Chem Factsheet

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Fuel Cells

Previous knowledge

Oxidation and reduction, half equations, standard conditions, standard electrode potential ($E^\ominus$), calculating standard cell potential ($E^\ominus_{cell}$), cell diagrams, thermodynamic feasibility of a reaction, kinetic stability, non-standard conditions and the equation $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$.

Introduction

The fuel cell was originally conceived by a German scientist, Christian Schoenbein, but Sir W. R. Grove developed the first working fuel cell in about 1842. In his cell he reacted hydrogen (the "fuel") with oxygen and obtained an electric current. Today, almost 170 years later, most fuel cells use this same reaction to create a voltage and, as in 1842, it is much more expensive than normal batteries. In the late 60's and early 70's the Apollo and Gemini spacecrafts also obtained their electrical power from hydrogen-oxygen fuel cells. The extra expense being justified since, unlike a storage battery, a fuel cell continues to supply current as long as the reactants are available or replenished (even while the cell is operating). The Apollo crew also used the product of the chemical reaction for drinking! For space applications, fuel cells have another big advantage over batteries in that they produce several times as much energy per equivalent unit of weight. Today, global warming and oil supplies are major environmental and economic issues. Fuel cells offer a way of reducing both greenhouse gas emissions and reliance on oil.

Some Important Related Terms

Electrochemical cell: a device for converting chemical energy into electrical energy by a spontaneous redox reaction. It generates a voltage that can produce a direct current through an external circuit.

In such cells the reduction and the oxidation reactions are physically separated. The electrons produced by the oxidation reaction flow out of the cell and around the external circuit. Here they can do useful work (e.g. light up a bulb) before returning to the cell to allow the reduction reaction to occur.

Anode: the electrode of an electrochemical cell where **oxidation** occurs. The anode is the **negative** electrode.

Cathode: the electrode of an electrochemical cell where **reduction** occurs. The cathode is the **positive** electrode.

Electrolyte: a compound which, when in solution or melted, will conduct electricity.

Fuel cell: an electrochemical cell for converting chemical energy into electrical energy by a spontaneous redox reaction between a fuel (e.g. hydrogen) and an oxidant (e.g. oxygen), both of which are being continuously supplied to the cell in the presence of an electrolyte. A fuel cell does not need to be electrically recharged.

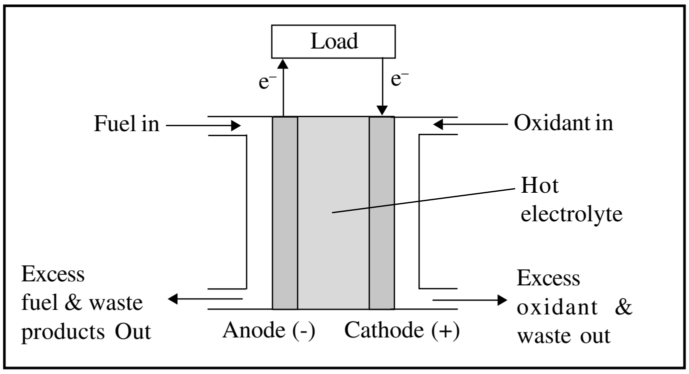
Primary cell : an electrochemical cell for converting chemical energy into electrical energy that cannot be recharged as the redox reaction cannot be reversed easily.

Secondary cell : an electrochemical cell for converting chemical energy into electrical energy that can be recharged as the redox reaction can be reversed by putting current (e.g. from the mains) through the cell in the opposite direction to that of the discharge current. Also referred to as storage cells.

Non-rechargeable (primary) and rechargeable (secondary) cells have their oxidants and reductants in a closed system. When either one of these is used up the cell no longer produces a voltage. The fuel cell is an open system as the fuel and oxygen are being continuously supplied and this allows continuous operation.

