

# Strong electrolytes

- For strong electrolytes,  $\Lambda_m$  increases slowly with dilution and can be represented by the equation:

$$\Lambda_m = \ddot{E}_m^\circ - Ac^{1/2}$$

if we plot  $\ddot{E}_m$  against  $c^{1/2}$ , we obtain a straight line with intercept equal to  $\ddot{E}_m^\circ$  and slope equal to  $-A$ . The value of the constant  $A$  for a given solvent and temperature depends on the type of electrolyte i.e., the charges on the cation and anion produced on the dissociation of the electrolyte in the solution. Thus, NaCl, CaCl<sub>2</sub>, MgSO<sub>4</sub> are known as 1-1, 2-1 and 2-2 electrolytes respectively. All electrolytes of a particular type have the same value for  $A$ .

- Kohlrausch examined  $\ddot{E}_m^\circ$  values for a number of strong electrolytes and observed certain regularities.
- He noted that the difference in  $\ddot{E}_m^\circ$  of the electrolytes NaX and KX for any X is nearly constant. For example at 298 K:
- $\ddot{E}_{m(\text{KCl})}^\circ - \ddot{E}_{m(\text{NaCl})}^\circ = \ddot{E}_{m(\text{KBr})}^\circ - \ddot{E}_{m(\text{NaBr})}^\circ = \ddot{E}_{m(\text{KI})}^\circ - \ddot{E}_{m(\text{NaI})}^\circ \approx 23.4 \text{ S cm}^2 \text{ mol}^{-1}$

and similarly it was found that

$$\ddot{E}_{m(\text{NaBr})}^\circ - \ddot{E}_{m(\text{NaCl})}^\circ = \ddot{E}_{m(\text{KBr})}^\circ - \ddot{E}_{m(\text{KCl})}^\circ \approx 1.8 \text{ S cm}^2 \text{ mol}^{-1}$$

# Law of independent migration of ions

- The law states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte. Thus, if  $\lambda_{\text{Na}^+}^{\circ}$  and  $\lambda_{\text{Cl}^-}^{\circ}$  are limiting molar conductivity of the sodium and chloride ions respectively, then the limiting molar conductivity for sodium chloride is given by the equation:

$$\Lambda_{(\text{NaCl})}^{\circ} = \lambda_{\text{Na}^+}^{\circ} + \lambda_{\text{Cl}^-}^{\circ}$$

- In general, if an electrolyte on dissociation gives  $v_+$  cations and  $v_-$  anions then its limiting molar conductivity is given by:
- $\Lambda^\circ = v_+ \lambda_+^0 + v_- \lambda_-^0$

Here,  $\lambda_+^0$  and  $\lambda_-^0$  are the limiting molar conductivities of the cation and anion respectively.

# Weak electrolytes

- Weak electrolytes like acetic acid have lower degree of dissociation at higher concentrations and hence for such electrolytes, the change in  $\Lambda_m$  with dilution is due to increase in the degree of dissociation and consequently the number of ions in total volume of solution that contains 1 mol of electrolyte.
- In such cases  $\ddot{E}_m^\circ$  increases steeply on dilution, especially near lower concentrations. Therefore,  $\ddot{E}_m^\circ$  cannot be obtained by extrapolation of  $\Lambda_m$  to zero concentration.
- At infinite dilution i.e., concentration  $c \rightarrow$  zero electrolyte dissociates completely ( $\alpha = 1$ ), but at such low concentration the conductivity of the solution is so low that it cannot be measured accurately.
- Therefore,  $\ddot{E}_m^\circ$  for weak electrolytes is obtained by using Kohlrausch law of independent migration of ions. At any concentration  $c$ , if  $\alpha$  is the degree of dissociation then it can be approximated to the ratio of molar conductivity  $\ddot{E}_m$  at the concentration  $c$  to limiting molar conductivity,  $\ddot{E}_m^\circ$ . Thus we have:

- $$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$$

But for weak electrolytes like acetic acid, the equation of  $K_a$  becomes

$$K_a = \frac{c\alpha^2}{(1-\alpha)} = \frac{c\Lambda_m^2}{A_m^{\circ 2} \left(1 - \frac{A_m}{A_m^{\circ}}\right)} = \frac{c\Lambda_m^2}{A_m^{\circ} (A_m^{\circ} - A_m)}$$

Aç

Using Kohlrausch law of independent migration of ions, it is possible to calculate  $\ddot{E}_m^{\circ}$  for any electrolyte from the  $\lambda^{\circ}$  of individual ions. Moreover, for weak electrolytes like acetic acid it is possible to determine the value of its dissociation constant once we know the  $\ddot{E}_m^{\circ}$  and  $\Lambda_m$  at a given concentration  $c$ .

