EMS717U/EMS717P
Renewable Energy Sources

Fuel Cells and Fuel Cell Systems

Fuel cell technology

Content

- What are fuel cells?
- Types of fuel cells
- Fuel cell performance
- Efficiency of fuel cell
- Actual fuel cell performance
- Efficiency of actual fuel cell and fuel utilisation
- Fuel cell systems
- Methods of hydrogen production
- Hydrogen storage

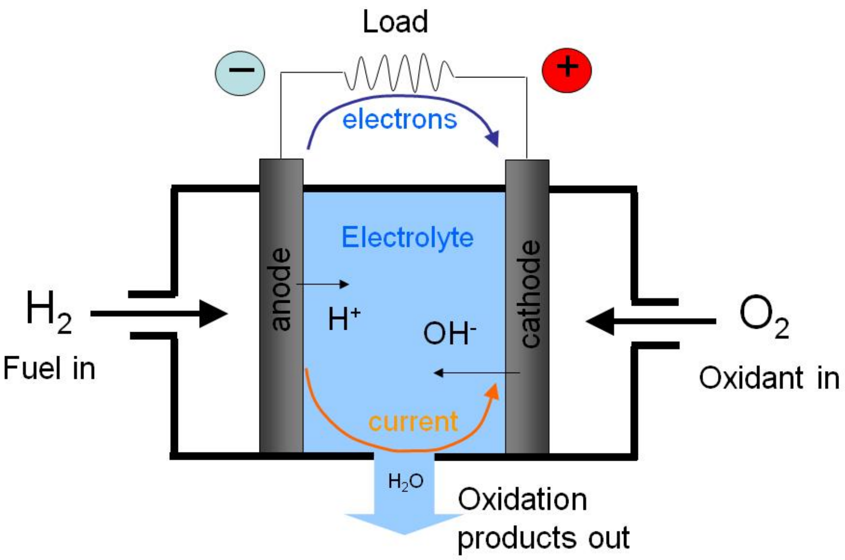
What are fuel cells?

Fuel cells are electrochemical devices that convert chemical energy directly into electrical energy

What are Fuel Cells?

Fuel cells are electrochemical devices that convert the chemical energy of a reaction directly into electrical energy

Example: H_2/O_2 fuel cell



Overall reaction:

$$H_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$$

Note: Same as that of the combustion reaction

Basic elements include:

a) Porous anode and cathode electrodes

The electrodes provide a surface site for electrochemical reactions to take place and conduct ions away from reaction site. They also provide a physical barrier to separate the bulk gas and electrolyte phase

b) Electrolyte layer is sandwiched between the porous electrodes

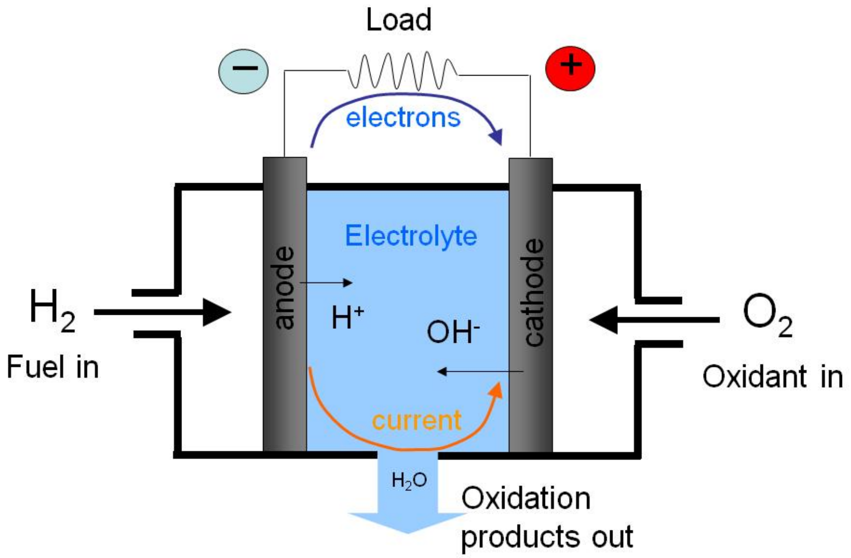
Gaseous fuels are continuously supplied to anode (negative electrode) and gaseous oxidant is supplied to the cathode (positive electrode) .

Electrochemical reactions produce electric current

Fuel and oxidant molecules are oxidized (loss of electrons) and reduced (gain of electrons) to produce ionic species. The ionic species migrate through the electrolyte carrying charge and completing the electrical circuit.

Comparison to Batteries

Fuel Cell



Energy conversion device

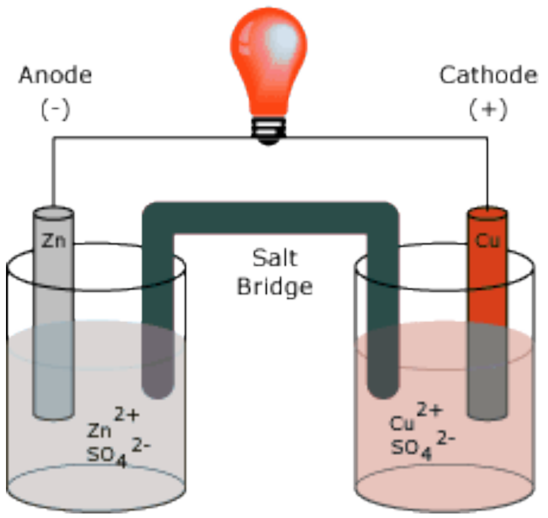
Continually operate as long as fuel and oxidant are supplied

In practice, degradation of the fuel cell electrodes occur and the operating performance decreases with time

Usually consider gaseous H_2/O_2 fuel cells.

Gas or liquid or any substance capable of oxidation/ reduction reactions - known as flow cell batteries

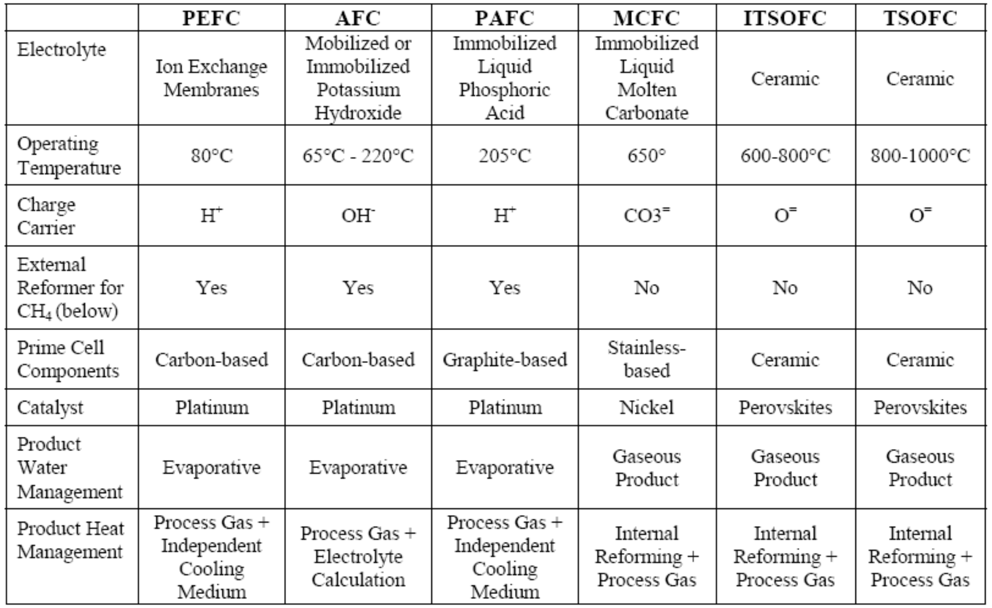
Electrolytic Battery



- energy storage device
- Energy available is related to amount of chemical reactant stored.
- Once discharged, no more power available
- Some batteries can be recharged from external power supply to regenerate reactants

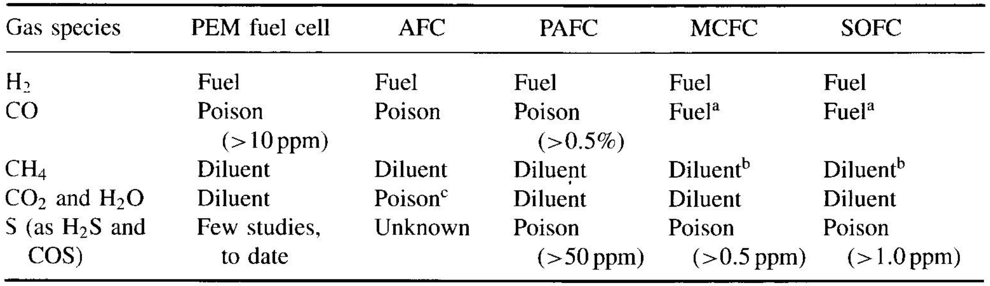
Different Types of Fuel Cells

Variety of fuel cell in development. Most common classification is by the type of **electrolyte used** in the fuel cell.



	PEFC	AFC	PAFC	MCFC	ITSOFC	TSOFC
Electrolyte	Ion Exchange Membranes	Mobilized or Immobilized Potassium Hydroxide	Immobilized Liquid Phosphoric Acid	Immobilized Liquid Molten Carbonate	Ceramic	Ceramic
Operating Temperature	80°C	65°C - 220°C	205°C	650°	600-800°C	800-1000°C
Charge Carrier	H^+	OH^-	H^+	$CO3^=$	$O^=$	$O^=$
External Reformer for CH_4 (below)	Yes	Yes	Yes	No	No	No
Prime Cell Components	Carbon-based	Carbon-based	Graphite-based	Stainless-based	Ceramic	Ceramic
Catalyst	Platinum	Platinum	Platinum	Nickel	Perovskites	Perovskites
Product Water Management	Evaporative	Evaporative	Evaporative	Gaseous Product	Gaseous Product	Gaseous Product
Product Heat Management	Process Gas + Independent Cooling Medium	Process Gas + Electrolyte Calculation	Process Gas + Independent Cooling Medium	Internal Reforming + Process Gas	Internal Reforming + Process Gas	Internal Reforming + Process Gas

Source: *Fuel cell handbook*, (2004)



Gas species	PEM fuel cell	AFC	PAFC	MCFC	SOFC
H_2	Fuel	Fuel	Fuel	Fuel	Fuel
CO	Poison (>10 ppm)	Poison	Poison (>0.5%)	Fuel[a]	Fuel[a]
CH_4	Diluent	Diluent	Diluent	Diluent[b]	Diluent[b]
CO_2 and H_2O	Diluent	Poison[c]	Diluent	Diluent	Diluent
S (as H_2S and COS)	Few studies, to date	Unknown	Poison (>50 ppm)	Poison (>0.5 ppm)	Poison (>1.0 ppm)

Source: *Fuel cell systems explained*, Larminie (2003)

Polymer Electrolyte Fuel Cell (PEFC):

Uses ion exchange polymer membrane as the electrolyte which is a solid proton conductor. Only liquid within FC is water, keeping corrosion problems to a minimum. Polymer has temperature limit of 120 ºC and high catalyst loading is required (higher cost).

