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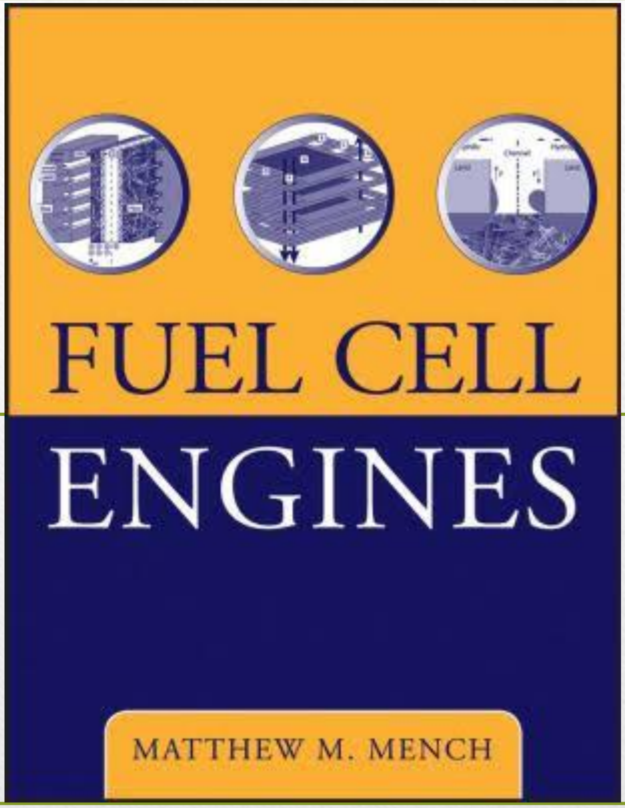


FUEL CELL
ENGINES
MATTHEW M. MENCH

Hydrogen Energy
And
Fuel Cell Technology

Instructor: Dr. Wisam J. Khudhayer

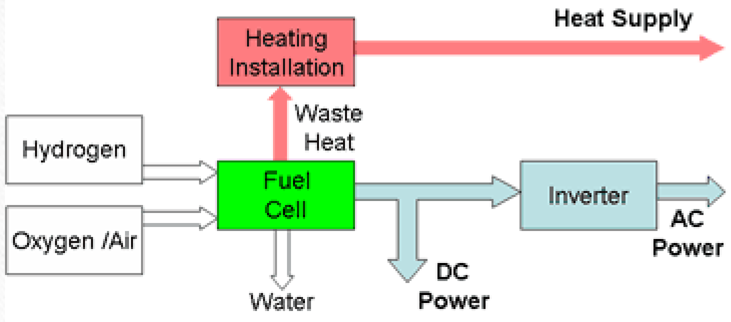
Textbook
Fuel Cell Engines
By
Matthew M. Mench

Chapter One: Introduction

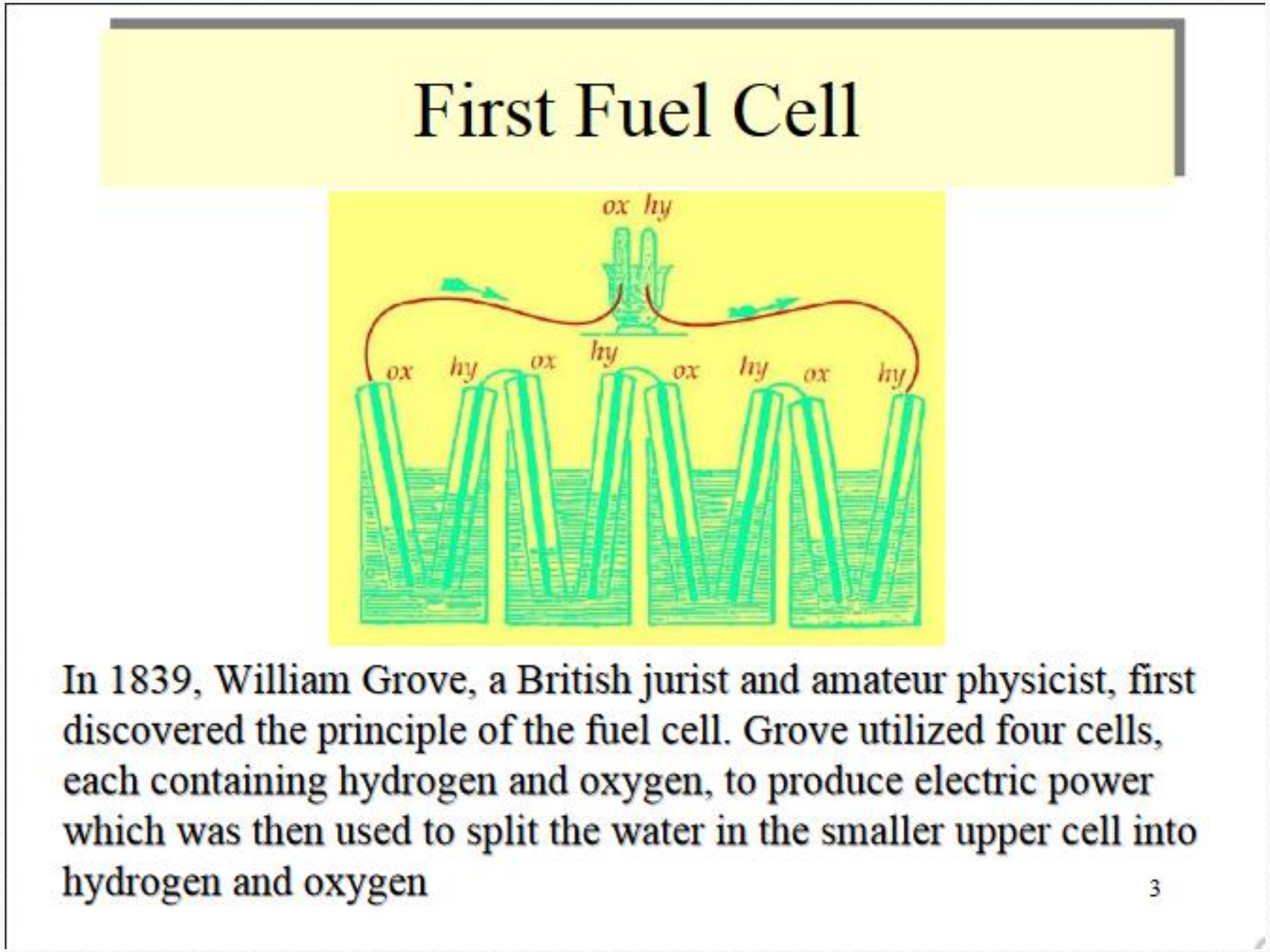
1.1 What is a fuel cell?