# summary

## Uses of Kohlrausch's law

→ Calculation of molar conductivity at infinite dilution for weak electrolytes

→ Calculation of degree of dissociation.

→ Calculation of dissociation constant for a weak electrolyte

→ Calculation of solubility of sparingly soluble salt.

# Electrolytic cells and electrolysis

- In an electrolytic cell external source of voltage is used to bring about a chemical reaction.
- One of the simplest electrolytic cell consists of two copper strips dipping in an aqueous solution of copper sulphate.
- If a DC voltage is applied to the two electrodes, then  $\text{Cu}^{2+}$  ions discharge at the cathode (negatively charged) and the following reaction takes place:
- $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$  Copper metal is deposited on the cathode. At the anode, copper is converted into  $\text{Cu}^{2+}$  ions by the reaction:  
 $\text{Cu}(\text{s}) \rightarrow \text{Cu}^{2+}(\text{s}) + 2\text{e}^-$
- Thus copper is dissolved (oxidised) at anode and deposited (reduced) at cathode. This is the basis for an industrial process in which impure copper is converted into copper of high purity. The impure copper is made an anode that dissolves on passing current and pure copper is deposited at the cathode.
- Sodium and magnesium metals are produced by the electrolysis of their fused chlorides and aluminium is produced by electrolysis of aluminium oxide in presence of cryolite.



# Faraday's law of electrolysis

Faraday's two laws of electrolysis are:

- **i) First Law:** The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or melt).
- **(ii) Second Law:** The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights (Atomic Mass of Metal ÷ Number of electrons required to reduce the cation).

According to faraday  $Q=It$

# Products of electrolysis

- Products of electrolysis depend on the nature of material being electrolysed and the type of electrodes being used.
- If the electrode is inert (e.g:-platinum or gold), it does not participate in the chemical reaction and acts only as source or sink for electrons. On the other hand, if the electrode is reactive, it participates in the electrode reaction. Thus, the products of electrolysis may be different for reactive and inert. electrodes.
- The products of electrolysis depend on the different oxidising and reducing species present in the electrolytic cell and their standard electrode potentials.
- Moreover, some of the electrochemical processes although feasible, are so slow kinetically that at lower voltages these do not seem to take place and extra potential which is called overpotential has to be applied, which makes such process more difficult to occur.