Alkaline Fuel Cell (AFC):

Electrolyte is conc. KOH. Can operate up to ~250 ºC with range of catalysts (Ni, Ag, metal oxides) but poisoned by CO_2 – can't use air as oxidant.

Phosphoric Acid Fuel Cell (PAFC):

Uses 100% Phosphoric acid electrolyte operating typically at 150-220 ºC.

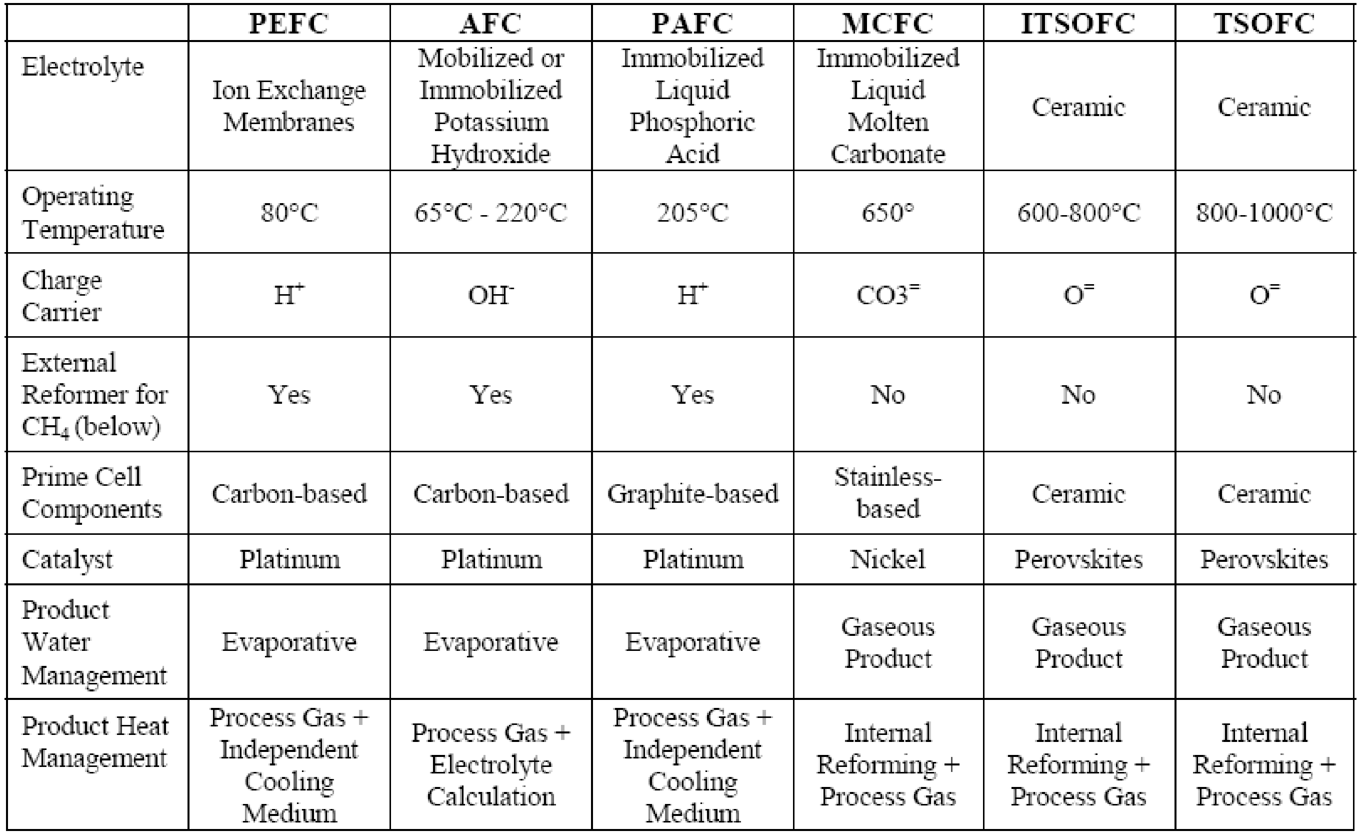
Molten Carbonate Fuel Cell (MCFC):

Uses alkali carbonates in a ceramic $LiAlO_2$ matrix operating between 600-700 ºC where the carbonates are conductive molten salts. At these elevated temperatures non-noble metal catalysts such as Nickel (anode) and nickel oxide (cathode) can be used – reduced cost.

Solid Oxide Fuel Cells (SOFC):

Use a solid, nonporous metal oxide, typically Y_2O_3 – stabilized ZrO_2. Fuel cell can operate at high temperature of ~1000 ºC where ionic conduction via oxygen ions occurs.

Different Types of Fuel Cells



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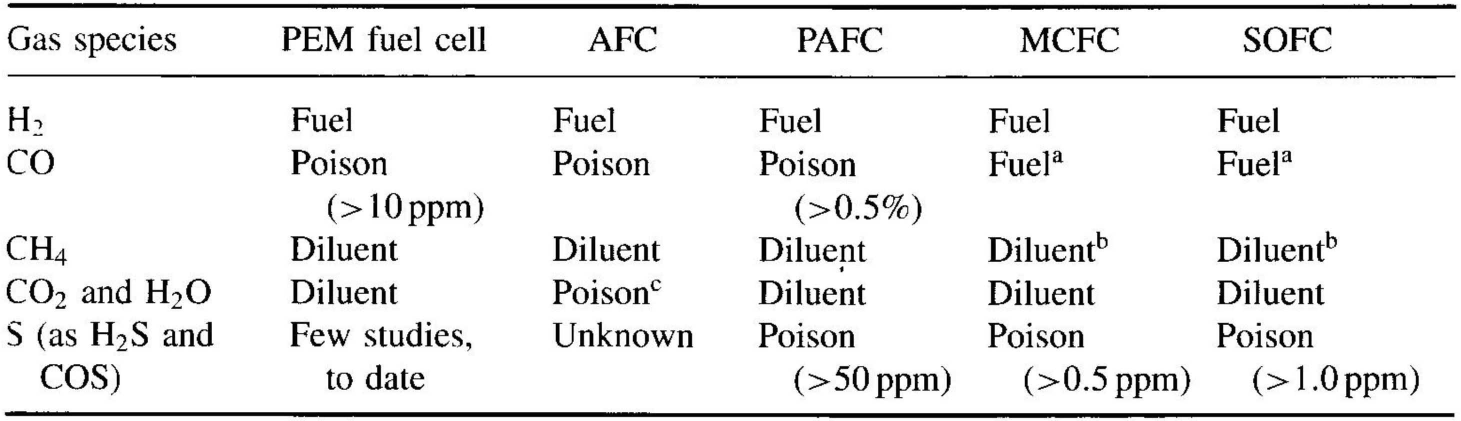
Catalyst	Platinum	Platinum	Platinum	Nickel	Perovskites	Perovskites
Product Water Management	Evaporative	Evaporative	Evaporative	Gaseous Product	Gaseous Product	Gaseous Product
Product Heat Management	Process Gas + Independent Cooling Medium	Process Gas + Electrolyte Calculation	Process Gas + Independent Cooling Medium	Internal Reforming + Process Gas	Internal Reforming + Process Gas	Internal Reforming + Process Gas



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Fuel Cell Performance

Consider the ideal performance of a fuel cell which will depend on the electrochemical reactions occurring within the fuel cell

The ideal performance of the fuel cell is defined by its Nernst potential.

The Nernst equation relates the ideal standard cell potential, ϕ^{o}_{cell}, to the ideal equilibrium potential, ϕ_{eq} , at a temperature and pressure other than standard conditions.

Considering a general reaction

$$jA + kB \rightarrow mC$$

where *j* moles of A react with *k* moles of B to produce *m* moles of C. Each species involved has an activity designated by a_A, a_B and a_C and in the case of ‘ideal’ gases it can be shown that

$$activity, a = \frac{P}{P^{o}}$$

where *P* is the pressure or partial pressure of the gas and P^{o} is the total pressure

Fuel Cell	Anode Reaction	Cathode Reaction
Proton Exchange Membrane and Phosphoric Acid	$H_2 \rightarrow 2H^+ + 2e^-$	$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Alkaline	$H_2 + 2(OH)^- \rightarrow 2H_2O + 2e^-$	$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$
Molten Carbonate	$H_2 + CO_3^= \rightarrow H_2O + CO_2 + 2e^-$ $CO + CO_3^= \rightarrow 2CO_2 + 2e^-$	$\frac{1}{2} O_2 + CO_2 + 2e^- \rightarrow CO_3^=$
Solid Oxide	$H_2 + O^= \rightarrow H_2O + 2e^-$ $CO + O^= \rightarrow CO_2 + 2e^-$ $CH_4 + 4O^= \rightarrow 2H_2O + CO_2 + 8e^-$	$\frac{1}{2} O_2 + 2e^- \rightarrow O^=$

CO - carbon monoxide
CO_2 - carbon dioxide
$CO_3^=$ - carbonate ion
e^- - electron
H^+ - hydrogen ion
H_2 - hydrogen
H_2O - water
O_2 - oxygen
OH^- - hydroxyl ion

Source: *Fuel cell handbook*, (2004)

$$\phi_{eq} = \phi^{o}_{cell} + \frac{RT}{nF} \ln\left(\frac{a_A^j \times a_B^k}{a_C^m} \right) \qquad (1)$$

Nernst equation in generic form

where *R* is the gas constant (8.314 J/kmol), *T* is thermodynamic temperature, *n* is the number of electrons transferred in reaction and *F* is Faraday constant (96485 C/mol).
a_A, a_B and a_C are activities of each species

