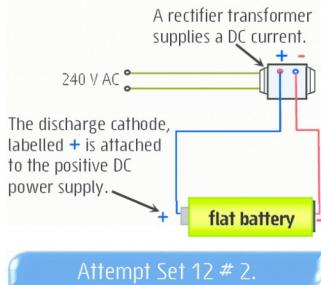


\*The cells examined in 8.3-8.5 are typical examples of the various cell types. These are not intended to be prescriptive of the WACE Chemistry course. Consult the Chemistry WACE manual for more specific guidance.

**Figure 3 Recharging a secondary cell.**



Attempt Set 12 # 2.

## 8.2 Types of galvanic cells\*

**Non-rechargeable** galvanic cells like the **dry cell** (p83) are known as **primary cells**. These contain a fixed amount of oxidant and reductant which once consumed cannot be replaced or regenerated. These single use cells are discarded once 'flat'.

**Secondary cells** like the **lead-acid cell** (typically called a car battery, p84-5) are **rechargeable**.

When galvanic cells like this go flat they can be recharged by applying a DC voltage that forces current through the cell in an opposite direction to that which occurs spontaneously during its discharge. (See Fig 3.) Recharging is essentially a process of electrolysis where electrical energy is used to force the spontaneous discharge reactions to be **reversed** and in the process regenerate the oxidant and reductant originally present in the charged cell. Although secondary cells are rechargeable there is a limit to the number of recharge cycles they will undergo before their electrodes become physically degraded and no longer able to be recharged.

A third type of galvanic cell is the **fuel cell**. In these cells the oxidant and reductant are continuously fed into the cell. The reductant is typically a fuel (ie a combustible substance) such as hydrogen, methane or methanol for example. The oxidant is usually oxygen gas. Fuel cells have a very long life and can theoretically operate without limit as long as the oxidant (oxygen) and reductant (fuel) are supplied into the cell.

## 8.3 Primary cells

**The dry cell:** Originally patented in 1866 by Georges Leclanché, the dry cell is the simplest and most inexpensive of the non-rechargeable cells in use today. It produces a maximum voltage of 1.5 V. Its design, however, is such that the voltage produced by the cell slowly decreases over the life of the cell. A further disadvantage of this cell is its very low energy to mass ratio (energy density). However, these batteries are inexpensive and ideal for use in flashlights, portable radios and calculators where low currents are required and a decreasing voltage is not an issue.

Primary cells like the dry cell, are not able to be recharged, so flat batteries are discarded. The materials used in a dry cell (Zn, MnO<sub>2</sub>, NH<sub>4</sub>Cl and C) pose **negligible environmental impact**. Thus spent dry cells are considered non-hazardous waste and can be disposed of in the normal household waste stream, though this is becoming increasingly discouraged. (See Fig 4.) At present there is no economic process for recycling spent dry cells.

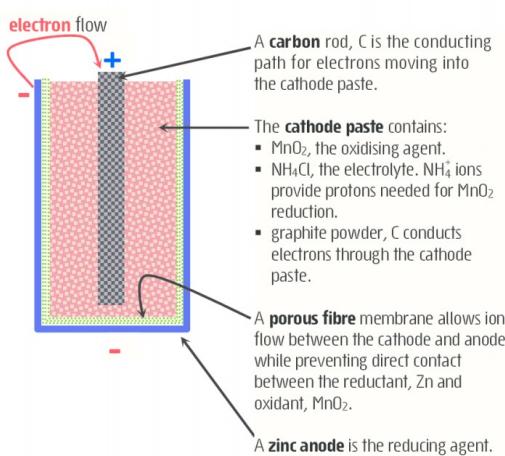


**Figure 4** While **dry cell batteries** are considered **non-hazardous** waste, they do contain large quantities of zinc, which upon disposal can leach into the soil and groundwater. The toxicity of zinc in the environment is a complex issue as the element **zinc** is actually an important dietary component while also being potentially toxic.

It is normal for wheat, for example, to contain up to 60 ppm zinc. In fact diets lacking in zinc can result in a variety of illnesses. However, **excessive intake** of zinc is **harmful** and potentially fatal. In particular even low concentrations of zinc ions, Zn<sup>2+</sup>(aq) are known to be **toxic** to plants and some animals.