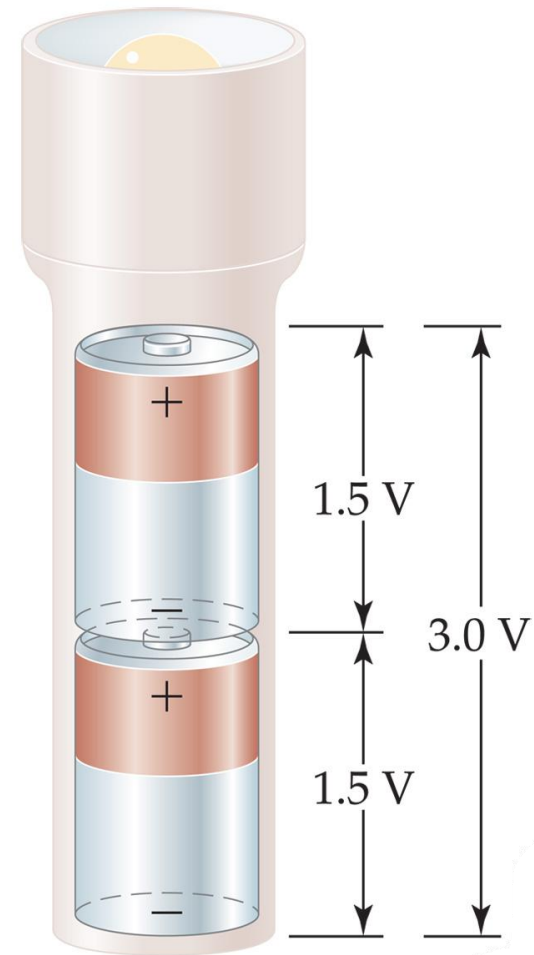
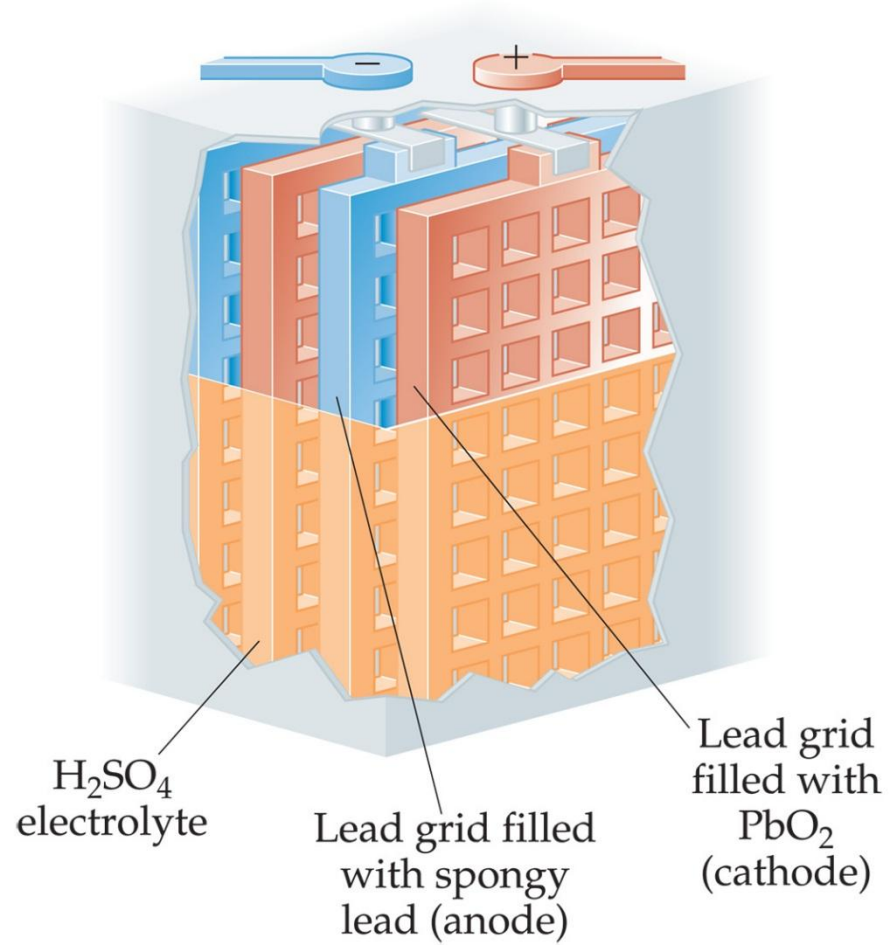
# Batteries

Any battery (actually it may have one or more than one cell connected in series) or cell that we use as a source of electrical energy is basically a galvanic cell where the chemical energy of the redox reaction is converted into electrical energy .

There are 2 types of batteries

- a) Primary batteries
- b) Secondary batteries

# Batteries



# Primary batteries

- In the primary batteries, the reaction occurs only once and after use over a period of time battery becomes dead and cannot be reused again.

The most familiar example of this type is the dry cell is also known as Leclanche cell after its discoverer which is used commonly in our transistors and clocks.