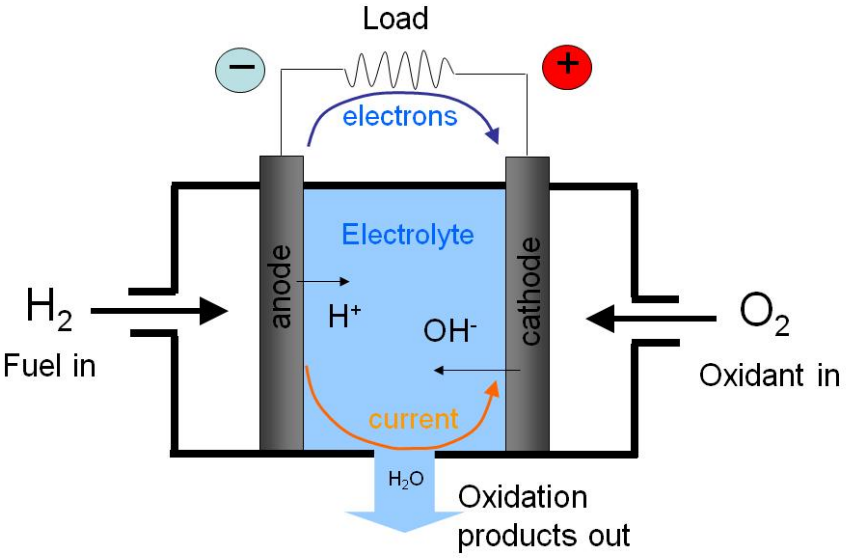
Standard conditions: 1 atm pressure and temperature of 298 K

Fuel Cell Performance

Then if we consider the H_2/O_2 fuel cell

Half cell reactions:

Anode = electrode at which oxidation occurs



At anode:

$$H_{2(g)} \rightarrow 2H^+{}_{(aq)} + 2e^-{}_{(M)}$$

Cathode = electrode at which reduction occurs

At cathode:

$$\tfrac{1}{2}O_{2(g)} + 2e^-{}_{(M)} + 2H^+{}_{(aq)} \rightarrow H_2O_{(l)}$$

Overall reaction:

$$H_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$$

$$\phi_{eq} = \phi^o_{cell} + \frac{RT}{2F}\ln\left(\frac{a_{H_2} \times a^{0.5}_{O_2}}{a_{H_2O}}\right)$$

Nernst equation for the Hydrogen:Oxygen reaction

Now the ideal cell potential can be calculated for any temperature and activity or pressure of reactants

Also, the standard cell potential can be calculated from the standard half cell potentials

Standard conditions: 1 atm pressure and temperature of 298 K

Fuel Cell Performance

Then if we consider the H_2/O_2 fuel cell

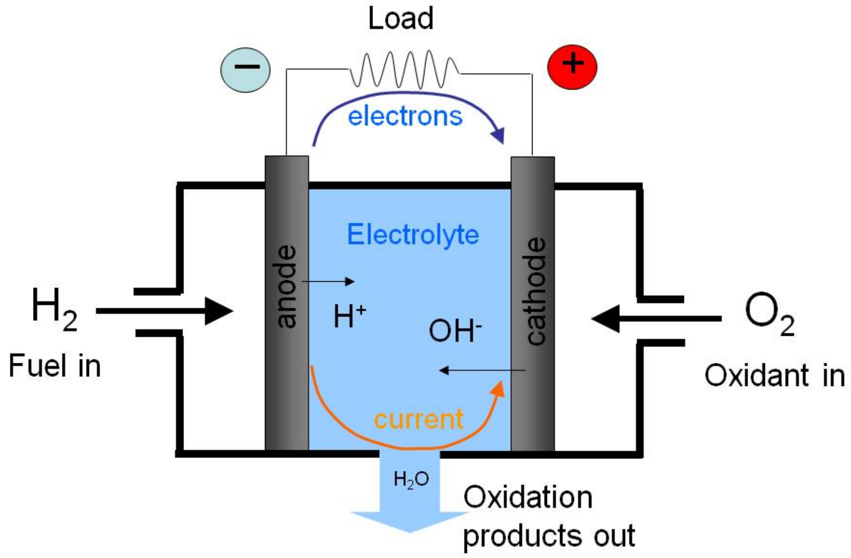
Half cell reactions:

Anode = electrode at which oxidation occurs

At anode:

$$H_{2(g)} \rightarrow 2H^+{}_{(aq)} + 2e^-{}_{(M)}$$

$$\phi_A^o = 0.00V$$



Cathode = electrode at which reduction occurs

At cathode:

$$\tfrac{1}{2}O_{2(g)} + 2e^-{}_{(M)} + 2H^+{}_{(aq)} \rightarrow H_2O_{(l)}$$

$$\phi_C^o = +1.23V$$

Overall reaction:

$$H_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$$

The standard cell potential for a reaction is then given by

$$\phi_{cell}^o = \phi_C^o - \phi_A^o \qquad (2)$$

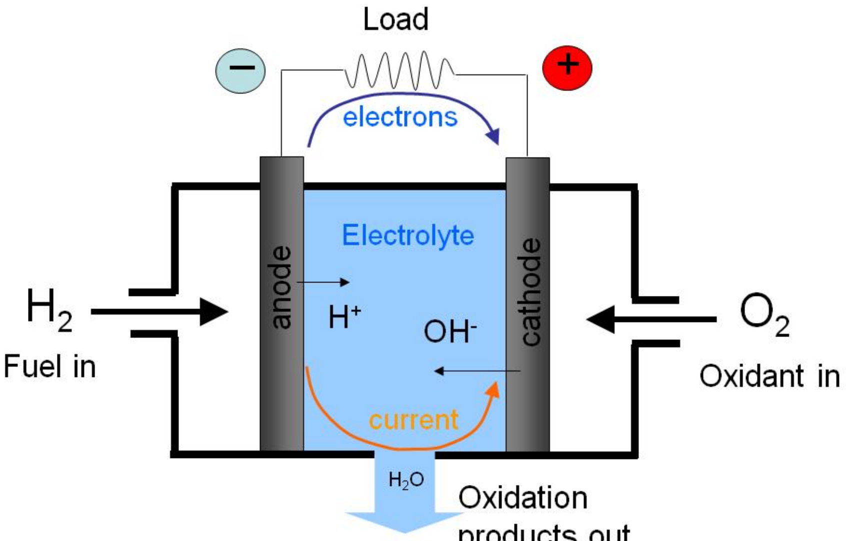
The standard cell potential for H_2/O_2 is then given by

$$\phi_{cell}^o = \phi_C^o - \phi_A^o = [1.23 - (-0.00)]V = 1.23V$$

Fuel Cell Performance

The potential energy can be expressed as a change in the Gibbs free energy, related to the ideal cell potential as follows:

$$\Delta G = -nF\phi_{cell} \qquad (3)$$



Hence, the Nernst equation can be expressed in terms of the Gibbs free energy change in general form:

$$\Delta G = \Delta G^\circ - RT\ln\left(\frac{a_A^j \times a_B^k}{a_C^m}\right) \qquad (4)$$

And for the H_2/O_2 fuel cell reaction can as follows:

$$\Delta G = \Delta G^\circ - RT\ln\left(\frac{a_{H_2} \times a_{O_2}^{0.5}}{a_{H_2O}}\right)$$

Efficiency of Fuel Cells

The thermal efficiency, *η*, is the ratio of the useful energy produced to the amount of chemical energy released

$$\eta = \frac{useful\ energy}{\Delta H}$$

In an ideal cell, Δ*G*, is equivalent to the useful electrical energy available.

$$\eta^{ideal} = \frac{\Delta G}{\Delta H} \qquad (5)$$

Heat lost to the surroundings is

$$\Delta Q = T\Delta S = \Delta H - \Delta G$$

where *T* is temperature and Δ*S* is the entropy change

Hydrogen/Oxygen fuel cell:

Hydrogen/oxygen reaction under STP:

Δ*H* is -285.3 kJ/mole and Δ*G* is -237.1 kJ/mole.

The ideal cell efficiency is

$$\eta^{ideal} = \frac{\Delta G}{\Delta H} = \frac{237.1}{285.3} = 0.83$$

The efficiency of an ideal fuel cell operating under **non-standard** conditions can be expressed in terms of the operating cell potential, from Nernst equation and standard ideal cell potential

From $\Delta G = -nF\phi_{cell}$ we have $\eta^{ideal} = \frac{\Delta G}{\Delta H} = \frac{-nF\phi_{cell}}{\Delta H} = \frac{It\phi_{cell}}{\Delta H}$

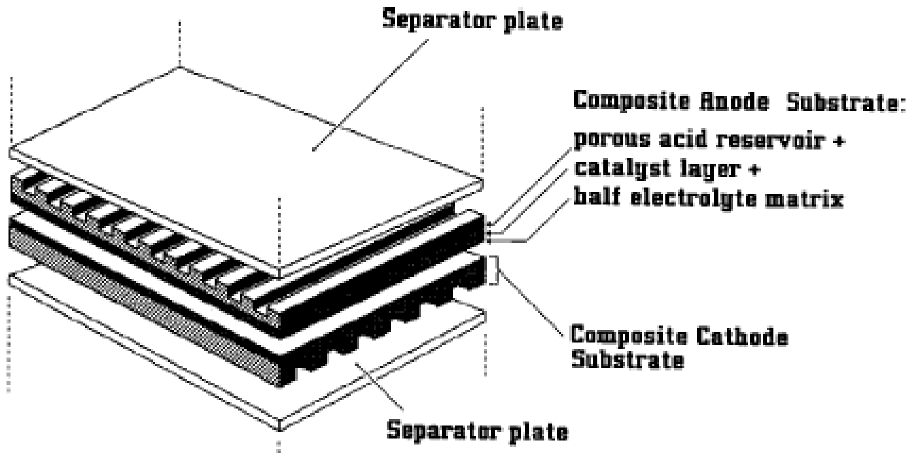
where *I* is the current and *t* is the time for which the current *I* flows

Fuel Cell Systems and Cell Stacking

Individual fuel cells can be combined in series to achieve appreciable voltage levels

The separator plate
a) provides an electrical connection between adjacent fuel cells, and

b) provides an impermeable gas barrier



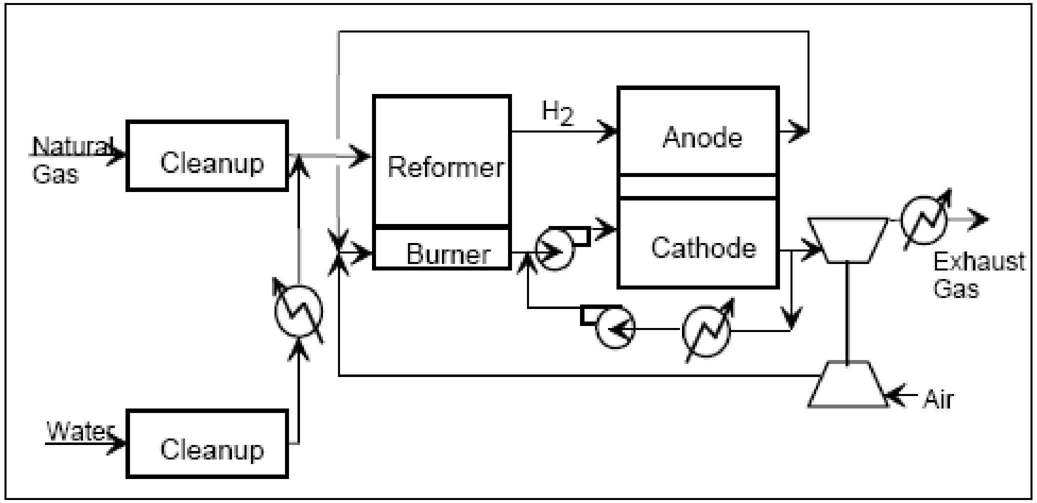
Basic fuel cell repeating unit for fuel cell stack

the initial fuel feed can be natural gas.

