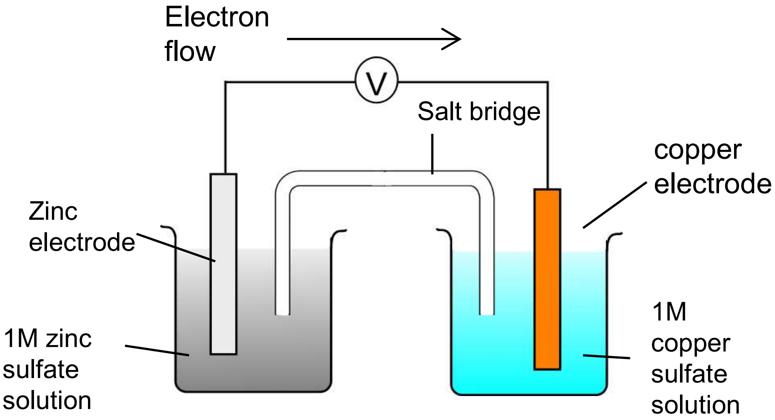
1.11 Redox Equilibria

Electrochemical cells

- A cell has two half–cells.
- The two half cells have to be connected with a salt bridge.
- Simple half cells will consist of a metal (acts an electrode) and a solution of a compound containing that metal (eg Cu and $CuSO_4$).
- These two half cells will produce a small voltage if connected into a circuit. (i.e. become a Battery or cell).



Why does a voltage form?
In the cell pictured above
When connected together the zinc half-cell has more of a tendency to oxidise to the Zn^{2+} ion and release electrons than the copper half-cell. ($Zn \rightarrow Zn^{2+} + 2e^-$)
More electrons will therefore build up on the zinc electrode than the copper electrode.
A potential difference is created between the two electrodes.
The zinc strip is the negative terminal and the copper strip is the positive terminal.

This potential difference is measured with a high resistance voltmeter, and is given the symbol **E**. The E for the above cell is E= +1.1V.

Why use a high resistance voltmeter?
The voltmeter needs to be of very high resistance to stop the current from flowing in the circuit. In this state it is possible to measure the maximum possible potential difference (E).
The reactions will not be occurring because the very high resistance voltmeter stops the current from flowing.

Salt bridge
The salt bridge is used to connect up the circuit. The **free moving ions** conduct the charge.

A salt bridge is usually made from a piece of filter paper (or material) soaked in a salt solution, usually **potassium nitrate**.

The salt should be **unreactive with the electrodes and electrode** solutions. E.g. potassium chloride would not be suitable for copper systems because chloride ions can form complexes with copper ions.

A wire is not used because the metal wire would set up its own electrode system with the solutions.

What happens if current is allowed to flow?
If the voltmeter is removed and replaced with a bulb or if the circuit is short circuited, a current flows. The reactions will then occur separately at each electrode. The voltage will fall to zero as the reactants are used up.

The most positive electrode will always undergo reduction.
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ (positive as electrons are used up)

The most negative electrode will always undergo oxidation.
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ (negative as electrons are given off)

Practical set up
When constructing a cell practically electrical contact between the electrodes and solutions can be improved by:
- Rubbing electrode with sandpaper to remove any oxide layer on the surface of the electrode.
- Wiping the electrodes with propanone to remove any grease on the surface of the metal.

Cell Diagrams

Electrochemical cells can be represented by a **cell diagram:**

$Zn(s)\ |\ Zn^{2+}(aq)\ ||\ Cu^{2+}(aq)\ |\ Cu(s)$ E= +1.1V

Most oxidised form is put next to the double line

- The solid vertical line represents the boundary between **phases** e.g. solid (electrode) and solution (electrolyte)
- The double line represents the **salt bridge** between the two half cells
- the voltage produced is indicated
- the more positive half cell is written on the right if possible (but this is not essential)

Systems that do not include metals.

If a system does not include a metal that can act as an electrode, then a **platinum electrode** must be used and included in the cell diagram. It provides a **conducting surface for electron transfer.**
A platinum electrode is used because it is **unreactive** and **can conduct electricity.**

e.g. for $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$ there is no solid conducting surface, a platinum electrode must be used.

The cell diagram is drawn as:

$||\ Fe^{3+}(aq), Fe^{2+}(aq)\ |Pt$

Still with more oxidised form near the double line
A comma separates the oxidised from the reduced species.

If the system contains several species
e.g. $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
then in the cell diagram the balancing numbers, H^+ ions and H_2O can be left out.