- The cell consists of a zinc container that also acts as anode and the cathode is a carbon (graphite) rod surrounded by powdered manganese dioxide and carbon . The space between the electrodes is filled by a moist paste of ammonium chloride ( $\text{NH}_4\text{Cl}$ ) and zinc chloride ( $\text{ZnCl}_2$ ). The electrode reactions are complex, but they can be written approximately as follows :
- Anode:  $\text{Zn(s)} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$
- Cathode:  $\text{MnO}_2 + \text{NH}_4^+ + \text{e}^- \rightarrow \text{MnO(OH)} + \text{NH}_3$

- In the reaction at cathode, manganese is reduced from the + 4 oxidation state to the +3 state. Ammonia produced in the reaction forms a complex with  $\text{Zn}^{2+}$  to give  $[\text{Zn}(\text{NH}_3)_4]^{2+}$ . The cell has a potential of nearly 1.5 V.
- Mercury cell, suitable for low current devices like hearing aids, watches, etc. consists of zinc – mercury amalgam as anode and a paste of  $\text{HgO}$  and carbon as the cathode. The electrolyte is a paste of  $\text{KOH}$  and  $\text{ZnO}$ . The electrode reactions for the cell are given below:

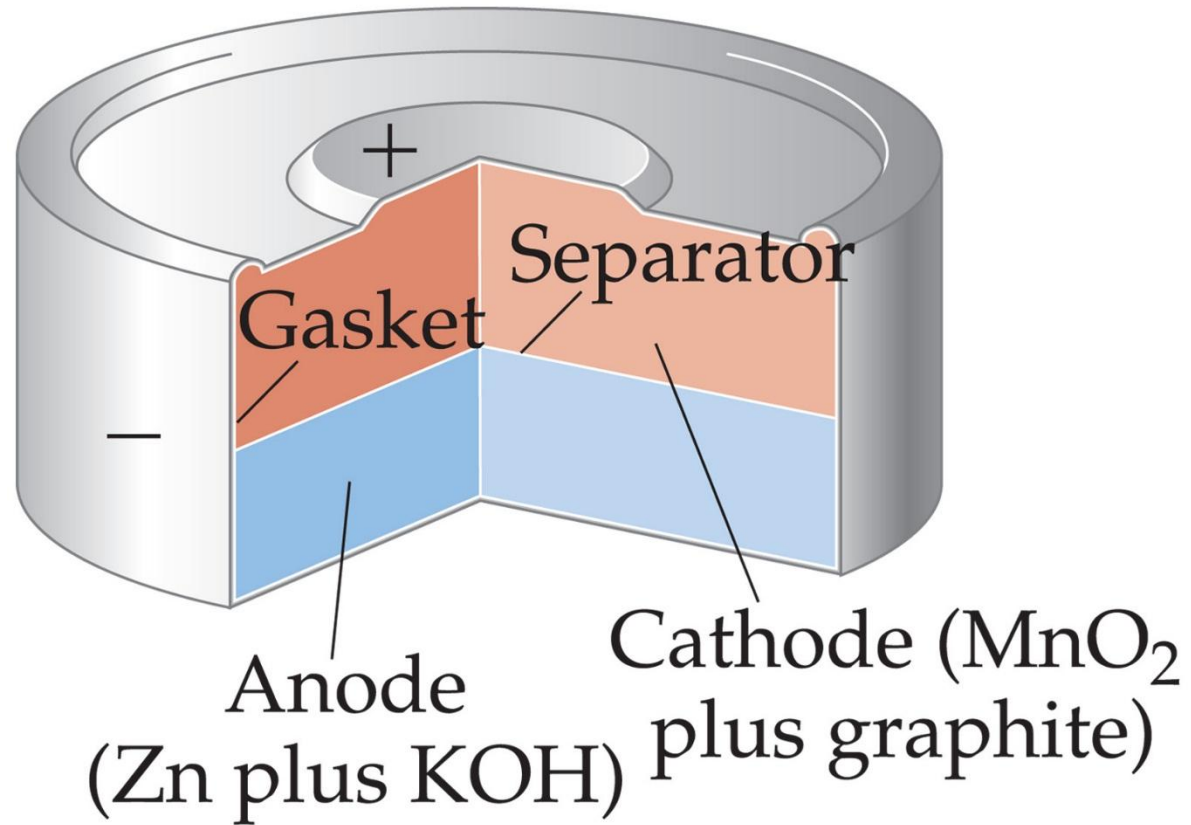
Anode:



Cathode:

- $\text{HgO} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Hg(l)} + 2\text{OH}^-$
- The overall reaction is represented by
- $\text{Zn(Hg)} + \text{HgO(s)} \rightarrow \text{ZnO(s)} + \text{Hg(l)}$
- The cell potential is approximately 1.35 V and remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its life time.