**Figure 5** The dry cell uses zinc as the reducing agent and manganese(IV) oxide, MnO<sub>2</sub> as the oxidising agent. A graphite rod, C and powdered graphite, C conduct electrons to the surface of individual MnO<sub>2</sub> particles within the cathode paste. Ammonium chloride is also incorporated into the cathode paste and serves as a salt bridge as well as providing protons (NH<sub>4</sub><sup>+</sup> is a weak acid) needed in the reduction of MnO<sub>2</sub>.

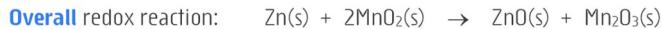
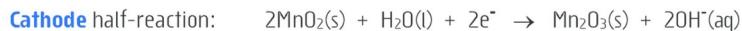
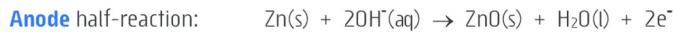
However, the use of ammonium ions is problematic, as over time their acidic nature causes the zinc anode to dissolve forming Zn<sup>2+</sup> ions. For this reason dry cells have a low shelf life of around a year.



The overall cell reactions for a dry cell are:

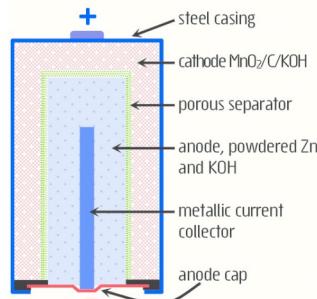


**The alkaline cell:** As in the dry cell, zinc is used as the reducing agent and manganese dioxide,  $\text{MnO}_2$  as the oxidising agent. Instead of an ammonium chloride electrolyte, it uses potassium hydroxide, KOH in the electrolyte paste. (See Fig 6.) This considerably improves its shelf life by eliminating the effect of acidic ammonium ions that ultimately dissolve the zinc anode of a dry cell. The zinc anode is in the form of powdered zinc, instead of Zn foil as in the dry cell. These design features allow the alkaline cell to achieve faster reaction rates thus giving it the ability to sustain a high current flow without the fall in voltage that happens in a dry cell. Typically an alkaline cell contains a greater mass of reductant, Zn and oxidant,  $\text{MnO}_2$  than a dry cell of similar size. This gives the cell a higher energy density and a longer operating life. The discharge cell reactions for an alkaline  $\text{Zn}/\text{MnO}_2$  cell are:

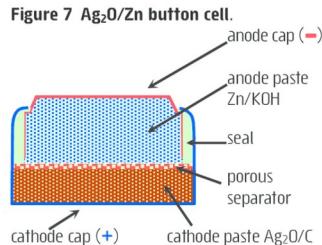


Alkaline cells are ideal for use in devices that require a higher current flow, eg toys, portable radios, CD players, electronic games and torches. As with the dry cell, spent alkaline cells pose minimal environmental impact. They are considered non-hazardous waste. While at present these cells are disposed of in the normal household waste stream, in the future it is hoped they can be recycled. At present there is no economic process for recycling the materials in these cells.

**Figure 6** A simplified view showing the arrangement of chemical components in an alkaline  $\text{Zn}/\text{MnO}_2$  cell.



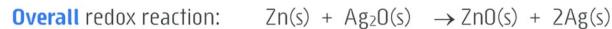
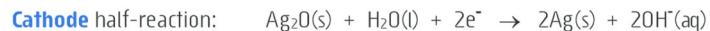
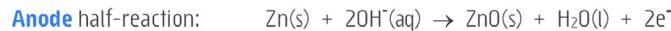
Attempt Set 12 # 3.



Most silver button cells contain small amounts of **mercury** and as such should be considered **hazardous waste**. These cells should not be disposed of in the normal household waste stream. Instead they can be recycled by returning them to retailers or jeweller's and watchmaker's stores.

Manufacturers and regulators are currently working to eliminate mercury use in these cells.