$||\ MnO_4^-(aq), Mn^{2+}(aq)\ |Pt$
or if on left hand side
$Pt\ |\ Mn^{2+}(aq), MnO_4^-(aq)\ ||$

If a half equation has several physical states then the solid vertical line should be used between each different state boundary.

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

$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ $||\ Cl_2(g)|\ Cl^-(aq)\ |\ Pt$

As the phase line also separates the oxidised and reduced terms a comma is not necessary here.

Measuring the electrode potential of a cell

- It is not possible to measure the absolute potential of a half electrode on its own. It is only possible to measure the potential difference between two electrodes.
- To measure it, it has to be connected to another half-cell of known potential, and the potential difference between the two half-cells measured.
- by convention we can assign a relative potential to each electrode by linking it to a reference electrode (hydrogen electrode), which is given a potential of zero Volts

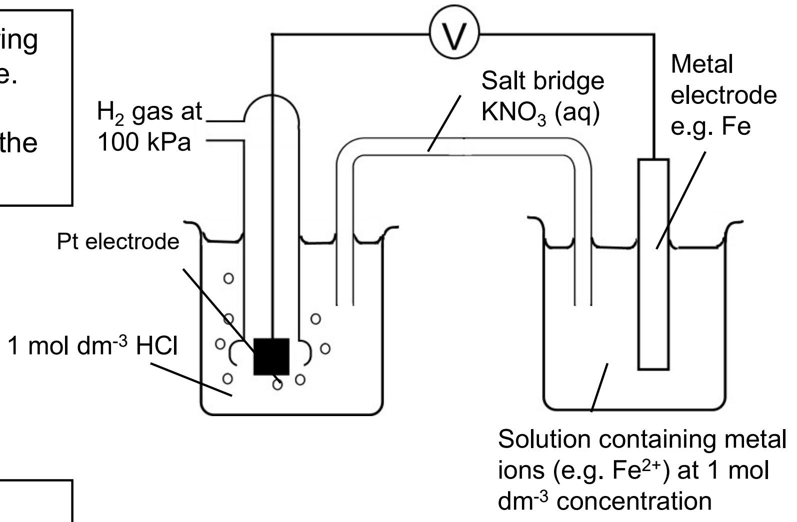
The Standard Hydrogen Electrode

The potential of all electrodes are measured by comparing their potential to that of the standard hydrogen electrode.

The **standard hydrogen electrode (SHE)** is assigned the potential of 0 volts.

The hydrogen electrode equilibrium is:
$H_2 (g) \rightleftharpoons 2H^+ (aq) + 2e^-$

In a cell diagram the hydrogen electrode is represented by: $Pt \,|H_{2\,(g)}\,|\, H^+_{(aq)}$



Components of a standard hydrogen electrode.
To make the electrode a standard reference electrode some conditions apply:
1. **Hydrogen gas** at **pressure of 100kPa**
2. Solution containing the **hydrogen ion at 1.0 mol dm^{-3}** (solution is usually 1 mol dm^{-3} HCl)
3. Temperature at **298K**
4. Platinum electrode

Because the equilibrium does not include a conducting metal surface, a platinum wire is used which is coated in finely divided platinum. (The platinum black is used because it is porous and can absorb the hydrogen gas.)

Standard conditions are needed because the position of the redox equilibrium will change with conditions.
For example, in the equilibrium:
$M^{n+}(aq) + n e^- \rightleftharpoons M(s)$

An increase in the concentration of M^{n+} would move the equilibrium to the right, so making the potential more positive.

Secondary standards
The standard hydrogen electrode is difficult to use, so often a different standard is used which is easier to use.
These other standards are themselves calibrated against the SHE. This is known as using a **secondary standard -** i.e. a standard electrode that has been calibrated against the primary standard.
The common ones are:

silver / silver chloride	E = +0.22 V
calomel electrode	E = +0.27 V

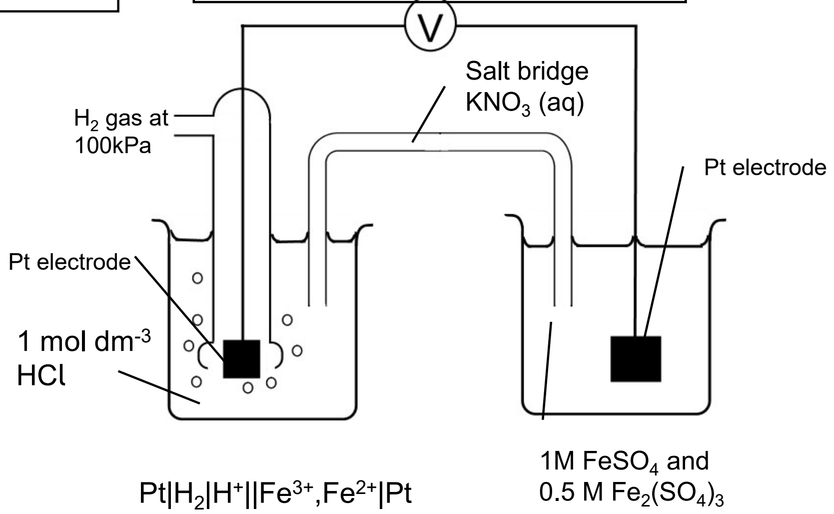
Standard Electrode Potentials $E^{\ominus}$

When an electrode system is connected to the hydrogen electrode system, and standard conditions apply the potential difference measured is called the **standard electrode potential**,

The standard conditions are :
•all ion solutions at 1 mol dm^{-3}
•temperature 298 K
•gases at 100 kPa pressure
•no current flowing

Standard electrode potentials are found in data books and are quoted as:
$Li^+(aq) \,|\, Li (s)$ E= -3.03V
more oxidised form on left

They may also be quoted as half equations
$Li^+ (aq) + e^- \rightleftharpoons Li (s)$ E= -3.03V
but again the more oxidised form is on the left



$Pt|H_2|H^+||Fe^{3+},Fe^{2+}|Pt$

Note: in the electrode system containing two solutions it is necessary to use a platinum electrode and **both** ion solutions must be of a 1 mol dm^{-3} concentration, so $[Fe^{2+}]$ = 1 mol dm^{-3} and $[Fe^{3+}]$ = 1 mol dm^{-3} .

Calculating the EMF of a cell

$Mg(s) \mid Mg^{2+}(aq) \mid\mid Cu^{2+}(aq) \mid Cu(s)$ E= +1.1V

use the equation

Ecell= Erhs - Elhs

For the cell diagram above
Ecell = 0.34 - -2.37
= + 2.71 V

In order to calculate the Ecell, we must use '**standard electrode potentials'** for the half cells.

Each half cell has a **standard electrode potential** value
$Mg^{2+}(aq) \mid Mg(s)$ $E^\ominus = -2.37V$
$Cu^{2+}(aq) \mid Cu(s)$ $E^\ominus = +0.34V$

Using Electrode Potentials

The most useful application of electrode potentials is to show the direction of spontaneous change for redox reactions.

The easiest way to use electrode potentials is as follows:

For any two half equations

The more **negative** half cell will always **oxidise** (go backwards)

$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$ E= -2.37V
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ E = +0.34V

The more **positive** half cell will always **reduce** (go forwards)

The reaction would be
$Mg + Cu^{2+} \rightarrow Cu + Mg^{2+}$

To work out the Ecell that corresponds to this spontaneous change then use
Ecell = Ered – Eox
A spontaneous change will always have a positive Ecell.

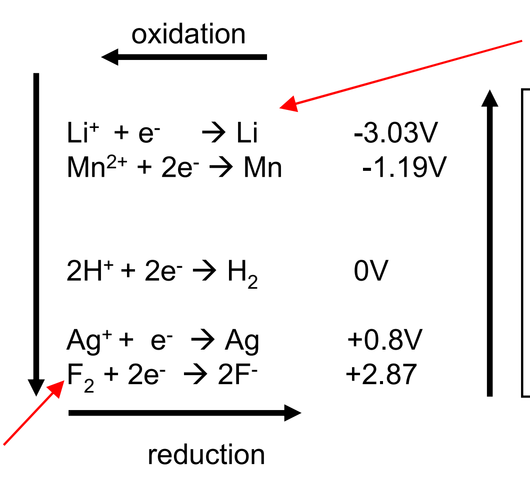
The most **negative** electrode will **oxidise** and go from **right to left**
The half equation is therefore $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
Electrons are given off (lost) and travel to positive electrode.