- Electrochemical cells can be non-rechargeable (primary cells), rechargeable (secondary cells) or fuel cells.
- All electrochemical cells can be used as a commercial source of electrical energy.

A general diagram of a fuel cell



Possible Fuels: hydrogen and hydrogen rich fuels such as methanol, ethanol, natural gas and petrol.

Only natural gas occurs naturally in vast quantities; petrol can be obtained from crude oil by fractional distillation and by cracking longer chain alkane fractions. Both hydrogen and methanol can be manufactured by reforming natural gas with steam.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \text{ and } CO + 2H_2 \rightarrow CH_3OH.$$

Ethanol is obtained either by catalytic hydration of ethene or by fermentation of crops such as sugar beat which is a renewable resource.

$$CH_2CH_2 + H_2O \rightarrow CH_3CH_2OH$$
$$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2$$

Direct Fuel Cell: a fuel cell in which the fuel is fed directly into the fuel cell without being reformed.

Reformed or Indirect Fuel Cell: a fuel cell that has a reformer unit attached to the fuel cell. The hydrogen rich fuel is reformed to produce a hydrogen-rich gas stream that is passed into the fuel cell.

Possible Oxidants: oxygen from the air or pure oxygen is most commonly used but other possibilities include Cl_2 and ClO_2.

A Hydrogen-Oxygen Fuel Cell

There are various types of these fuel cells. One type is called an alkaline fuel cell because the electrolyte is an alkali such as potassium hydroxide solution. The electrodes are porous graphite coated with for example nickel. The fuel is pure hydrogen (H_2) and the oxidant is pure oxygen (O_2).

The relevant standard electrode potentials for this fuel cell are:

$H_2O(l) + e^- \rightarrow ½H_2(g) + OH^-(aq)$; $E^\ominus = -0.83V.$

$½O_2(g) + H_2O(l) + 2e^- \rightarrow 2OH^-(aq)$; $E^\ominus = +0.40 V.$

Since - 0.83 V is more negative than + 0.40 V, $H_2(g) / OH^-(aq)$ is a better reductant than $OH^-(aq)$. $H_2(g) / OH^-(aq)$ will therefore reduce $½O_2(g) / H_2O(l)$ to $OH^-(aq)$

The hydrogen diffuses through the porous anode and is adsorbed.

This H_2 in contact with the KOH(aq) is oxidised to water (electron loss):

$½H_2(g) + OH^-(aq) \rightarrow H_2O(l) + e^-$ --- (1)

The electrons flow through the external circuit to the porous cathode. The adsorbed oxygen in the cathode is then reduced to hydroxide ions, (electron gain).

$½O_2(g) + H_2O(l) + 2e^- \rightarrow 2OH^-(aq)$ --- (2)

The hydroxide ions move towards the anode. (Both of these half-reactions are catalysed by nickel.)

The overall equation is the formation of water. {2 × (1) + 2}.

$H_2(g) + ½O_2(g) \rightarrow H_2O(l)$ --- (A)

Cell Diagram

$C(s) \,|\, [½H_2(g) \,|\, OH^-(aq)], H_2O(l) \,||\, [½O_2(g) \,|\, H_2O(l)], 2OH^-(aq) \,|\, C(s)$

LHE Salt bridge RHE

$E^\ominus_{cell} = (E^\ominus_{RHE} - E^\ominus_{LHE}) = +0.40 - (-0.87) = +1.23\ V.$

or $E^\ominus_{cell} = (E^\ominus_{cathode} - E^\ominus_{anode}) = +0.40 - (-0.87) = +1.23\ V.$

Since $E^\ominus_{cell}$ is positive, the oxidation of hydrogen by oxygen is feasible / spontaneous under standard conditions.

The conditions actually used are not standard, so the cell voltage will not be + 1.23V.