hydrogen is then obtained by the reforming reactions between natural gas and steam in the presence of a catalyst at temperature of ~760 oC

The operating temperature of most fuel cells are too low to make internal reforming viable and a separate external reformer stage is required

Finally, power conditioning is required to convert the DC output power from the fuel cell stack into AC power for consumer use



Example of external fuel reforming fuel cell

Actual Fuel Cell Performance

Only considered ideal fuel cell performance with no irreversible losses in energy

In real systems, useful power is only obtained from the fuel cell when a reasonable current is drawn. This leads to a loss in cell potential due to irreversible losses in the system

Irreversible losses in fuel cell systems originate primarily from three sources

1) Activation polarisation:

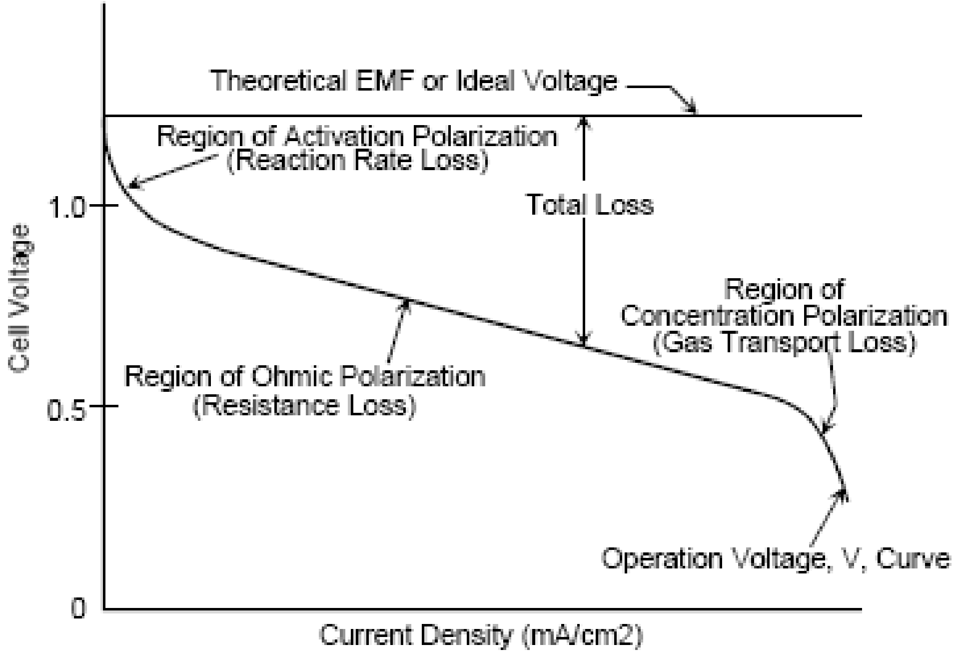
Activation polarisation due to slow electrode kinetics. Activation polarisation can be described by the general Tafel equation

$$\Delta\phi_{act} = a\log\left(\frac{i}{i_o}\right) = A\ln\left(\frac{i}{i_o}\right)$$

where *i* is the current density, i_o is the *exchange current density* and

$$A = \frac{RT}{\alpha nF}$$

where α is the *charge transfer coefficient* typically ~0.5



Ideal and actual fuel cell voltages

2) Ohmic polarisation:

Ohmic polarisation is due to the resistance to flow of ions. These resistive losses can be expressed by an Ohmic relationship

$$\Delta\phi_{ohm} = ir$$

where *i* is the current flowing through the cell and *r* is the total cell resistance

Actual Fuel Cell Performance

Thus far we have only considered ideal fuel cell performance with no irreversible losses in energy

In real systems, useful power is only obtained from the fuel cell when a reasonable current is drawn. For this to occur the actual cell potential decreases from its ideal potential value due to irreversible losses in the system

Irreversible losses in fuel cell systems originate primarily from three sources

1) **Activation polarisation**
2) **Ohmic polarisation**
3) **Concentration polarisation:**

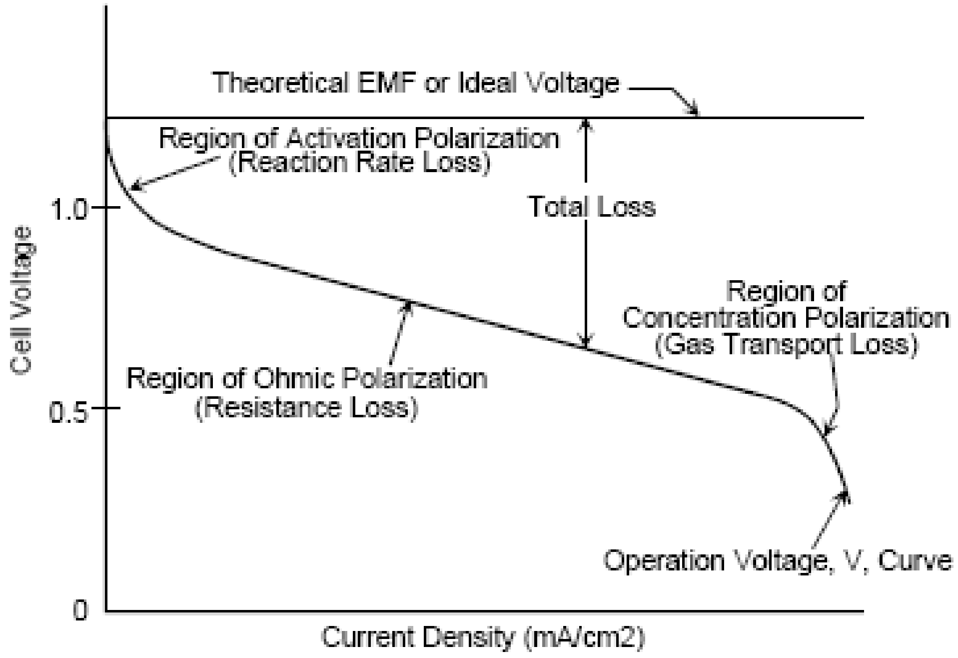
Concentration polarisation occurs when the reaction rate is limited by the rate of arrival of reactants to the electrode surface.

$$\Delta\phi_{trans} = -\frac{RT}{nF}\ln\left(1-\frac{i}{i_L}\right)$$

where i_L is the *limiting current density*

$$i_L = \frac{nFDC_{bulk}}{\delta}$$

where D is the diffusion coefficient, δ is the Nernst diffusion layer thickness and C_{bulk} is the bulk concentration



Ideal and actual fuel cell voltages

Note: Concentration polarisation is reduced by higher reactant bulk concentrations and increased mixing or flow rate of the electrolyte to decrease the Nernst diffusion layer thickness

Actual Fuel Cell Performance

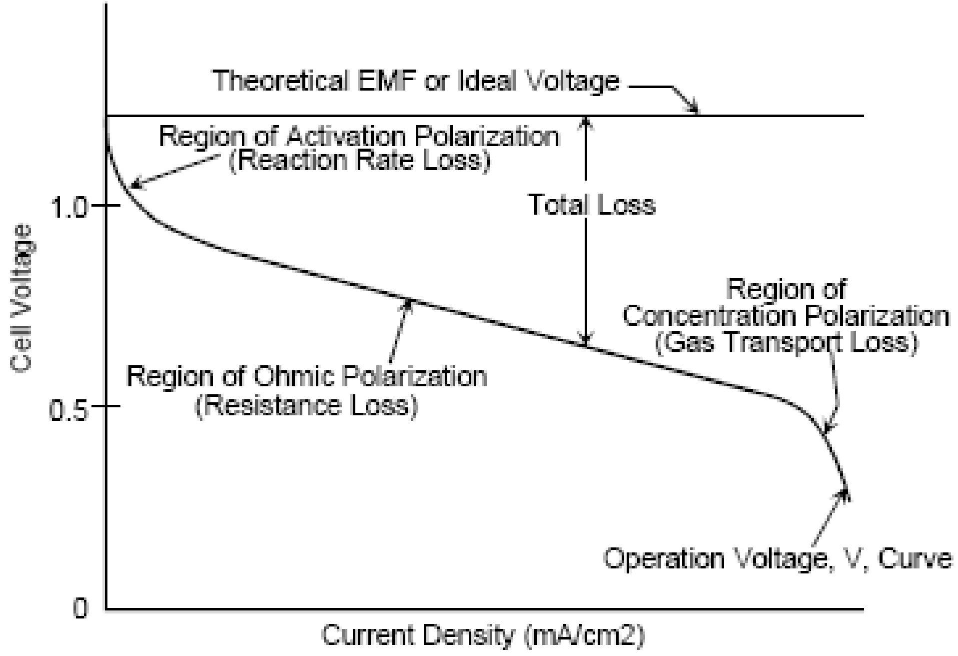
Combined irreversible losses:

It is useful to combine the voltage losses due to irreversibilities in the fuel cell system to give one expression for the fuel cell operating voltage, Φ_{ac}, at a particular current density, I

$$\phi_{ac} = \phi_{eq} - \Delta\phi_{ohm} - \Delta\phi_{act} - \Delta\phi_{trans}$$

Substituting in the individual voltage loss terms gives

$$\phi_{ac} = \phi_{eq} - ir - A\ln\left(\frac{i}{i_o}\right) + \frac{RT}{nF}\ln\left(1 - \frac{i}{i_L}\right)$$



Ideal and actual fuel cell voltages

Actual fuel cell efficiency and fuel utilization:

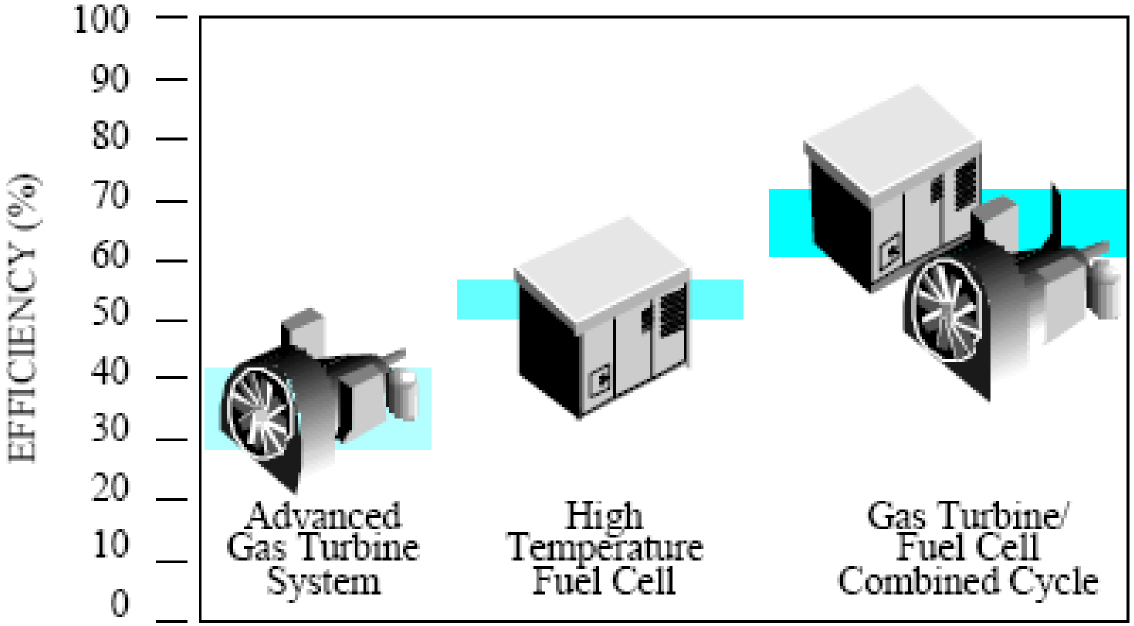
In practice some portion of the fuel will pass through the cell without being oxidized. Thus a *fuel utilization coefficient* is defined as

$$\mu_F = \frac{\text{Mass of fuel reacted}}{\text{Mass of fuel input to cell}}$$

Finally, the actual fuel cell performance can be expressed as

$$\eta_{ac} = \mu_F \frac{-nF\phi_{ac}}{\Delta H} \qquad (6)$$

Different Types of Fuel Cells



Typical fuel cell plant efficiencies

Typical efficiency:

High temperature fuel cell plants can achieve efficiencies of 50-60%

Higher efficiencies of ~ 70% can be achieved in gas turbine/fuel cell combined cycle systems

Further reading: Fuel cell systems explained (2000), Larminie, J.

Fuel Cells – Worked Examples

Problem 1: What volumetric hydrogen flow rate (assuming 100% utilization at anode and 1 atm pressure) is required to generate 1 A of current from a fuel cell?

Problem 2: A fuel cell stack is operated at 298 K and a cell voltage of 0.85 V on pure hydrogen fed at 1 atm pressure. The fuel utilization coefficient, μ_F, is 0.90 and the value of enthalpy change, ΔH, for the reaction is -285.3 kJ/mole.

A) What is the actual efficiency of the fuel cell stack?

B) What hydrogen mass flow rate must be supplied to the fuel cell stack to generate 2.0 MW_{DC} of power?

Definitions of Charge and Current

The Electronic Charge

The charge carried by each electron, e, is 1.602 x 10^{-19} C

Therefore the charge of 1 mole of electrons = N_A x e = 96,487 C

(Faraday constant is 96,487 C/mole)

Electric current is a measure of the rate of charge collection where:

1 ampere = 1 Coulomb of charge per second = 1 C/s

Considering the H_2:O_2 fuel cell reaction

At the anode:

$$H_{2(g)} \rightarrow 2H^{+}{}_{(aq)} + 2e^{-}{}_{(M)}$$

1 mole hydrogen molecules	2 moles aqueous protons	2 moles electrons

Note: For every mole of hydrogen fuel consumed at anode you generate 2 moles of electrons

Problem 1

Problem 1: What volumetric hydrogen flow rate (assuming 100% utilization at anode and 1 atm pressure) is required to generate 1 amp of current from a fuel cell?

For a general oxidation half cell reaction:

$$jR \rightarrow kO + ne^-$$

The number of moles of fuel can be related to the current by

$$\text{No moles of fuel consumed} = \frac{jI}{nF}$$

So for the hydrogen reaction, where *n* = 2 and *j* = 1, the number of moles of hydrogen required to produce 1 A of current is given by

$$\text{No mole of } H_2 = \frac{1 \times 1 (C/\sec)}{2 \times 96485 (C/mole)} = 5.18 \times 10^{-6} (mole/\text{s})$$

Problem 1

Problem 1: What volumetric hydrogen flow rate (assuming 100% utilization at anode and 1 atm pressure) is required to generate 1 amp of current from a fuel cell?

1 mole of ideal gas at standard temperature and pressure (1 atm and 298 K) occupies 24,465 cm^3. Therefore, the volumetric flow rate of hydrogen required to generate 1 A is:

$$\text{Flow rate of } H_2 = 5.18\text{x}10^{-6}(\text{mole/s}) \text{ x } 24{,}465(\text{cm}^3/\text{mole})$$

$$\underline{= 0.127 \text{ cm}^3/\text{s}}$$

Alternatively, since 1 mole of H_2 has a mass of 2.0 g, converting to a mass flow rate gives

$$\text{Mass flow rate of } H_2 = 5.18\text{x}10^{-6}(\text{mole/s}) \text{ x } 2.0(\text{g/mole})$$

$$\underline{=1.036\text{x}10^{-5}(\text{g/s}) \ = \ 0.037(\text{g/hr}) \text{ of } H_2}$$

Problem 2

Problem 2: A fuel cell stack is operated at 298 K and a cell voltage of 0.85 V on pure hydrogen fed at 1atm pressure. The fuel utilization coefficient, μ_F, is 0.90 and the value of enthalpy change, ΔH, for the reaction is -285.3 kJ/mole.

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A) What is the actual efficiency of the fuel cell stack?

Recalling Eq. (6)

$$\eta_{ac} = \mu_F \frac{-nF\phi_{ac}}{\Delta H} \qquad (6)$$

We have

$$\eta_{ac} = (0.90) \times \frac{-2 \times 96485(C/mole) \times 0.85(V)}{-285300(J/mole)} = 0.517$$

Note: As the ideal efficiency is 0.83, the fuel cell stack is operation at only 62% of the ideal efficiency

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B) What hydrogen mass flow rate must be supplied to the fuel cell stack to generate 2.0 MW_{DC} of power?

Firstly we can calculate the generated current as follows:

$$Power, P = I\phi \text{ Therefore } I = \frac{P}{\phi} = \frac{2\times10^6(W)}{0.85(V)} = 2.35\times10^6(C/\text{s})$$

Then the rate of fuel consumption can be calculated from

Rate of H_2 consumption = $\frac{1\times2.35\times10^6(C/\text{s})\times2.0(g/mole)}{2\times96485(C/mole)} = 24.36(g/s)$

Note: as μ_F is not equal to 1 the fuel flow rate supplied to fuel cell is given by

Mass of fuel supplied = mass of fuel reacted/μ_F = $\frac{24.36}{0.90}(g/\text{s}) = 27.07\,g/\text{s}$

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Fuel Cell Systems

Fuel Cell Systems

What fuels can be used?

Most types of fuel cells employ hydrogen as the fuel but this can be produced by reforming of other fuels

Fuel reforming:

Large interest in devices operating on liquid fuels - accelerated introduction to market due to reduced infrastructure needs in order to supply fuel

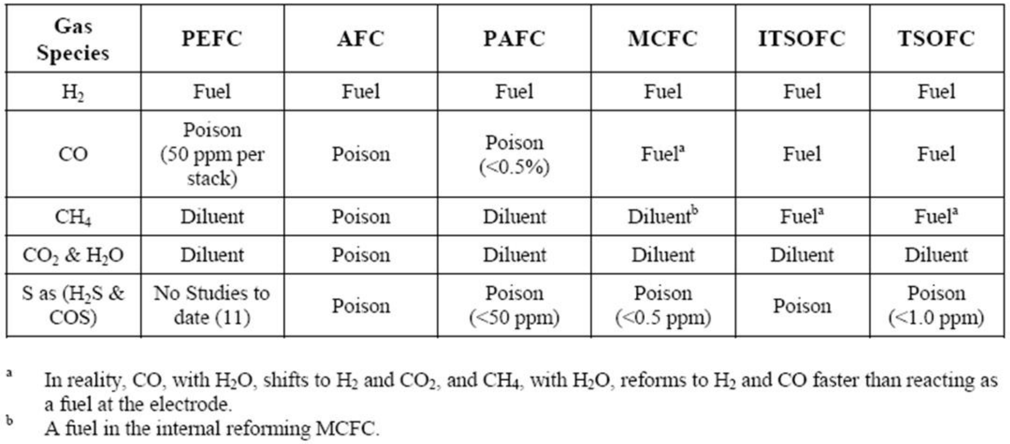
Fossil fuels such as natural gas and gasoline and liquid alcohols need to undergo reforming reactions to be used in conventional fuel cells

These fuel reformers add complexity and mass to the overall system

Natural gas common starting fuel for stationary fuel cell power systems

However, the extra size/mass of the reformer a major drawback in most mobile applications and hydrogen as fuel is preferred

Major fuel constituent effects on fuel cells

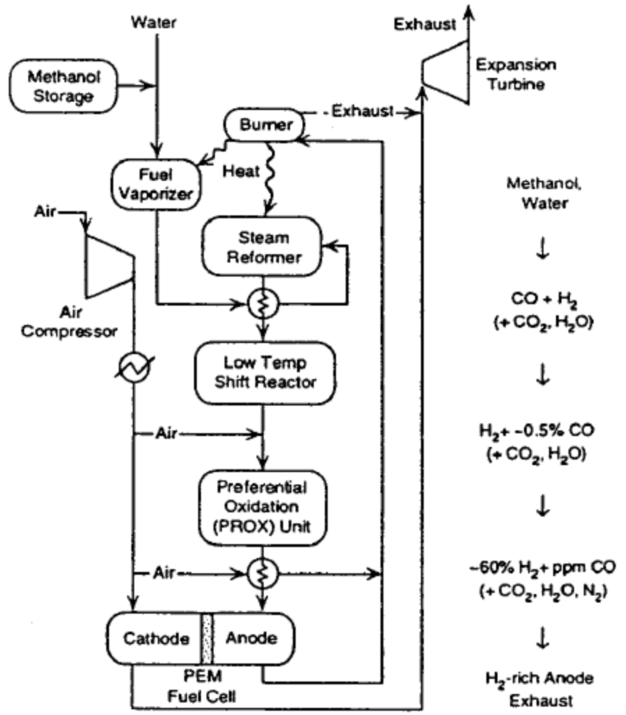


Gas Species	PEFC	AFC	PAFC	MCFC	ITSOFC	TSOFC
H_2	Fuel	Fuel	Fuel	Fuel	Fuel	Fuel
CO	Poison (50 ppm per stack)	Poison	Poison (<0.5%)	Fuel[a]	Fuel	Fuel
CH_4	Diluent	Poison	Diluent	Diluent[b]	Fuel[a]	Fuel[a]
CO_2 & H_2O	Diluent	Poison	Diluent	Diluent	Diluent	Diluent
S as (H_2S & COS)	No Studies to date (11)	Poison	Poison (<50 ppm)	Poison (<0.5 ppm)	Poison	Poison (<1.0 ppm)

[a] In reality, CO, with H_2O, shifts to H_2 and CO_2, and CH_4, with H_2O, reforms to H_2 and CO faster than reacting as a fuel at the electrode.
[b] A fuel in the internal reforming MCFC.