The more **positive** electrode will **reduce** and go from **left to right** $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$
Electrons arrive at this electrode and are absorbed (gained)

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $E^\ominus = -0.76V$
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ $E^\ominus = -0.44V$

To get the full equation of the reaction add the two half reactions together, cancelling out the electrons.
$Zn + Fe^{2+} \rightarrow Fe + Zn^{2+}$

Using series of standard electrode potentials



oxidation

$Li^+ + e^- \rightarrow Li$ -3.03V
$Mn^{2+} + 2e^- \rightarrow Mn$ -1.19V
$2H^+ + 2e^- \rightarrow H_2$ 0V
$Ag^+ + e^- \rightarrow Ag$ +0.8V
$F_2 + 2e^- \rightarrow 2F^-$ +2.87

reduction

Most strong reducing agents found here on the **right**

As more **+ve** increasing tendency for species on left to **reduce**, and act as **oxidising agents**

As more **-ve** increasing tendency for species on right to **oxidise**, and act as **reducing agents**

Most strong oxidising agents found here on the **left**

To work out the Ecell from two standard electrode potentials then use
Ecell = Ered – Eox

The most **powerful reducing agents** will be found at the most **negative** end of the series on the right (i.e. the one with the lower oxidation number).
The most **powerful oxidising agents** will be found at the most **positive** end of the series on the left (i.e. the one with the higher oxidation number).

Example 1

Use electrode data to explain why fluorine reacts with water.
Write an equation for the reaction that occurs.

$\xleftarrow{\text{oxidise}}$

$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ $E^o{+1.23V}$
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$ E^o +2.87V

$\xrightarrow[\text{reduce}]{}$

First apply idea that more positive $E^\ominus$ will reduce (go forward) and more negative $E^\ominus$ will oxidise (go backwards)

Explanation to write

As $E^\ominus$ F_2/F^- > $E^\ominus$ O_2/H_2O, F_2 will oxidise H_2O to O_2

Can also work out Ecell and quote it as part of your answer
Ecell = Ered - Eox = 2.87-1.23 =1.64V

Equation

$2F_2(g) + 2H_2O(l) \rightarrow 4F^-(aq) + O_2(g) + 4H^+(aq)$

Remember to cancel out electrons in full equation

Conventional cell diagram for above example

$Pt|H_2O|O_2 \,||\, F_2|F^-|Pt$

Example 2

Use data from the table to explain why chlorine should undergo a redox reaction with water. Write an equation for this reaction.

$Cl_2(aq) + 2e^- \rightarrow 2Cl^-(aq)$ E^o+1.36V
$2HOCl(aq) + 2H^+(aq) + 2e^- \rightarrow Cl_2(aq) + 2H_2O(l)$ E^o+1.64V
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$ E^o +1.77V
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ E^o +1.23V

First select relevant half equations by considering the $E^\ominus$ values and applying the idea that more positive $E^\ominus$ will reduce (go forward) and more negative $E^\ominus$ will oxidise (go backwards).

$\xrightarrow{\text{reduce}}$

$Cl_2(aq) + 2e^- \rightarrow 2Cl^-(aq)$ E^o+1.36V
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ E^o +1.23V

$\xleftarrow[\text{oxidise}]{}$

Explanation to write

As $E^\ominus$ Cl_2/Cl^- > $E^\ominus$ O_2/H_2O, Cl_2 will oxidise H_2O to O_2

Equation

$2Cl_2(g) + 2H_2O(l) \rightarrow 4Cl^-(aq) + O_2(g) + 4H^+(aq)$

Example 3

Suggest what reactions occur, if any, when hydrogen gas is bubbled into a solution containing a mixture of iron(II) and iron(III) ions. Explain your answer.

$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ E^o +0.77V
$2H^+(aq) + 2e^- \rightarrow H_2(g)$ E^o 0.00V
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ E^o–0.44V

First select relevant half equations by considering the $E^\ominus$ values and applying the idea that more positive $E^\ominus$ will reduce (go forward) and more negative $E^\ominus$ will oxidise (go backwards)

$\xrightarrow{\text{reduce}}$

$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ E^o +0.77V
$2H^+(aq) + 2e^- \rightarrow H_2(g)$ E^o 0.00V

$\xleftarrow[\text{oxidise}]{}$

Explanation to write

Fe^{3+} will be reduced to Fe^{2+} by H_2 oxidising to H^+
because $E^\ominus$ Fe^{3+}/Fe^{2+} > $E^\ominus$ H^+/H_2

Equation

$2Fe^{3+}(aq) + H_2(g) \rightarrow 2Fe^{2+}(aq) + 2H^+(aq)$

Example 4

Use the half-equations to explain in terms of oxidation states what happens to hydrogen peroxide when it is reduced.