Free Energy Considerations

> ***Remember**: The standard free energy change ($\Delta G^\ominus$) is calculated using $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$. A reaction is energetically feasible if $\Delta G^\ominus$ is negative.*

The reaction of hydrogen with oxygen (reaction A) is very exothermic; hence the enthalpy change ($\Delta H^\ominus$) is very negative.

The entropy change of the system ($\Delta S^\ominus$) is negative since 1.5 moles of highly disordered gases form one mole of liquid. Hence the term - $T\Delta S^\ominus$ is positive.

Since the reaction is known to be feasible ($\Delta G^\ominus$ negative), $\Delta H^\ominus$ must be more negative than - $T\Delta S^\ominus$ is positive to make $\Delta G^\ominus$ negative.

The higher the temperature the less negative ΔG becomes, since - $T\Delta S$ will be more positive. Hence, the higher the temperature the less feasible reaction A becomes. (This ignores any changes in ΔH and ΔS with temperature).

However, hydrogen and oxygen *do not react* on mixing even though the reaction is energetically feasible. This is because the activation energy is very high making the mixture kinetically stable.

Fuel Cell Vehicles, (FCVs)

Scientists and engineers in the car industry are developing FCVs. The fuel is either hydrogen gas or a hydrogen rich fuel such as natural gas, methanol, ethanol or petrol. The oxidant is oxygen from the air. The electricity produced drives an electric motor.

If hydrogen gas is the fuel only water and heat are produced so there are *no chemical pollutants*. As hydrogen rich fuels such as methane and lower alcohols also contain carbon, they also produce carbon dioxide. However, it is less than petrol or diesel do in current vehicles and FCVs can be more than twice as efficient.

Ways of Storing Hydrogen

(a) as a compressed gas (e.g. 35 MPa) in special pressurised tanks,
(b) as a liquid under pressure in special heat-insulated tanks below 253°C,
(c) adsorbed on the surface of a solid highly porous material (e.g. using carbon nanotubes and zeolites.),
(d) absorbed within a solid material. The hydrogen is desorbed by heating.

Limitations of Hydrogen Fuel Cells

(a) Hydrogen has a low energy-density so it is difficult to store enough hydrogen for a FCV to travel more than 300 miles before refuelling. Pressurised cylinders of hydrogen would need to be a lot larger and heavier than current petrol / diesel tanks. They are also more expensive because of the intricate technology involved to efficiently store hydrogen. This is especially true for pressurised liquid hydrogen; there must be doubt that such a system is feasible.

(b) Solid adsorbers or absorbers will need replacing periodically.

(c) A compressed hydrogen fuel tank can be at risk of developing pressure leaks either through accidents (e.g. car crash) or through normal wear, which could result in explosions.

(d) Fuel cells are expensive to manufacture. They could last for about 150,000 miles in a FCV. Used fuel cell would require safe disposal.

(e) The production of fuel cells involves the use of toxic chemicals. (e.g. Ni, Pt catalysts for the electrodes.)

At present, FCVs need much research and development to reduce costs, improve performance and allow safe handling and maintenance of a hydrogen system. This is a desirable goal since success would mean much less reliance on oil. To run cars on hydrogen seems ideal in terms of being pollution free but would you drive a car powered by flammable hydrogen gas? The hydrogen gas itself must be made and this is generally done by steam reforming of methane as electrolysis of water at present is too expensive.

Ethanol Fuel Cell - Breathalyser

$CH_3COOH(aq) + 4H^+(aq) + 4e^- \rightarrow CH_3CH_2OH(l) + H_2O(l) \quad E^\ominus = +0.06\ V.$ ----- (1)

$\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O(l) \quad E^\ominus = +1.23\ V.$ ----- (2)

If exhaled air from a suspect contains ethanol, this is oxidised at a platinum anode (negative) to ethanoic acid, hydrogen ions and electrons. These electrons pass externally to a platinum cathode (positive) and the hydrogen ions pass internally through a porous acid-electrolyte to the cathode. At the cathode oxygen is reduced to water. The more ethanol that becomes oxidized, the more electrons are produced and hence the greater the electrical current produced. A microprocessor measures the electrical current and calculates the blood alcohol concentration (BAC). A BAC of 0.09 means 0.09 g of alcohol per 100 cm^3 of blood.