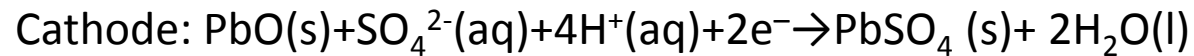
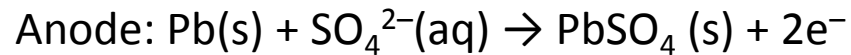
# Alkaline Batteries



# Secondary batteries

- A secondary cell after use can be recharged by passing current through it in the opposite direction so that it can be used again. A good secondary cell can undergo a large number of discharging and charging cycles.
- The most important secondary cell is the lead storage battery commonly used in automobiles and invertors. It consists of a lead anode and a grid of lead packed with lead dioxide (PbO<sub>2</sub>) as cathode. A 38% solution of sulphuric acid is used as an electrolyte.

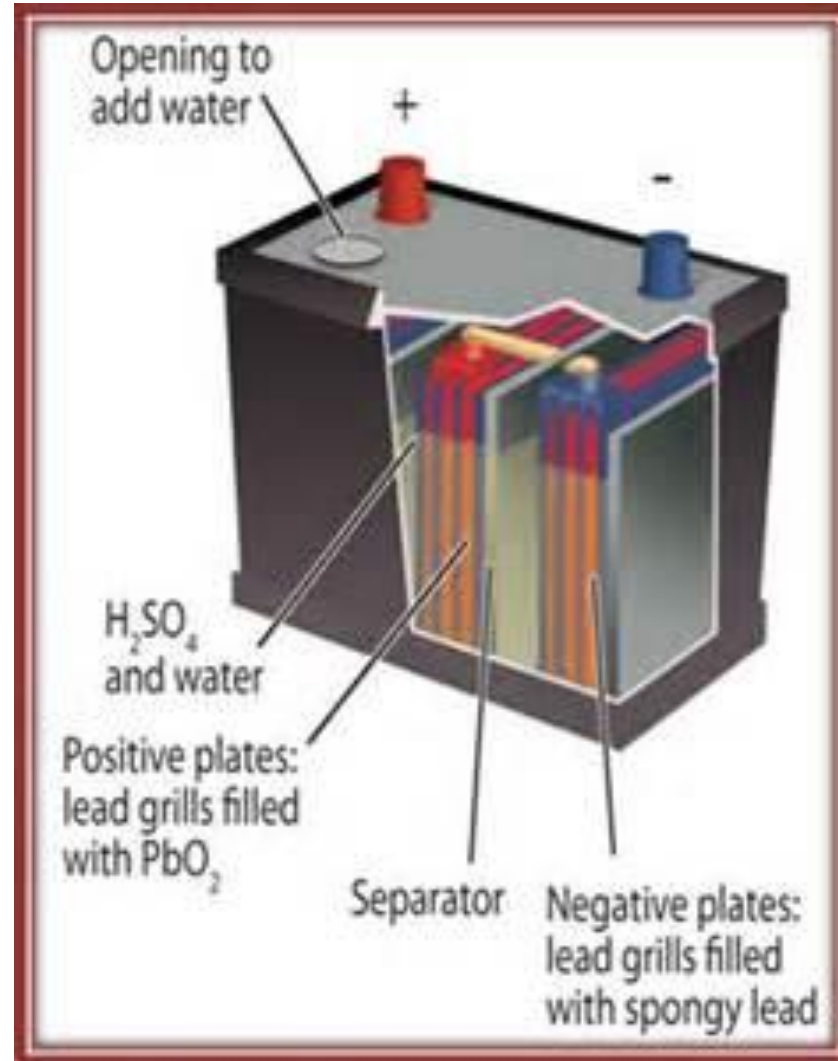
- The cell reactions when the battery is in use are given below:



