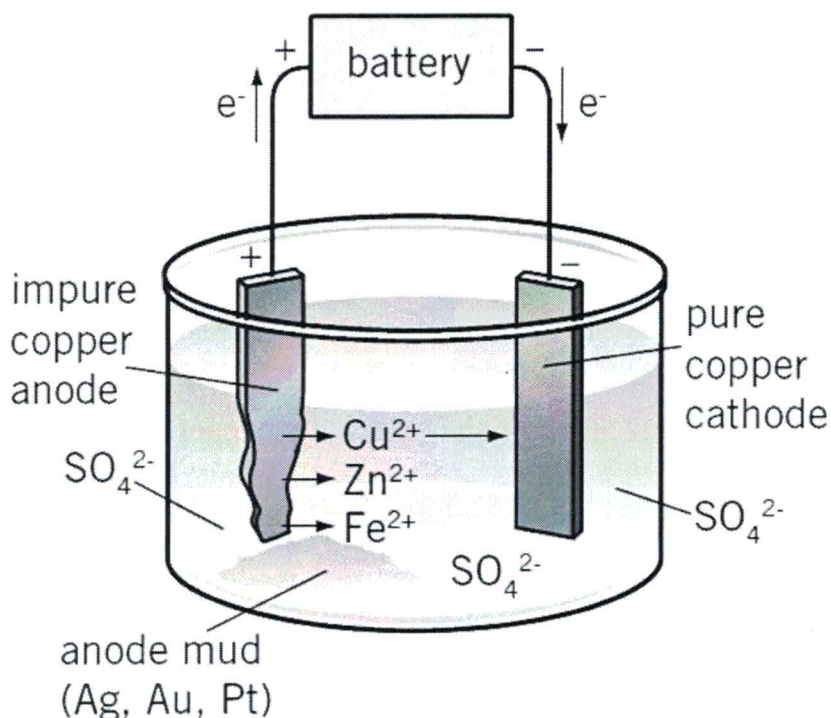
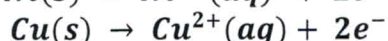
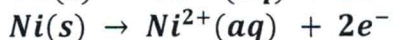
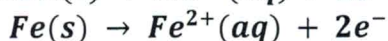
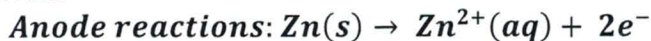


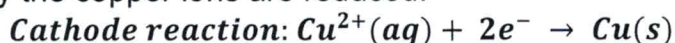
Figure 4 Electrorefining of copper

The crude copper is made into anodes in an electrolytic cell. Thin pure copper electrodes form the cathode and both electrodes are placed in an acidic solution of copper (II) sulfate.

By careful adjustment of the voltage applied to the cell, the copper is oxidised, together with the more reactive metal impurities such as iron, zinc and nickel. The less reactive metals such as silver, gold and platinum do not undergo oxidation and as the anode oxidises and dissolves, these precious metals fall to the bottom of the cell as a sludge or mud.



At the cathode only the copper ions are reduced.



This is partly because of the much higher concentration of copper ions in the electrolyte, and partly because the copper ion is a stronger oxidant than the ions of the more reactive metals.

In this process, copper with purity in excess of 99.99% is plated onto the cathode.

Electroplating of silver

The process of electroplating involves depositing a thin layer of one metal over another. The coating may serve as protection for the metal beneath or may provide a surface with a nicer appearance than the original.

A layer of silver can be deposited onto another metal object by making that object the cathode in an electrolytic cell. A piece of pure silver is used as the anode and the two metals are immersed in a solution containing silver ions. In commercial silver-plating the nature of the electrolyte needs to be carefully controlled using cyanide ion, CN^- , to keep the concentration of the silver ion low enough to allow the silver metal that forms on the surface to be a thin, controlled layer. The electrode reactions for this cell are:



Application of Redox

Corrosion of metals

All metals (except perhaps gold and platinum) react with oxygen. Some, like sodium, react vigorously while others, such as copper, need to be strongly heated to react. While aluminium is quite a reactive metal, its reaction with oxygen produces a continuous and impervious coating of aluminium oxide that prevents further reaction, even at the high temperatures used in cooking. Stainless steel also forms a similar protective oxide coating (chromium oxide dominates, but other metals in the steel alloy such as nickel also play a part).