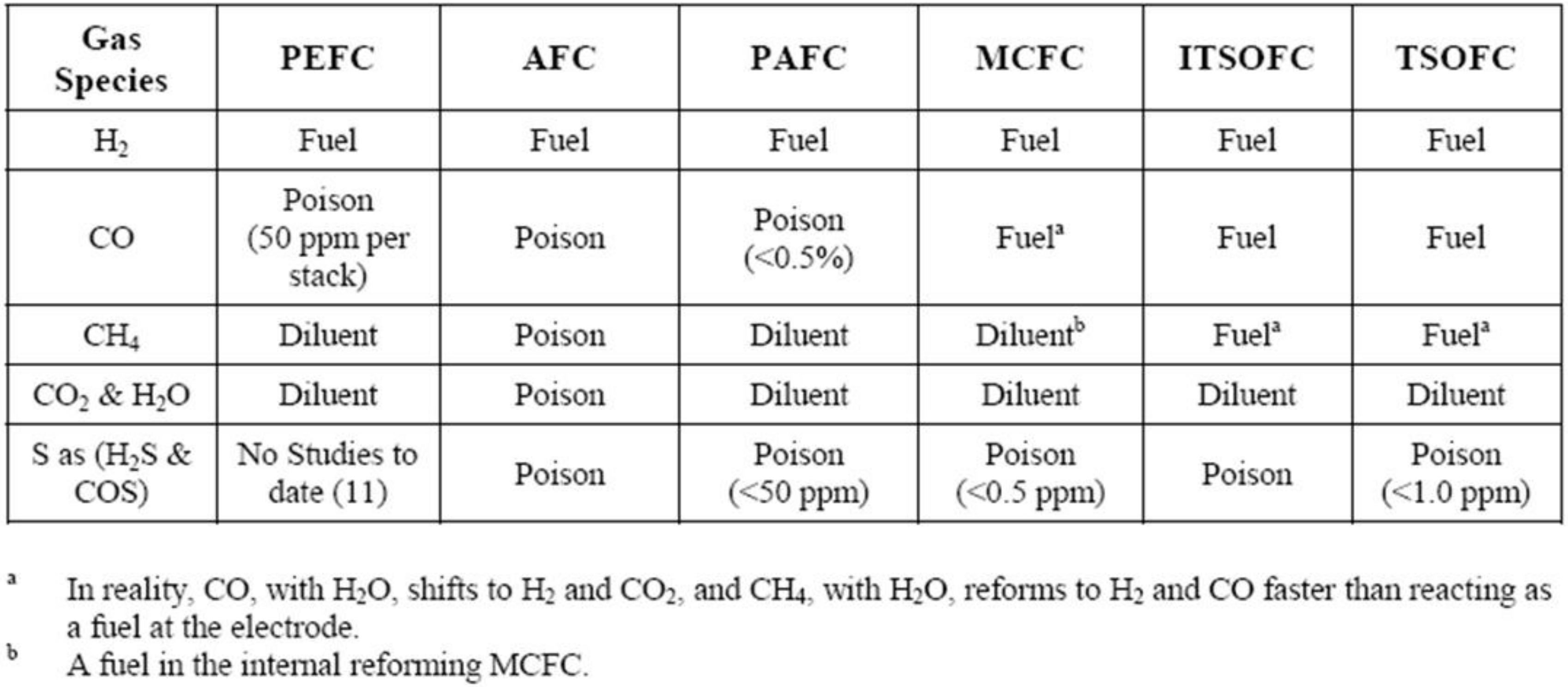
Source: *Fuel cell handbook*, (2000)

Methanol Steam Reformer System



Fuel Cell Systems

Major fuel constituent effects on fuel cells



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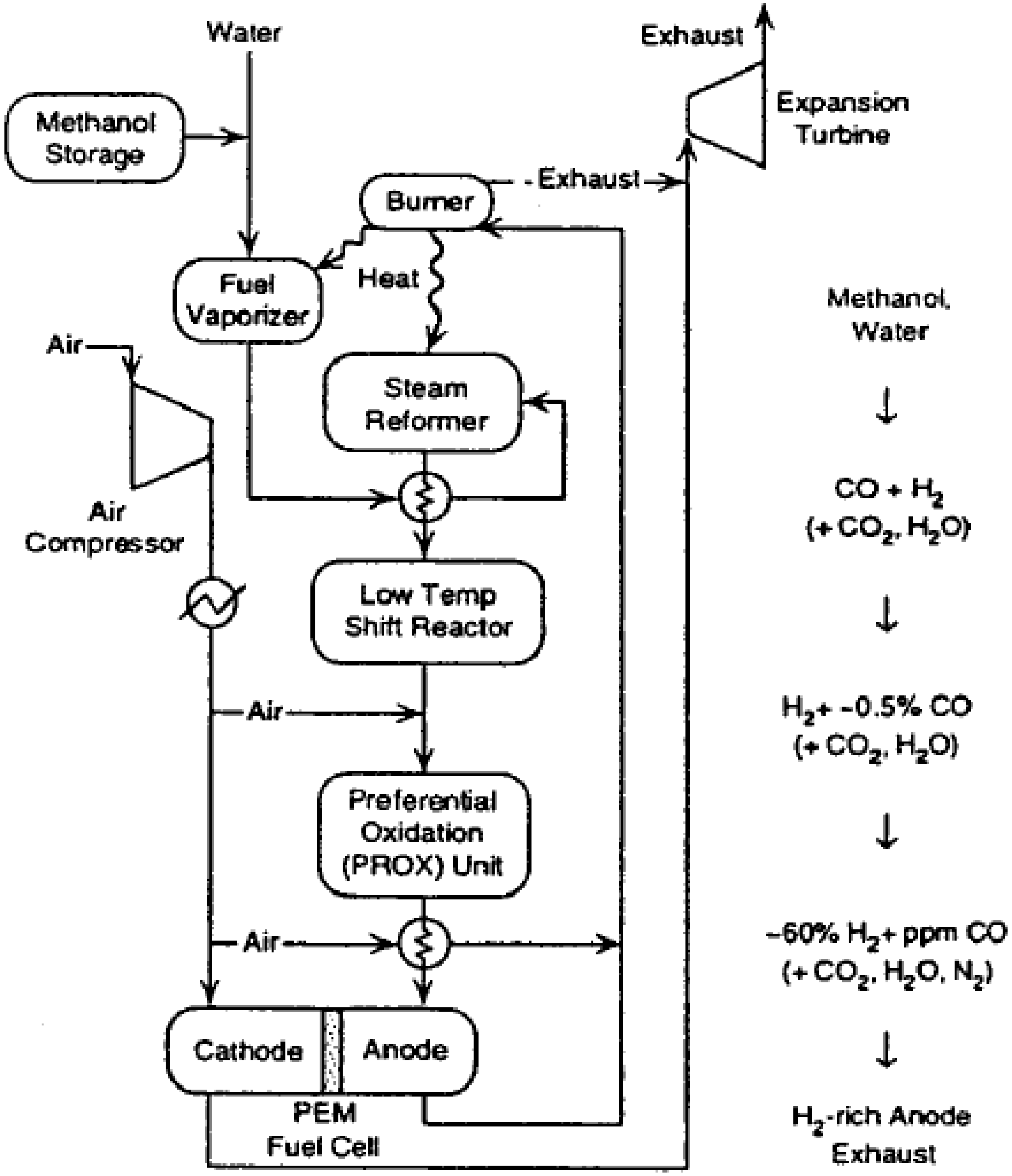
Fuel Cell Systems

Methanol Steam Reformer System



Fuel Cell Systems

What fuels can be used?

Most types of fuel cells employ hydrogen as the fuel but other fuel types can be used, including

Direct Methanol Fuel Cell (DMFC):
These fuel cells allow the direct conversion of the chemical energy stored in methanol into electrical energy – without need of reforming

They are based on polymer electrolyte fuel cells (PEFC) with a proton exchange polymer membrane

Direct methanol fuel cell reactions

Anode:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$$

Cathode:

$$\frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$$

Overall reaction:

$$CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$$

Large interest in devices operating on liquid fuels - accelerated introduction to market due to less complex system and reduced infrastructure needs in order to supply fuel

Key advantages:
Fuel storage as methanol – liquid at room T & P
Ease of refuelling, distribution and reduced infrastructure required
High energy density of methanol

Key disadvantages:
Low efficiency due to fuel crossover (permeation through membrane), dynamic response sluggish

Recent developments include Toshiba's (above) DMFC weighing only 8.5g capable of producing 100mW power. This is enough for small portable consumer products such as mobile phones, mP3 players and laptops. A 2cc charge of methanol can power an MP3 player continuously for 20 hours

Fuel Cell Systems

Why hydrogen?