$\xrightarrow{\text{reduce}}$

$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$ E^o+1.77V
$O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O_2(aq)$ E^o +0.68V

$\xleftarrow[\text{oxidise}]{}$

Explanation to write

As $E^\ominus$ H_2O_2/H_2O > $E^\ominus$ O_2/H_2O_2 , H_2O_2 disproportionates from -1 oxidation state to 0 in O_2 and -2 in H_2O

Equation

$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

Effect of conditions on Cell voltage Ecell

The effects of changing conditions on E cell can be made by applying le Chatelier's principle.

Ecell is a measure of how far from equilibrium the cell reaction lies. The more positive the Ecell the more likely the reaction is to occur.

If current is allowed to flow, the cell reaction will occur and the Ecell will fall to zero as the reaction proceeds and the reactant concentrations drop.

Effect of concentration on Ecell

Looking at cell reactions is a straight forward application of le Chatelier. So increasing concentration of 'reactants' would increase Ecell and decreasing them would cause Ecell to decrease.

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ E= - 0.76V
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ E= -0.44V

$Zn + Fe^{2+} \rightarrow Fe + Zn^{2+}$ E= +0.32

Increasing the concentration of Fe^{2+} and decreasing the concentration of Zn^{2+} would cause Ecell to increase.

Effect of temperature on Ecell

Most cells are exothermic in the spontaneous direction so applying Le Chatelier to a temperature rise to these would result in a decrease in Ecell because the equilibrium reactions would shift backwards.

If the Ecell positive it indicates a reaction might occur. There is still a possibility, however, that the reaction will not occur or will occur so slowly that effectively it does not happen.
If the reaction has a high activation energy the reaction will not occur.

Cells

Electrochemical cells can be used as a commercial source of electrical energy
Cells can be non-rechargeable (irreversible), rechargeable and fuel cells.

You should be able to work out Ecell for given half reactions.

You do not need to learn the details of most of these cells. Relevant cell information will be given. You should be able to convert between standard electrode potential half cells, full cell reactions and cell diagrams and be able to calculate potentials from given data.

Example primary non rechargeable cells

Cells are non-rechargeable when the reactions that occur with in them are non-reversible.

Dry Cell $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ E = - 0.76 V More negative half equation will oxidise

$2MnO_2(s) + 2NH_4^+(aq) + 2\ e^- \rightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$ E = 0.75 V

Overall reaction $2MnO_2 + 2NH_4^+ + Zn \rightarrow Mn_2O_3 + 2NH_3 + H_2O + Zn^{2+}$ Ecell =+1.51V

Example primary Lithium –manganese dioxide cell- non rechargeable

$Li^+_{(aq)} + e^- \rightarrow Li_{(s)}$ E = - 3.04 V More negative half equation will oxidise

$Li^+_{(aq)} + MnO_{2\,(s)} + e^- \rightarrow LiMnO_{2(s)}$ E = - 0.13 V *(Mn will reduce changing oxidation state from +4 to +3)*

Overall reaction $Li + MnO_2 \rightarrow LiMnO_2$

Ecell = E red- Eox = -0.13 - - 3.04 = 2.91 V

Conventional cell diagram $Li_{(s)} | Li^+_{(aq)} || Li^+_{(aq)} | MnO_{2\,(s)} , LiMnO_{2(s)} | Pt_{(s)}$ Ecell =+2.91V

Example secondary rechargeable cells

The forward reaction occurs on discharge giving out charge. Charging causes the reaction to reverse

Lead acid cell $PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$ E= -0.356V

$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$ E= +1.685 V

Overall reaction $PbO_2 + Pb + 2SO_4^{2-} + 4H^+ \rightarrow 2\ PbSO_4 + 2H_2O$ Ecell= +2.04V

Reversible cells only work if the product stays attached to the electrode and does not disperse

Example secondary nickel–cadmium cells are used to power electrical equipment such as drills and shavers. They are rechargeable cells.
The electrode reactions are shown below.
$NiO(OH) + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$ *E = +0.52 V (Ni will reduce changing oxidation state from 3 to 2)*
$Cd(OH)_2 + 2e^- \rightarrow Cd + 2OH^-$ *E = –0.88 V (Cd will oxidise changing oxidation state from 0 to 2)*

Overall reaction **discharge** $2NiO(OH) + Cd + 2H_2O \rightarrow 2Ni(OH)_2 + Cd(OH)_2$ E= +1.40V

Ecell = E red- Eox = +0.52 - - 0.88 = + 1.40 V

The overall reaction would be reversed in the **recharging** state
$2Ni(OH)_2 + Cd(OH)_2 \rightarrow 2NiO(OH) + Cd + 2H_2O$

Example secondary Lithium ion cells are used to power cameras and mobile phones.