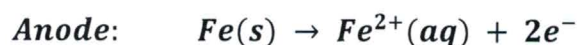
Iron and copper are somewhat less reactive than aluminium, but they will oxidise, particularly on heating. Unlike aluminium, however, the oxide coating of these two metals allows further reaction of the metal. The oxide coating is 'flaky' and exposes fresh metal to the air and water, and so allows further oxidation.

Rusting of iron

The most common example of corrosion, rusting of iron, differs from dry corrosion (reaction of iron with air, in the absence of water) in a number of respects. The major requirement for 'wet' corrosion or rusting is the presence of oxygen and water, although other factors, such as impurities in the iron and the presence of electrolytes dissolved in the water, enhance the rate of the rusting process.

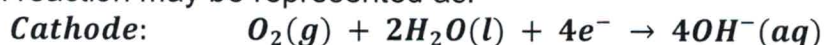
'Wet' corrosion also has an electrochemical nature because the oxidation and reduction processes can take place at different points on the metal. In addition, because the metal is an electrical conductor, it promotes the flow of electrons from the anode to the cathode.

In the rusting process, the iron acts as the anode where oxidation of Fe takes place, initially to form Fe^{2+} .



The cathode may be an impurity, such as carbon, in the iron, or a region of high oxygen concentration.

The reduction reaction may be represented as:



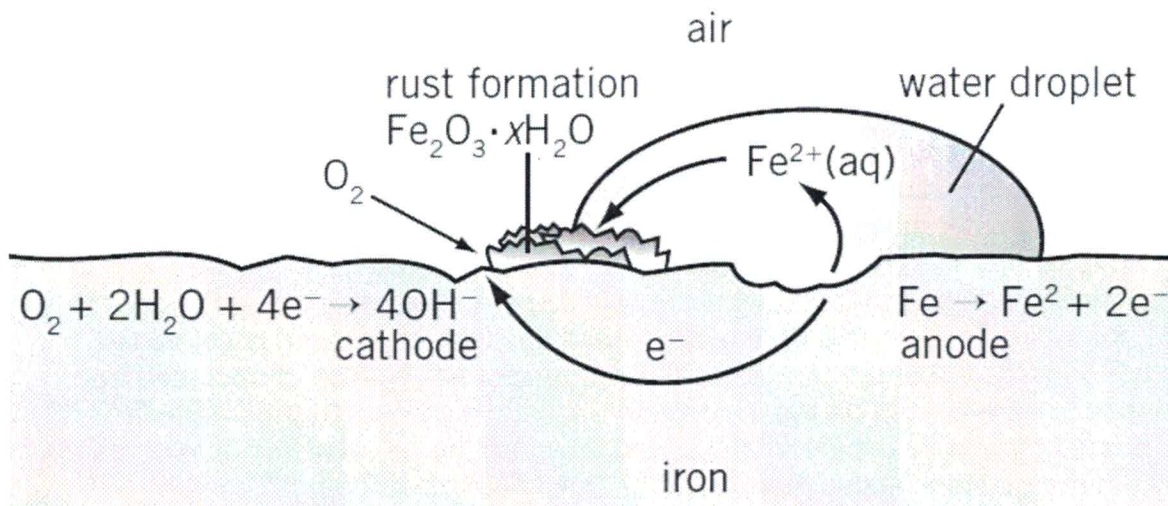
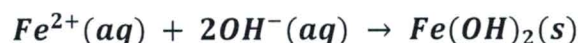


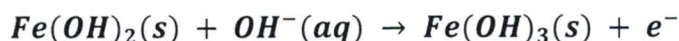
Figure 5 Corrosion of iron in the presence of water and air

The rusting process occurs most rapidly when iron or steel is exposed to the atmosphere and is covered with a film of water for a considerable period. The solid rust (see Figure 5) usually forms near the cathode where the hydroxide ions are produced. Since this reduction reaction takes place where there is an abundance of air (oxygen), the actual pitting or loss of iron (the anode reaction) is more likely to occur where there is a deficiency of air. This differential aeration effect can lead to the iron corroding below paintwork or where two metal surfaces are in contact. In the presence of other electrolytes, for example salts near the ocean, or pollutants such as SO_2 and NO_2 , solutions of greater conductivity are produced and so the rate of rusting will increase.