- High electrochemical reactivity at anode (much higher than methanol)
- Products of oxidation are environmentally benign, e.g. water and heat
- Hydrogen has one of the highest specific energies of 120 MJ/kg (compared to 42 MJ/kg for oil)

Therefore, a car running on a fuel cell and powered by hydrogen could be classed as *zero-emissions*!?

$$Specific\_Power = \frac{Power}{Mass}$$

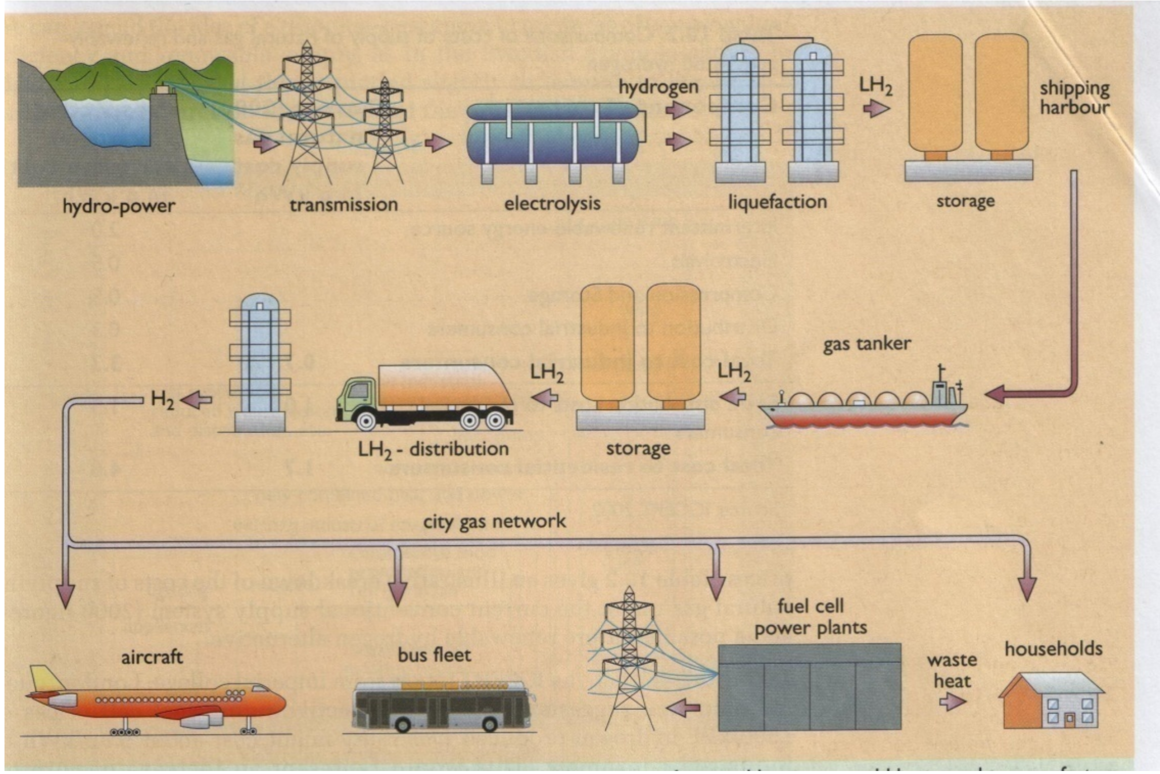
Note 1: However, unlike fossil fuels, hydrogen does not occur naturally so must be produced from a conversion process – **Energy required**

Note 2: These conversion processes may produce pollutants – **such as (CO_2)**

Hydrogen considered as a secondary fuel and an energy carrier - not a primary fuel

Fuel Cell Systems

The Hydrogen Economy



Source: Boyle, *Renewable energy*

Large-scale use of hydrogen would require many interdependent steps and large capital investment

Production: From surplus renewables

Distribution: Existing Pipelines, tankers

End use: Domestic cooking & heating

Fuel cell power stations

Fuel cell transportation

Transportation

As an energy carrier hydrogen is a convenient way to transport and store energy originating from other sources

Can be distributed and transported by pipeline over long distances – associated energy losses may be less than those associated with electricity distribution

Has been safely transported for many years due to ammonia production industry

Pipelines already operational - Some 1500 km of pipeline installed in Europe for carrying hydrogen and some 700 km in the US

Fuel Cell Systems

Methods of Hydrogen Production – Fossil Fuel Reforming

Steam reforming

Most commonly used technique and already extensively used in industry on large scale for hydrogen production

In late 1990's global production had reached ~500 billion cubic meters which is equivalent to 6.5 EJ energy or ~1.5% of world's primary energy

However, at present the hydrogen is seldom used for energy generation but instead used in fertilizer industry for ammonia production, for oil refining and for feedstock in chemical industry

Basic reforming reactions

$$CH_4 + H_2O \rightarrow CO + 3H_2$$ (ΔH = 206 kJ/mol)

$$C_nH_m + nH_2O \rightarrow nCO + (\frac{m}{2} + n)H_2$$

Reactions carried out over nickel catalyst at *T*>500 ºC

Steam reforming – what are the benefits?

Why not just burn the fossil fuels without conversion?

Fuel Cell Systems

Methods of Hydrogen Production – Fossil Fuel Reforming

Steam reforming

Basic reforming reactions

$CH_4 + H_2O \rightarrow CO + 3H_2$ (ΔH = 206 kJ/mol) $C_nH_m + nH_2O \rightarrow nCO + (\frac{m}{2} + n)H_2$

Reactions carried out over nickel catalyst at T > 500 ºC

Steam reforming – what are the benefits?

Why not just burn the fossil fuels without conversion?

Benefits include:

- Easier to separate and capture CO_2 from reforming process product gas than to capture CO_2 post combustion
- Therefore possible to use central large-scale hydrogen production combined with CO_2 removal
- Problem of point-of-use emissions is avoided
- Hydrogen can be utilised to produce electricity and burnt in air to produce heat with fewer pollutants – Nox at high temperature but no CO_2, SOx, VOC or CO

The CO_2 produced can be removed from gas stream using ethanolamine solution. CO_2 can then be recovered

The additional cost of CO_2 capture is estimated at ~25% to overall process

Fuel Cell Systems

Methods of Hydrogen Production – Biomass Conversion

Biomass can be converted to gaseous products by a number of processes

Thermochemical conversion to synthesis gas

biomass

Gasification

~900°C, O_2

H_2, CO

Partial oxidation to synthesis gas

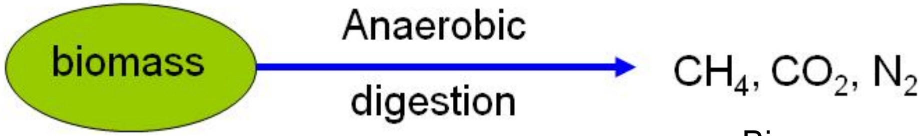
Gaseous product has low heating value of ~4-6 MJ/Nm^3

The product gas allows production of hydrogen (via the water-gas shift reaction below) and methanol – both of which are of use in fuel cell systems and for fuel transportation

$$CO + H_2O \rightarrow CO_2 + H_2$$

Water gas shift reaction

Anaerobic digestion of biomass to biogas



biomass

Anaerobic digestion

CH_4, CO_2, N_2

High moisture content biomass

Biogas

Varying composition

Biogases produced from anaerobic digestion and thermochemical treatments typically have low heating values (due to relatively high N_2 and COx levels) making them unattractive for use in gas engines

However, this is not an issue for fuel cells and the biogases can be used to generated electricity in the MCFC and SOFC without problems

Fuel Cell Systems

Methods of Hydrogen Production – Electrolysers

Use electricity to electrochemically disassociate water into H_2 and O_2 gases – the reverse of fuel cell reaction

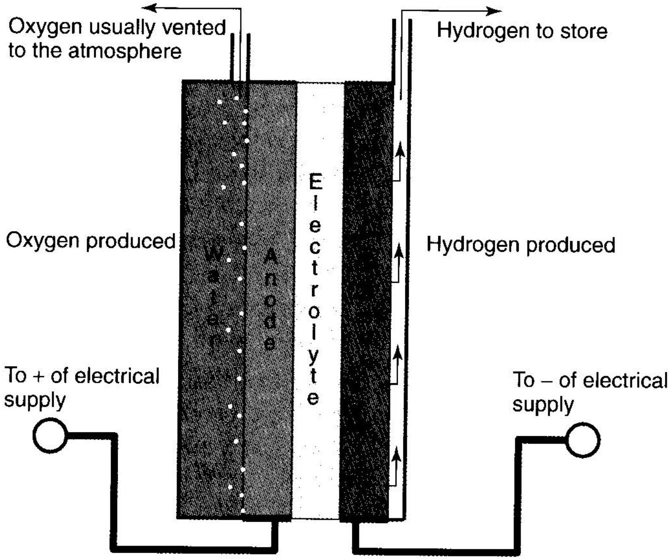


Diagram of PEM-based electrolyser system (source: *Fuel cell systems explained* 2nd Ed. Larminie (2003))

Electrolyte is usually alkaline potassium hydroxide or solid proton exchange membrane (PEM) which allows passage of protons between electrodes

At cathode – protons removed from electrolyte by reduction

$$2H^+ + 2e^- \rightarrow H_{2(g)}$$

At anode – water oxidised and oxygen formed

$$H_2O \rightarrow \tfrac{1}{2}O_{2(g)} + 2H^+ + 2e^-$$

Overall reaction:

$$H_2O_{(l)} \rightarrow H_{2(g)} + \tfrac{1}{2}O_{2(g)} \qquad \phi^o_{Cell} = -1.23V$$

$$\Delta G^\circ = -nF\phi^o_{cell} = -(2 \times 96485 \times -1.23)J = +237.2KJ$$

Gibbs free energy for reaction positive so process is not spontaneous

Electricity can come from renewable sources such as solar, wind, hydro.

Hydrogen produced by electrolysers is of high purity but there can be water vapour. Hence, gas stream may require drying before use

Fuel Cell Systems

Hydrogen Storage

- So far we have considered production of hydrogen by various methods.
- In most applications it is more convenient and efficient to store generated hydrogen fuel for later use when needed.
- This is also a convenient method to store energy supply from renewable sources such as solar, wind, hydro, where the supply may be out of phase with the peak demand (in combination with electrolysers for example)
- A small local store of hydrogen is also essential for use in mobile and portable fuel cell applications

Properties of hydrogen

- Hydrogen has high specific energies of 120 MJ/Kg (compared to 42 MJ/Kg for oil)
- However, it has one of the lowest energy densities of ~10 MJ/m^3 at atmospheric pressure (~one quarter that of natural gas)

Courtesy TFL – the fuel cell powered No.25 bus which ran during a two year trial from Oxford Circus to Ilford

Therefore, major drawback is that at normal temperature and pressure the use of hydrogen as fuel requires relatively large volumes for storage

- Reason why first applications in fuel cell powered vehicles have been for buses where a large roof space is available for hydrogen storage
- Improved hydrogen storage is still a major obstacle to the widespread use of fuel cells

Fuel Cell Systems

Hydrogen Storage

Principle storage methods at present

(a) Compressed gas

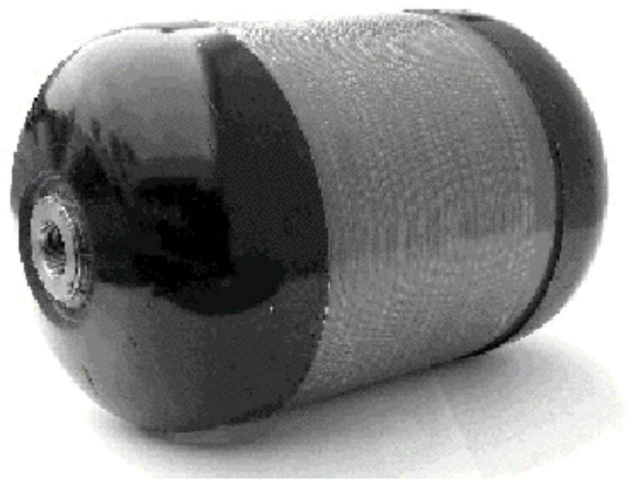
(b) Liquid hydrogen (LH_2)