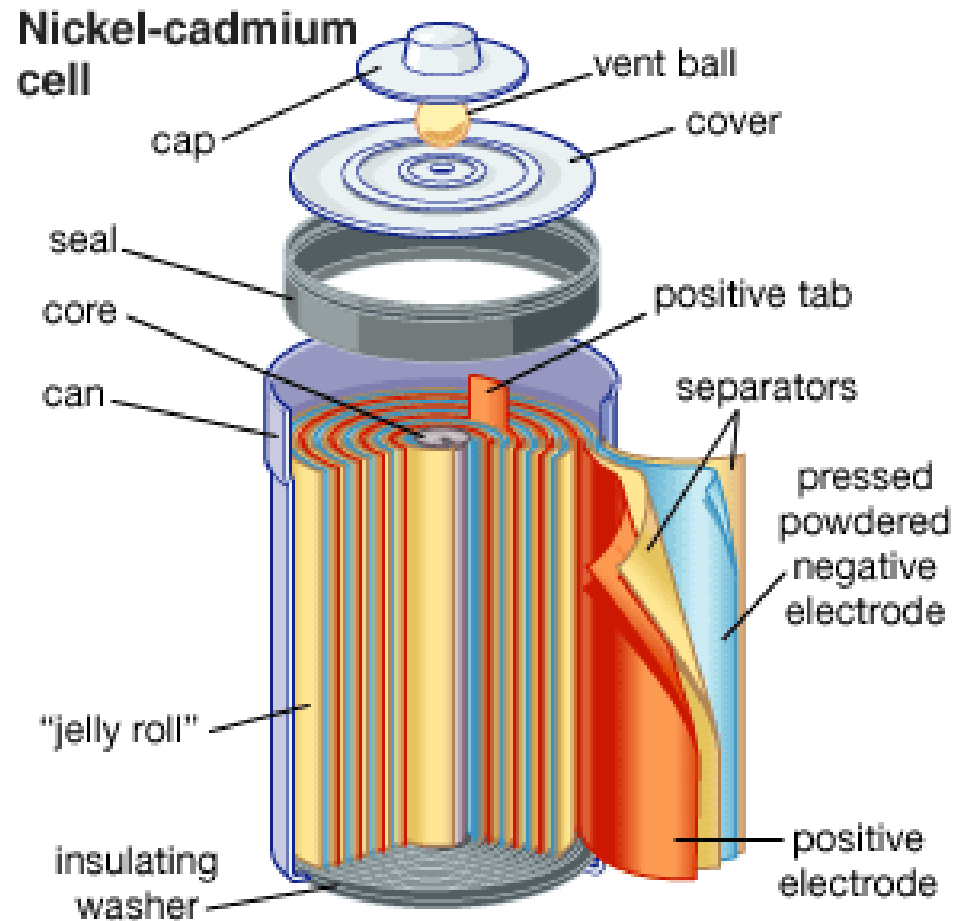
- i.e., overall cell reaction consisting of cathode and anode reactions is:  $\text{Pb}(s) + \text{PbO}_2(s) + 2\text{H}_2\text{SO}_4(aq) \rightarrow 2\text{PbSO}_4(s) + 2\text{H}_2\text{O}(l)$
- On charging the battery the reaction is reversed and PbSO<sub>4</sub>(s) on anode and cathode is converted into Pb and PbO<sub>2</sub>, respectively.



# A lead storage battery (secondary battery)



- Another important secondary cell is the nickel-cadmium cell which has longer life than the lead storage cell but more expensive to manufacture.
- The overall reaction during discharge is:
- $\text{Cd (s)} + 2\text{Ni(OH)}_3 \text{ (s)} \rightarrow \text{CdO (s)} + 2\text{Ni(OH)}_2 \text{ (s)} + \text{H}_2\text{O (l)}$



# Fuel cells

- Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy are called fuel cells.
- One of the most successful fuel cells uses the reaction of hydrogen with oxygen to form water.
- In the cell, hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution. Catalysts like finely divided platinum or palladium metal are incorporated into the electrodes for increasing the rate of electrode reactions. The electrode reactions are given below:
- Cathode:  $O_2 (g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$
- Anode:  $2H_2 (g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$
- Overall reaction being:  
 $2H_2(g) + O_2(g) \rightarrow 2 H_2O(l)$
- The cell runs continuously as long as the reactants are supplied. Fuel cells produce electricity with an efficiency of about 70 % compared to thermal plants whose efficiency is about 40%.

# Hydrogen Fuel Cells