$Li^+ + CoO_2 + e^- \rightarrow Li^+[CoO_2]^-$ E=+0.6V *(Co will reduce changing oxidation state from 4 to 3)*
$Li^+ + e^- \rightarrow Li$ E=-3.0V

Overall **discharge** reaction $Li + CoO_2 \rightarrow LiCoO_2$ E=3.6V

Conventional cell diagram $Li \mid Li^+ \parallel Li^+, CoO_2 \mid LiCoO_2 \mid Pt$

The overall reaction would be reversed in the **recharging** state

The reagents in the cell are absorbed onto powdered graphite that acts as a support medium. The support medium allows the ions to react in the absence of a solvent such as water.

Water would not be good as a solvent as it would react with the lithium metal.

Fuel cells

A fuel cell uses the energy from the reaction of a fuel with oxygen to create a voltage.

You should learn the details of the lithium cell and the hydrogen fuel cell in alkaline conditions

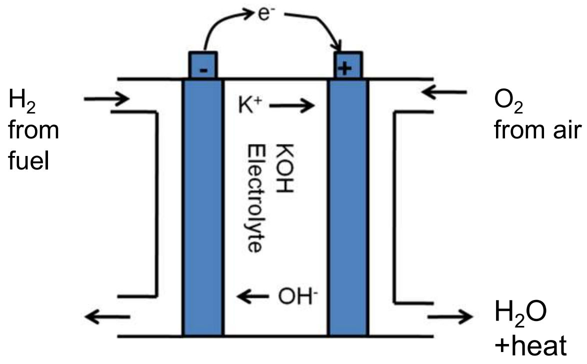
Hydrogen fuel cell (potassium hydroxide electrolyte)

Alkaline Conditions

Standard electrode potentials
$2e^- + 2H_2O \rightarrow H_2 + 2OH^-$ E=-0.83V
$4e^- + 2H_2O + O_2 \rightarrow 4OH^-$ E=+0.4V

Equations at electrodes
Negative: $H_2 + 2OH^- \rightarrow 2e^- + 2H_2O$
Positive: $4e^- + 2H_2O + O_2 \rightarrow 4OH^-$

Overall reaction $2H_2 + O_2 \rightarrow 2H_2O$ E=1.23V



Using standard conditions: The rate is too slow to produce an appreciable current.

Higher temperatures are therefore used to increase rate but the reaction is exothermic so by applying le Chatelier would mean the E cell falls.
A higher pressure can help counteract this.

Fuel cells will maintain a **constant voltage** over time because they are continuously fed with fresh O_2 and H_2 so maintaining **constant concentration** of reactants. This differs from ordinary cells where the voltage drops over time as the reactant concentrations drop.

Advantages of fuel cells over conventional petrol or diesel-powered vehicles
(i) less pollution and less CO_2. (Pure hydrogen emits only water whilst hydrogen-rich fuels produce only small amounts of air pollutants and CO_2).
(ii) greater efficiency

Limitations of hydrogen fuel cells
(i) expensive
(ii) storing and transporting hydrogen, in terms of safety, feasibility of a pressurised liquid and a limited life cycle of a solid 'adsorber' or 'absorber'
(iii) limited lifetime (requiring regular replacement and disposal) and high production costs,
(iv) use of toxic chemicals in their production

Hydrogen is readily available by the electrolysis of water, but this is expensive. To be a green fuel the electricity needed would need to be produced from renewable resources

Hydrogen can be stored in fuel cells
(i) as a liquid under pressure,
(ii) adsorbed on the surface of a solid material,
(iii) absorbed within a solid material;

Ethanol fuel cells

Ethanol fuel cells have also been developed. Compared to hydrogen fuel cells they have certain advantages including.
Ethanol can be made from renewable sources in a carbon neutral way.
Raw materials to produce ethanol by fermentation are abundant.
Ethanol is less explosive and easier to store than hydrogen.
New petrol stations would not be required as ethanol is a liquid fuel.

Equation that occurs at oxygen electrode
$4e^- + 4H^+ + O_2 \rightarrow 2H_2O \quad E=1.23V$

Equation that occurs at ethanol electrode
$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$

Overall equation
$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$