**Silver oxide button cells:** These are small primary cells with a very steady, constant voltage of 1.86 V. Their small size and reliable voltage output make them suitable for use in cameras, watches, hearing aids and pacemakers. Button cells have a good shelf life and a greater energy density than the alkaline cell. The reactions occurring in a button cell are:



**The lithium cell:** The high oxidation potential and low density of lithium, Li make it an ideal reducing agent for use in galvanic cells. One version of the **primary lithium cell** uses a lithium anode and manganese dioxide,  $\text{MnO}_2$  as the oxidising agent. The high reactivity of lithium with air and water means the cell must not contain water and needs to be of a robust airtight construction. For this reason lithium cells are potentially dangerous and can lead to accidental fires during use or especially if disposed of incorrectly.

Individual  $\text{Li}/\text{MnO}_2$  cells have an operating voltage of 3.0 V. The anode and cathode reactions for this cell are:



Although these cells are typically more expensive, they have a **very high energy density**, (see border note) long shelf life and a long operational life making them ideal for many applications. Lithium cells do not contain toxic metals, but they do pose a **fire hazard** if disposed of incorrectly. As lithium is a highly reactive metal they must be fully discharged, to consume all of the metallic lithium, before disposal. Disposable lithium cells are different to and should not be confused with the rechargeable **lithium-ion cell**. (See 8.4 p85.)

Attempt Set 12 # 4 and 5.

**Energy density** in a galvanic cell may be defined as the energy available per unit mass of the cell (eg  $\text{kJ kg}^{-1}$ ) or as the energy available per unit volume of the cell (eg  $\text{kJ L}^{-1}$ ). Thus, for a given application, the higher the energy density of a cell, the smaller its mass and or volume will be. For this reason, energy density is a very important aspect of a galvanic cell. This is especially true for cells in **portable** devices.

## 8.4 Secondary cells

**Figure 8** A typical car battery contains six lead-acid cells (Fig 9) connected in series in a single container producing 12 V.



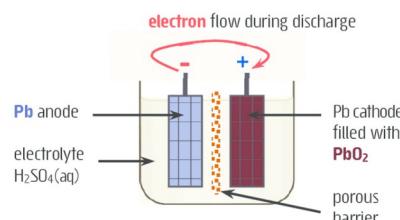
Batteries like this are low cost and have the advantage of being able to deliver high currents for prolonged periods. They are ideal for applications like car ignition and lighting systems.

A major limitation of these batteries is their **low energy density** ( $\approx 150 \text{ kJ kg}^{-1}$ ) and the **environmental and safety hazards** they pose. The sulfuric acid electrolyte is a corrosive and hazardous substance whilst lead and its compounds are acutely and chronically toxic. Although generally insoluble, lead compounds can be absorbed through ingestion and inhalation. Lead is also highly toxic to fish, other animals and plants.

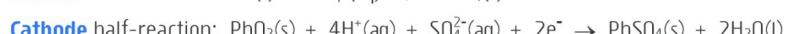
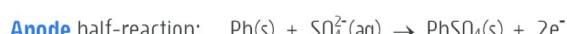
Spent lead-acid batteries are classified as **hazardous waste** by the Australian Government under the Hazardous Waste Act 1989.

**The lead-acid cell:** This **rechargeable** cell produces a voltage of 2 V and is typically used in the form of a battery consisting of several cells connected in a series. The **car battery**, for example, contains six of these cells connected in series to produce approximately 12 V. (See Fig 8.) The lead accumulator (lead-acid cell) used in most vehicles can undergo many **discharge-recharge cycles** over a period of several years before the internal components eventually lose their structure and the cell no longer functions. The ability to be recharged and to deliver **very large currents** makes this battery ideal for running the electric starter motor of cars and trucks, a purpose for which it has been used for over a century. These batteries also find application in electric vehicles like wheel chairs, fork lifts and golf carts as well as in emergency power systems and solar power storage systems.

**Figure 9** A simplified view of a single **lead-acid cell**. A porous separator ensures the oxidising agent and reducing agent do not make contact.