Other methods under development include

(c)Metal hydride storage

(d)Storage using carbon nanotubes/fibres

(a) Storage as compressed gas



Most technically simple method and most widely used for small-scale storage of gas

Gas pressure is typically ~300 atm. Moving to high pressure requires thicker cylinder walls and carries the corresponding weight penalty which is particular problem for mobile applications

Typical storage efficiencies are only 1-3% by mass H_2 – when including cylinder and associated equipment. This gives a specific energy of 0.5-1.2 kWh/kg for the overall system

This low specific energy and mass storage is due to low density of H_2 gas – even at elevated pressure

Main advantages are:

- Simplicity of systems - long storage lifetime - no limits on hydrogen purity

Most useful for applications where the demand is variable but not high

Fuel Cell Systems

Hydrogen Storage

Principle storage methods at present

(a) Compressed gas

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(b) Storage as liquid hydrogen (LH_2)

H_2 is difficult to liquefy and requires to be cooled to ~-253 ºC (20 K) "cryogenic hydrogen"

Only widely used method of storing large quantities of hydrogen which are currently used in petroleum refining and ammonia production industries

Due to low temperatures required LH_2 containers are typically large, strongly reinforced vacuum (or Dewar) flask designs with pressures in the tanks of ~ 3 bar

Despite being a liquid, the density of LH_2 is still low at only 71 kg/m^3

Considerable effort has been made by BMW (among others) to develop a mobile LH_2 storage system for use in cars. Their system has a maximum pressure of 5 bar and 120 L volume. At a density of 71 kg/m^3, this gives 8.5 kg of LH_2

The specific energy density of this storage system is 5.57 kWh/kg

Major disadvantage: energy intensive nature of liquefaction process where the energy required is ~25% of the heating value of hydrogen.

Hence, overall a very inefficient way of storing and transporting energy!

Fuel Cell Systems

Hydrogen Storage

Principle storage methods at present

(a) Compressed gas

(b) Liquid hydrogen (LH_2)

Other methods under development include

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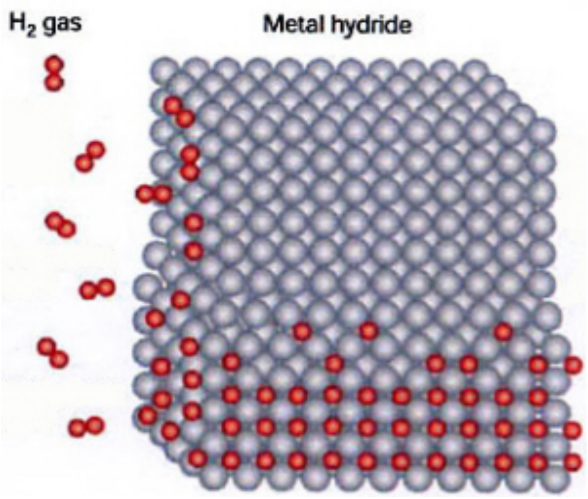
(c) Metal hydride stores

These involve the reversible absorption of hydrogen by certain metal alloys, for example titanium-iron alloy

The general reaction is $M + H_2 \leftrightarrow MH_2$

In terms of mass and specific energy density the storage system is not very promising with an specific energy density of 0.22 kWh/kg

However, benefits lie in having one of the lowest volumetric densities of H_2 storage where the hydrides can hold more H_2 per unit volume than pure LH_2



Operation simple - filled at room temp and just above 1atm pressure. Hydrogen released by gentle heating

Key advantages:

- Safety - as H_2 not stored at high pressure
- Simplicity of device and charging/discharging of H_2

Find a wide range of application where small quantities of H_2 are required and where mass is not a problem but where space is, e.g. fuel cell powered boats – ballast mass usually artificially added

Main disadvantages:

- Low specific energy
- High purity H_2 required to avoid contamination and degradation of metal alloy

Fuel Cell Systems


bjhaoyun.en.alibaba.com

Fuel Cell Systems

Secure Supplies Tank Kits

300 LITRE

METAL Hydride

Stackable 5 tanks (5x500=2500ltr)
or (10 tanks etc 10x 500L=5000Ltr)

Size W 67mm x
L 312mm
Parts Stainless
5 kg

System for 1-2 cylinder Generator engines
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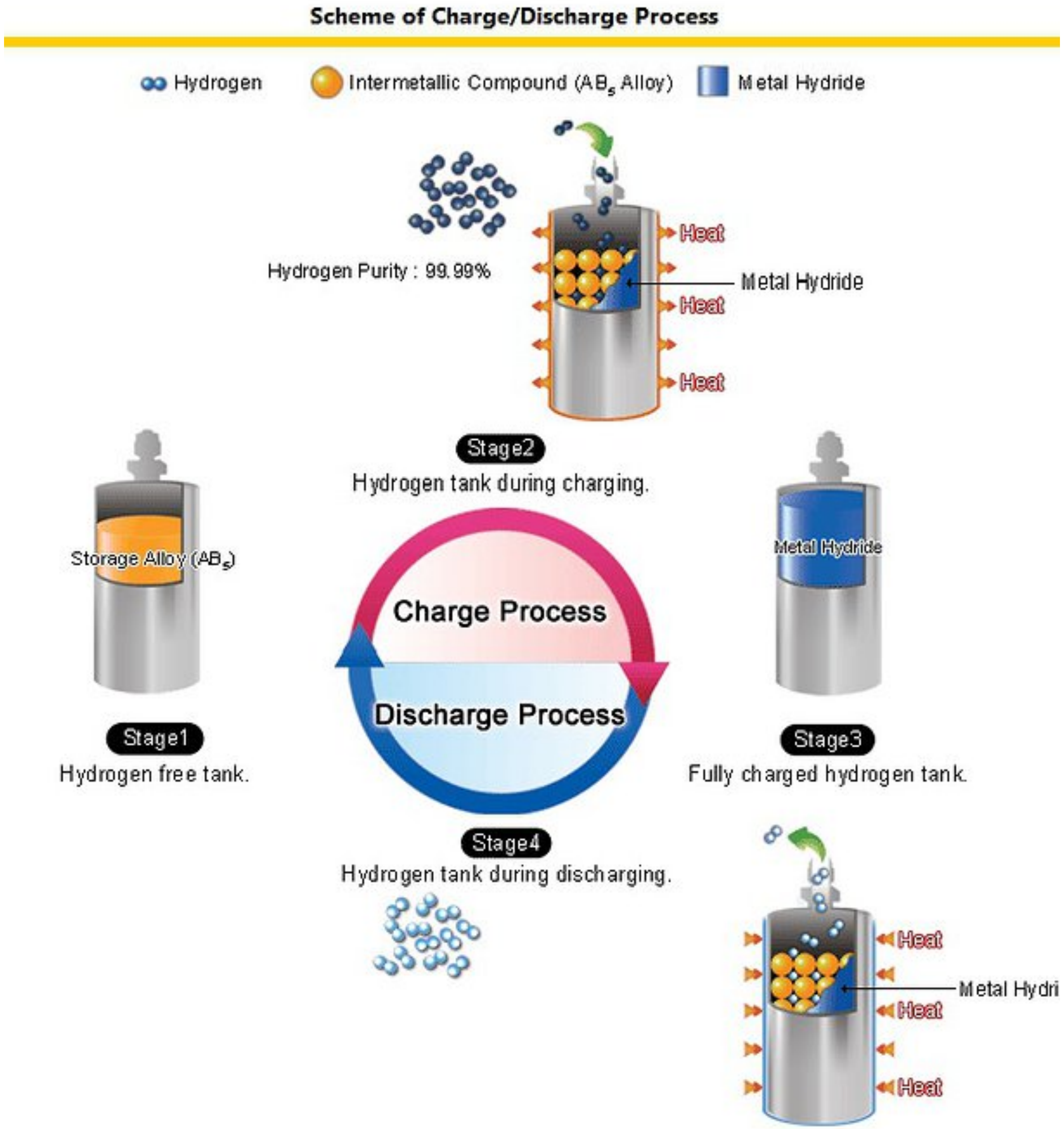
Fuel Cell Systems



Fuel Cell Systems

Hydrogen Storage

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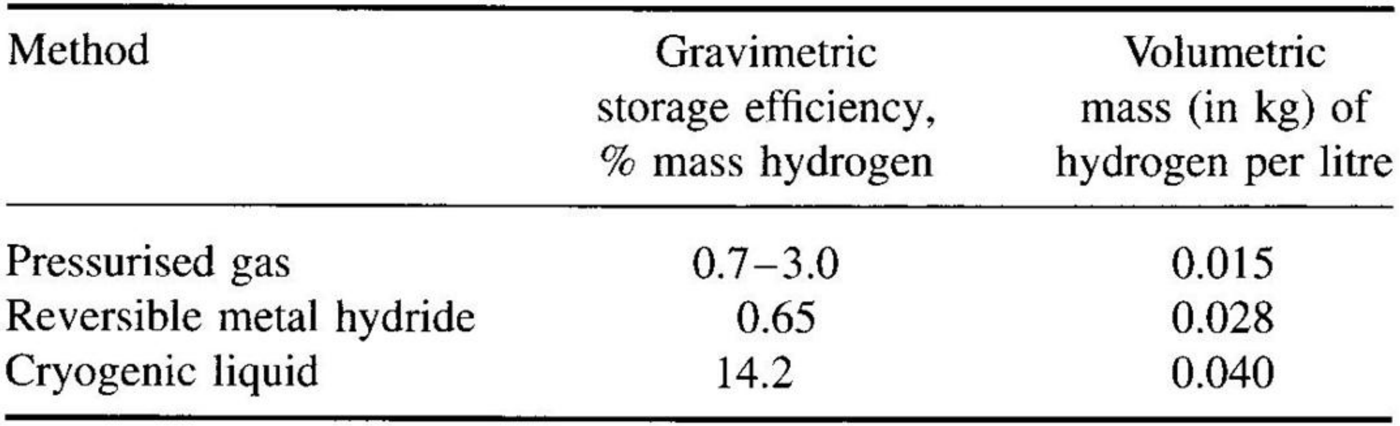
Comparison of storage methods for hydrogen



Method	Gravimetric storage efficiency, % mass hydrogen	Volumetric mass (in kg) of hydrogen per litre
Pressurised gas	0.7–3.0	0.015
Reversible metal hydride	0.65	0.028
Cryogenic liquid	14.2	0.040

Source: *Fuel cell systems explained*, Larminie (2003)