The iron (II) ions and the hydroxide ions produced diffuse towards each other and precipitate as iron (II) hydroxide, according to the following equation:

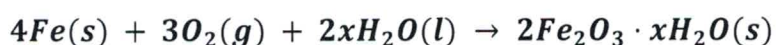


The iron (II) hydroxide is very easily oxidised by air (more readily than the original iron) to form iron (III) hydroxide:



The iron (III) hydroxide is then partially dehydrated to give rust, $Fe_2O_3 \cdot xH_2O$. The $Fe(OH)_2$ and $Fe(OH)_3$ are only sparingly soluble (the latter being the least soluble) and their formation removes Fe^{2+} from solution. This in turn shifts the position of equilibrium in favour of the rusting process.

The overall equation for the rusting of iron is:



Prevention of corrosion

The formation of rust on iron and steel can be slowed down or stopped by a number of methods.

i Application of a surface coating, either metal or non-metal, which prevents oxygen and water from coming in contact with the iron. Examples include painting and plating with tin, chromium or silver.

If a less reactive metal is used as the coating, then any scratch on the surface will lead to an increase in corrosion of the more reactive metal, namely the iron. For example, for an iron can coated on the inside with tin, if the tin coating is scratched, the iron will become the anode and will oxidise quicker than a piece of uncoated iron. Most cans today are coated on the inside with a plastic material. This increase in corrosion rate of iron also occurs in any situation where the piece of iron is in contact with any other metal less active than itself, for example, copper.

ii Galvanising the surface of the metal with a coating of a more reactive metal. For example, if a layer of zinc is coated onto an iron surface, the more reactive zinc will give up its electrons, i.e. it will oxidise more readily than the iron, even if the surface coating is scratched.

iii Connecting the iron or steel, by a conducting wire, to a piece of more reactive metal such as zinc, magnesium or aluminium. The more reactive metal is sacrificially oxidised instead of the iron being oxidised, i.e. the more reactive metal acts as the anode. The method is very similar to that in point ii, except that the reactive metal can be replaced easily after it has been consumed. The more reactive metal in this process is often called the sacrificial anode.

iv Making the iron or steel the cathode of an electrolytic cell. The cell consists of a DC (direct current) power source, an anode of scrap metal and the iron or steel cathode. The applied voltage makes the iron (steel) object negatively charged and so prevents its oxidation. The scrap metal anode must be replaced from time to time (or it can be made of an inert material if scrap metal is not available). This process is called **cathodic protection**.

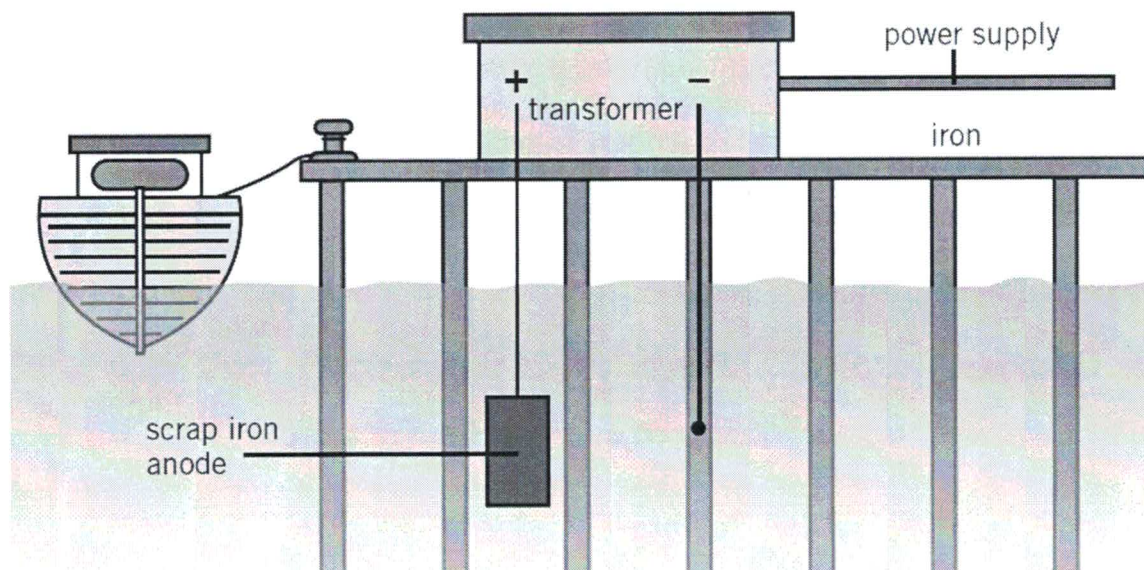


Figure 6 Cathodic protection of an iron wharf