A single lead-acid cell (Fig 9) has two lead grid electrodes, immersed in an electrolyte of  $\approx 4.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4(\text{aq})$ . The **anode** grid contains spongy **lead**, Pb while the **cathode** grid is packed with powdered **lead dioxide**,  $\text{PbO}_2$ . During discharge, spongy Pb at the anode is oxidised to  $\text{Pb}^{2+}$  which immediately precipitates onto the electrode as insoluble  $\text{PbSO}_4(s)$ . Simultaneously, at the cathode,  $\text{PbO}_2$  is reduced to  $\text{Pb}^{2+}$  which also precipitates onto the electrode as insoluble  $\text{PbSO}_4(s)$ . The **powdered** nature of the Pb and  $\text{PbO}_2$  on the anode and cathode give these reagents a high **surface area** (increases reaction rate) contributing to one of the cell's important features, its ability to produce high currents.



A lead-acid cell can be recharged by applying a direct current of slightly greater than 2 V to each cell. The recharging current is made to flow in a direction opposite to the discharge current. This has the effect of **reversing** the anode and cathode half-reactions that occur during discharge, thus regenerating Pb at the anode and  $\text{PbO}_2$  at the cathode.

A major drawback of the lead-acid cell is the high density of lead ( $11.3 \text{ kg L}^{-1}$ ) which results in the cells having a **very low energy density** of around  $150 \text{ kJ kg}^{-1}$ . This is especially an issue where the cells are used in transport situations. These batteries must be handled with care as lead and its compounds are acutely and chronically **toxic** whilst sulfuric acid is **corrosive**. Used lead-acid batteries are classed as **hazardous waste** and as such they must be disposed of appropriately. This usually involves **recycling**. An Australian Government estimate found about 70,000 to 80,000 tonnes of waste lead-acid batteries were produced in Australia in 2005; 65,000 tonnes of which were reprocessed at Australian smelters.

Attempt Set 12 # 6, 7 and 8.

**The lithium-ion cell:** As with the non-rechargeable lithium cell, the **lithium-ion cell** utilises lithium to produce a rechargeable cell with an **exceptional energy density**, good shelf life and the capability of many recharge cycles. Despite their higher cost, these cells are now extensively used in laptops, iPads, cameras, mobile phones and portable power tools. Ongoing research and improvement in lithium-ion cell technology is supporting the current growth in the electric vehicle industry (Fig 23 p91) and has also led to the introduction of large scale lithium-ion storage units for household and commercial use. (See Fig 10.)

These cells do not contain a metallic lithium anode, as in the non-rechargeable lithium cell. Instead the **anode** is made of porous graphite with lithium ions interspersed between the graphite layers, called intercalation, designated as  $\text{Li}_x\text{C}_6$ . The **cathode** is a porous lithium metal oxide such as  $\text{LiCoO}_2$ . (See Fig 11.) The electrodes are in sheet form with a porous separator sheet in between and rolled into a convenient shape. The electrode assembly is immersed in a **non-aqueous** organic electrolyte containing mobile  $\text{Li}^+$  ions.

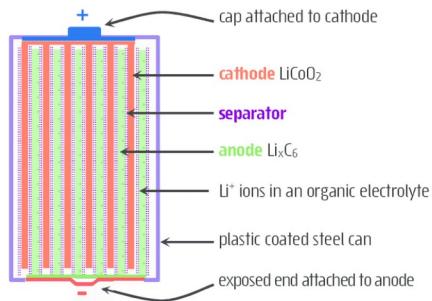
**Figure 10** Powerwall is a lithium-ion home battery that charges using electricity generated from solar panels or when utility rates are low and then returns power to your home in the evening.



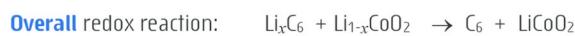
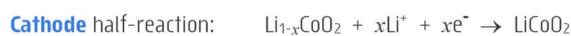
Image: Tesla Motors, Inc: Alexis Georgeson.

**Figure 11** A simplified view of a cylindrical Li-ion cell. The anode, cathode and separator are in sheet form and rolled into a cylinder housed in a pressurised steel can.