The overall equation {reversing (1) and adding 2 × (2)} is:

$CH_3CH_2OH(l) + O_2(g) \rightarrow CH_3COOH(aq) + H_2O(l).$

$E^\ominus_{cell} = +1.23 - (+0.06) = +1.17\ V.$

$\therefore \Delta S^\ominus_{Total}$ is positive since $E^\ominus_{cell} \propto \Delta S^\ominus_{Total}$. As $\Delta S^\ominus_{Total}$ is positive the reaction is feasible under standard conditions. However, due to high activation energy, the rate of the reaction is very low.

Practice Questions

1. Hydrogen gas to be used in fuel cells is usually made by reacting methane with steam. The products are hydrogen and carbon monoxide. Suggest why methane is used and write an equation for the reaction.

2. A fuel cell using methanol as fuel and air as oxidant is operated at 110^{0}C.
   The $E^\ominus$ values are:
   $CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O\ ;\ E^\ominus = +0.02\ V$
   and $\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O(l)\ ;\ E^\ominus = +1.23\ V.$

   Using the $E^\ominus$ values, explain which half-reaction occurs at each electrode. Write the cell diagram, calculate $E^\ominus_{cell}$ and write the overall equation.

3. Calculate the $E^\ominus$cell value for a fuel cell using ethanol as the fuel from the following data. Write the equations for the reactions that occur at each electrode and hence write the overall equation for the combustion of ethanol.
   $2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O\ ;\ E^\ominus = +0.084\ V.$

   $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O\ ;\ E^\ominus = +1.23\ V.$

   Given an environmental reason why ethanol is preferable to methanol in fuel cells.

4. Write balanced equations for the complete combustion of one mole of methanol and 1 mole of 2,2,4-trimethylpentane using molecular formulas.

   If the $\Delta H^\ominus_{comb.}$ values are -890 and -5461 kJ mol^{-1} respectively, calculate the percentage decrease in CO_2 for the same amount of energy released.

Answers

1. Methane is naturally occurring as natural gas and is plentiful.
   $CH_4 + H_2O \rightarrow CO + 3H_2$

2. +0.02 V is more negative than +1.23 V. Hence CH_3OH / H_2O will lose electrons at the negative electrode. The half-reaction here is: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$.

   At the positive electrode the half-reaction is:
   $\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O(l).$

   $Pt(s) \mid [CH_3OH(aq) + H_2O(l)] \mid\mid [\frac{1}{2}O_2(g) \mid H^+(aq)], H_2O(l) \mid Pt(s)$

   $E^\ominus_{cell} = 1.23 - (+0.02) = +1.21\ V.$

   Overall equation: $CH_3OH + 1\frac{1}{2}O_2 \rightarrow CO_2 + 2H_2O.$

3. $E^\ominus_{cell} = +1.23 - (+0.084) = +1.146\ V.$

   Anode (+): $C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$ --- (1)

   Cathode (-): $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$ --- (2)

   Equation {(1) + 6 × (2)}. $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O.$

   Methanol is manufactured by reforming natural gas with steam but ethanol can be obtained by fermentation which makes it a renewable resource.

4. $CH_4O + 1\frac{1}{2}O_2 \rightarrow CO_2 + 2H_2O$

   $C_8H_{18} + 12\frac{1}{2}O_2 \rightarrow 8CO_2 + 9H_2O$

   Moles of CH_4O required to produce 5461 kJ = 5461/890 = 6.134.
   So for every 8 moles of CO_2 produced by C_8H_{18} methanol would produce 6.134 moles.
   % Decrease = (8 – 6.134) / 8 × 100 = 23.3%.

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