Rechargeable Li-ion battery packs like those in a laptop must have an inbuilt microprocessor that manages its charging. Overcharging is dangerous and can lead to a process called venting and thermal runaway. This can also happen if spent cells are pierced or crushed.



During discharge lithium ions migrate out of the  $\text{Li}_x\text{C}_6$  anode and into the  $\text{LiCoO}_2$  cathode while electrons flow from the anode, via an external conducting path (through an appliance) to the cathode. This maintains a charge balance in both the anode and cathode.



During recharge these processes are reversed by applying a sufficient voltage to the cell so that electrons are forced to flow from the  $\text{LiCoO}_2$  electrode to the  $\text{Li}_x\text{C}_6$  electrode. This regenerates  $\text{Li}_x\text{C}_6$  at the anode and  $\text{LiCoO}_2$  at the cathode.

**Figure 12 Li-ion cells**, like these two, are becoming increasingly popular as a rechargeable power source for portable electrical devices. They can be produced in a variety of shapes and sizes, have a long shelf life and an exceptional energy density. Li-ion cells typically have an energy density of  $350\text{--}950 \text{ J kg}^{-1}$ . The upper level energy density is steadily increasing as researchers continue to improve cell design.





**Figure 13** A hydrogen refuelling pump.

**Hydrogen gas** is a desirable fuel as its combustion produces considerably more energy per gram of fuel than does the combustion of natural gas ( $\approx 120 \text{ kJ g}^{-1}$  for  $\text{H}_2$  compared to  $50 \text{ kJ g}^{-1}$  for  $\text{CH}_4$ ).

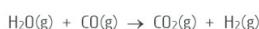
Furthermore the only waste product of its combustion is water. However, as **natural sources** of hydrogen gas do not occur on Earth it must be produced industrially and this is an energy intensive process.

The major method of hydrogen production is the steam methane reforming process.



Heat energy needed to drive this endothermic reaction is gained from the combustion of further methane.

The resulting  $\text{CO}/\text{H}_2$  gas mixture from this reaction is treated with steam at  $400^\circ\text{C}$  to further increase the yield of hydrogen gas.



Producing hydrogen gas this way is **not sustainable** as it uses natural gas, a non-renewable resource. Also this method generates a large amount of  $\text{CO}_2$ , a **greenhouse gas**.

**Electrolysis** of water is another method used to produce  $\text{H}_2(\text{g})$ .



It is most favourable where cheap sources of electrical energy are available. Electrolysis has the advantage of producing pure  $\text{O}_2(\text{g})$  as a valuable by-product.

Producing hydrogen gas this way can be a **sustainable** process if the electrical energy used is produced from **renewable sources** like hydro, wind, wave, geothermal or solar energy. Doing this avoids both the use of non-renewable hydrocarbon fuels and the production of the greenhouse gas  $\text{CO}_2$ .

Attempt Set 12 # 10 and 11.

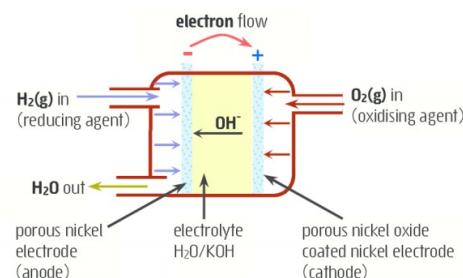
## 8.5 Fuel cells

**Alkaline hydrogen-oxygen fuel cell:** This is one of the earliest fuel cell designs. The Apollo space missions during the late 1960s and early 1970s used these cells to generate electricity and provide drinking water for the astronauts. NASA also used this technology on board its space shuttles.

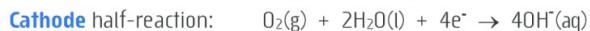
**Fuel cells** like this differ from primary cells and secondary cells in that they do not store the oxidising or reducing agent. Instead, these reactants are constantly fed into the cell to generate electricity. Chemical by-products of the cell reactions are expelled from the cell as it operates. The cell shown below uses gaseous **hydrogen** as the reductant and gaseous **oxygen** as the oxidant. These circulate under pressure over porous nickel electrodes that incorporate particles of a catalyst (eg platinum). A hot concentrated solution of KOH is used as the electrolyte. Some of the water formed at the anode can be seen leaving the cell as steam mixed with the circulating hydrogen gas.

**Figure 14** A simplified view of an **alkaline  $\text{H}_2/\text{O}_2$  fuel cell**.

The reducing agent,  $\text{H}_2$ , diffuses into the porous Ni electrode and is oxidised forming  $\text{H}^+$  ions and free electrons. These electrons are conducted by the Ni electrode out of the cell to the cathode. Oxygen absorbed into the cathode then gains electrons forming  $\text{OH}^-$  ions. The resulting  $\text{H}^+$  ions and  $\text{OH}^-$  ions migrate through the electrolyte to combine and form water, the only chemical product. This cell operates at  $\approx 150\text{--}200^\circ\text{C}$  with an efficiency of around 70%.



Half-reactions for this cell are:



The overall reaction occurring in the hydrogen-oxygen fuel cell is identical to burning hydrogen in air (or oxygen). Conducting the reaction in the fuel cell, however, is a much more efficient way of converting the available enthalpy change directly into electrical energy. Modern electrical power plants burning fossil fuels for example are typically constrained to energy conversion efficiencies of 35–40% (excluding cogeneration plants). Motor vehicles using fossil fuels to operate an internal combustion engine can achieve energy conversion efficiencies of around 25–30%. By comparison the hydrogen-oxygen fuel cell described here has an energy conversion efficiency of around 70%.

**Proton exchange membrane fuel cell (PEMFC):** The PEMFC was first developed in the US during the early 1960s. Its original intended uses were for military and space applications, though it was never widely commercialised. Research and development of this fuel cell technology continues today in the hope that it can find wide application and commercialisation as the fuel cell of choice for future hydrogen powered cars and buses. (See Fig 15.)

The **PEMFC** uses 99.999% pure  $\text{H}_2(\text{g})$  and  $\text{O}_2(\text{g})$ , from the air to produce a DC electric current, water and heat. A special PEMFC feature is the thin, **solid** polymer **proton exchange membrane (PEM)** used as the electrolyte and electrode separator. This avoids the use of a corrosive liquid electrolyte, as in the alkaline fuel cell. The PEM allows protons ( $\text{H}^+$  ions) to move through it, from the anode to the cathode, while preventing  $\text{H}_2(\text{g})$  or  $\text{O}_2(\text{g})$  from moving across the thin, solid electrolyte membrane.

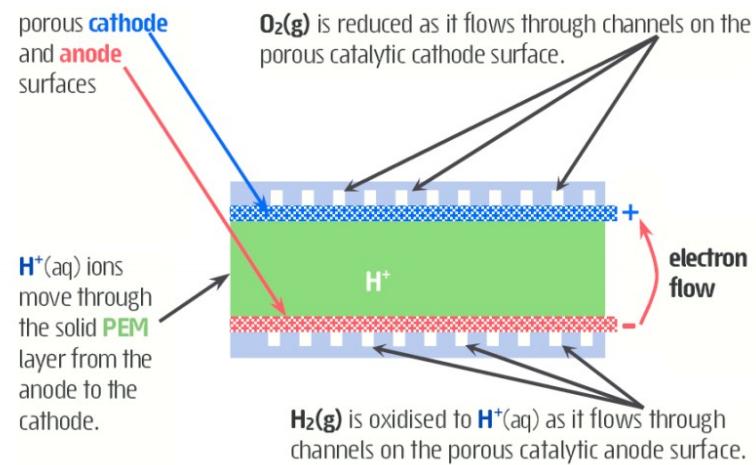


**Figure 15** This Toyota Fuel Cell Vehicle (FCV) is scheduled for selected release into the Japanese car market in early 2015 prior to its release in the US and Europe. It utilises solid polymer electrolyte membrane fuel cells (similar to the PEMFC) and a nickel metal hydride storage battery to power its electric motor. Hydrogen is stored at 70 MPa in several storage cylinders giving the vehicle a range of around 700 km.

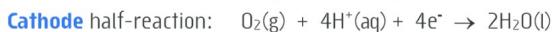
Image courtesy Toyota Motor Corporation, [http://www.toyota-global.com/innovation/environmental\\_technology/fuelcell\\_vehicle/](http://www.toyota-global.com/innovation/environmental_technology/fuelcell_vehicle/)

The solid nature of the electrolyte in a PEMFC allows a compact, flexible fuel cell design as the electrolyte layer (PEM) can be as thin as 0.050 mm with the entire cell (PEMFC) being around 1 mm thick. Both the anode and cathode consist of **nanoparticles** of **platinum** impregnated onto **porous carbon**. The platinum acts as a **catalyst**, speeding up the anode and cathode reactions, while the carbon conducts electrons from the electrode surface. Although each cell produces only 1.1 V, arranging the cells into stacks in series produces higher voltages.

**Figure 16** During the operation of a **PEMFC**, pure hydrogen gas is oxidised as it flows through channels on the anode surface. The resulting  $\text{H}^+$  ions migrate into the solid electrolyte membrane (**PEM**) and move towards the cathode. Electrons released at the anode move through an external circuit to the cathode. Oxygen gas passing through channels on the cathode surface gain these electrons and combine with the migrating  $\text{H}^+$  ions to form water.



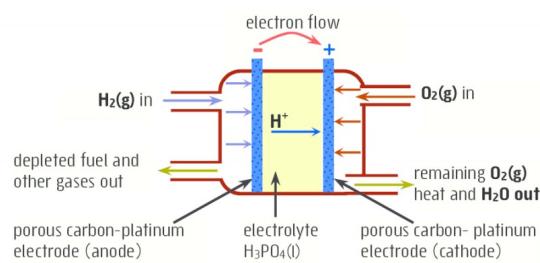
Half-reactions for this cell are:



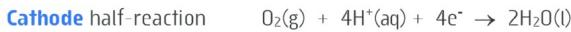
Attempt Set 12 # 12.

**Phosphoric acid fuel cell (PAFC):** The PAFC uses hydrogen gas from petroleum reforming and is able to tolerate the low levels of CO impurities that are often present. Oxygen gas from the air is the oxidising agent. The cells produce a DC potential (voltage), water and heat. These cells operate using a phosphoric acid electrolyte contained in a ceramic matrix of silicon carbide. They operate at temperatures of 150–220 °C. This high temperature increases  $\text{H}_3\text{PO}_4(\text{l})$  conductivity while minimising catalyst **poisoning** (rendering inactive due to CO absorption) from gas impurities like CO that are present in the hydrogen fuel stream. Both electrodes consist of **porous carbon** and **platinum catalyst** particles.

**Figure 17** A simplified view of a **phosphoric acid fuel cell**. The reducing agent  $\text{H}_2$  diffuses into the porous C/Pt electrode and is oxidised forming  $\text{H}^+$  ions and free electrons. These electrons are conducted by the C/Pt electrode out of the cell to the cathode.  $\text{H}^+$  ions migrate through the electrolyte to the cathode. Here they combine with oxygen absorbed into the cathode. In the process, oxygen gains electrons arriving from the anode and becomes reduced to form water, the only chemical product.



Half-reactions for this cell are:



The **phosphoric acid fuel cell** (PAFC) is one of the more widely developed commercial fuel cell technologies. These cells have an electrical output **efficiency** of around 40% but overall efficiency can rise to 85% with **cogeneration**, ie where the waste heat is also utilised.

While PAFCs are a costly way to produce electricity they are quiet, maintain good air quality and can run on hydrogen produced from traditional hydrocarbon fuels. The high operational temperature of these cells (150–220 °C) makes the platinum electrode catalyst reasonably tolerant of contaminants like carbon monoxide. In low temperature fuel cells, the electrode catalyst, platinum, is easily '**poisoned**' (made inactive) by even minute traces of impurity gases like CO.

PAFC is currently the dominant fuel cell system used for **static power generation** in applications like emergency power for banks, hotels, hospitals and police stations. Recent developments in commercial Li-ion cells however, may see these soon become the cell of choice for this type of application.

Attempt Set 12 # 13, 14 and 15.