Fuel cell is an electrochemical device that converts chemical energy of a fuel (hydrogen, natural gas, methanol...etc.) and an oxidant (air or oxygen) into electrical energy directly, promising power generation with high efficiency and low environmental impact. Most fuel cell power systems comprise a number of components:

- Unit cells, in which the electrochemical reactions take place
- Stacks, in which individual cells are modularly combined by electrically connecting the cells to form units with the desired output capacity
- Balance of plant which comprises components that provide feed stream conditioning (including a fuel processor if needed), thermal management, and electric power conditioning among other ancillary and interface functions



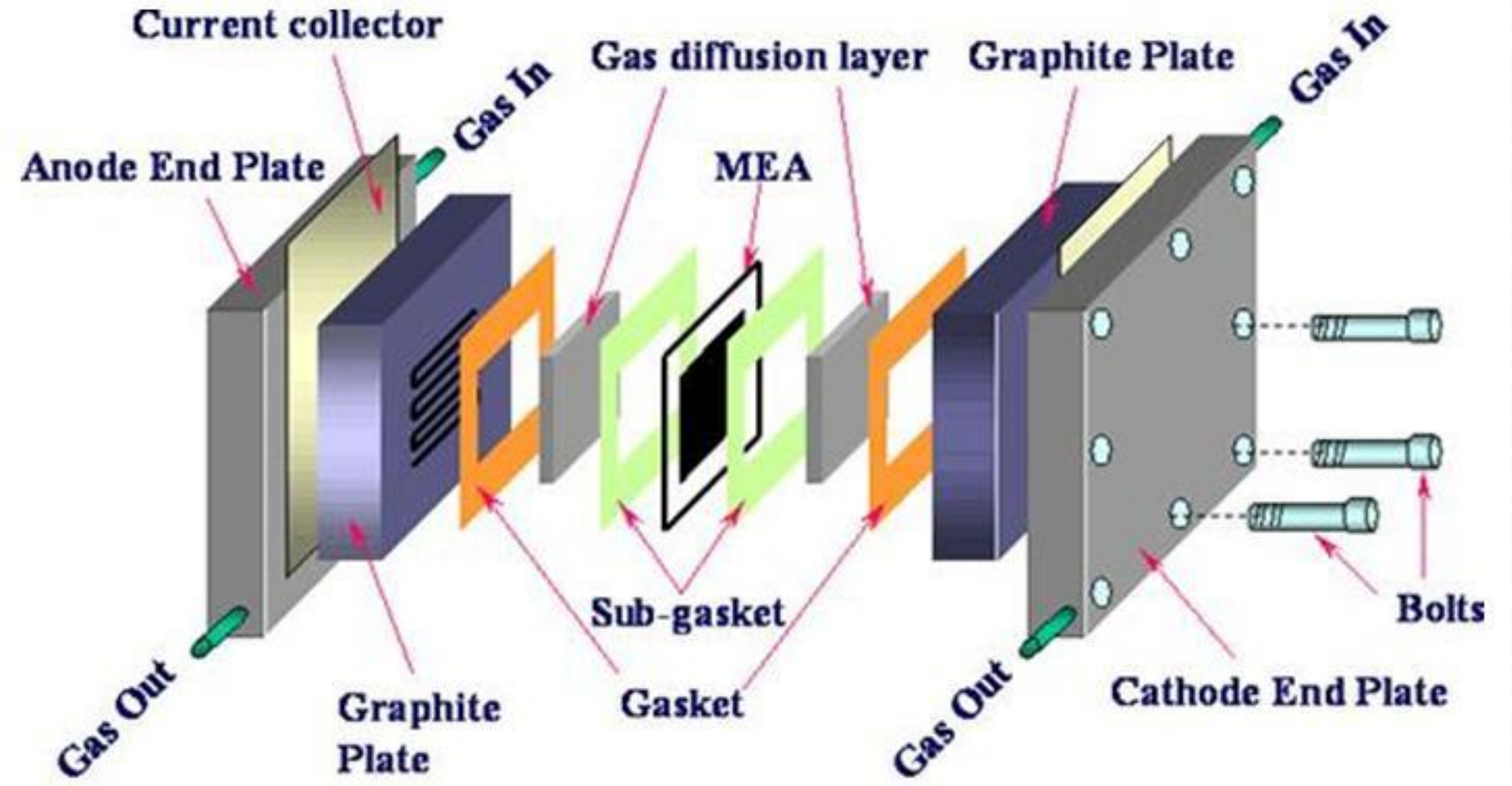
Fuel Cells used in CHP Applications



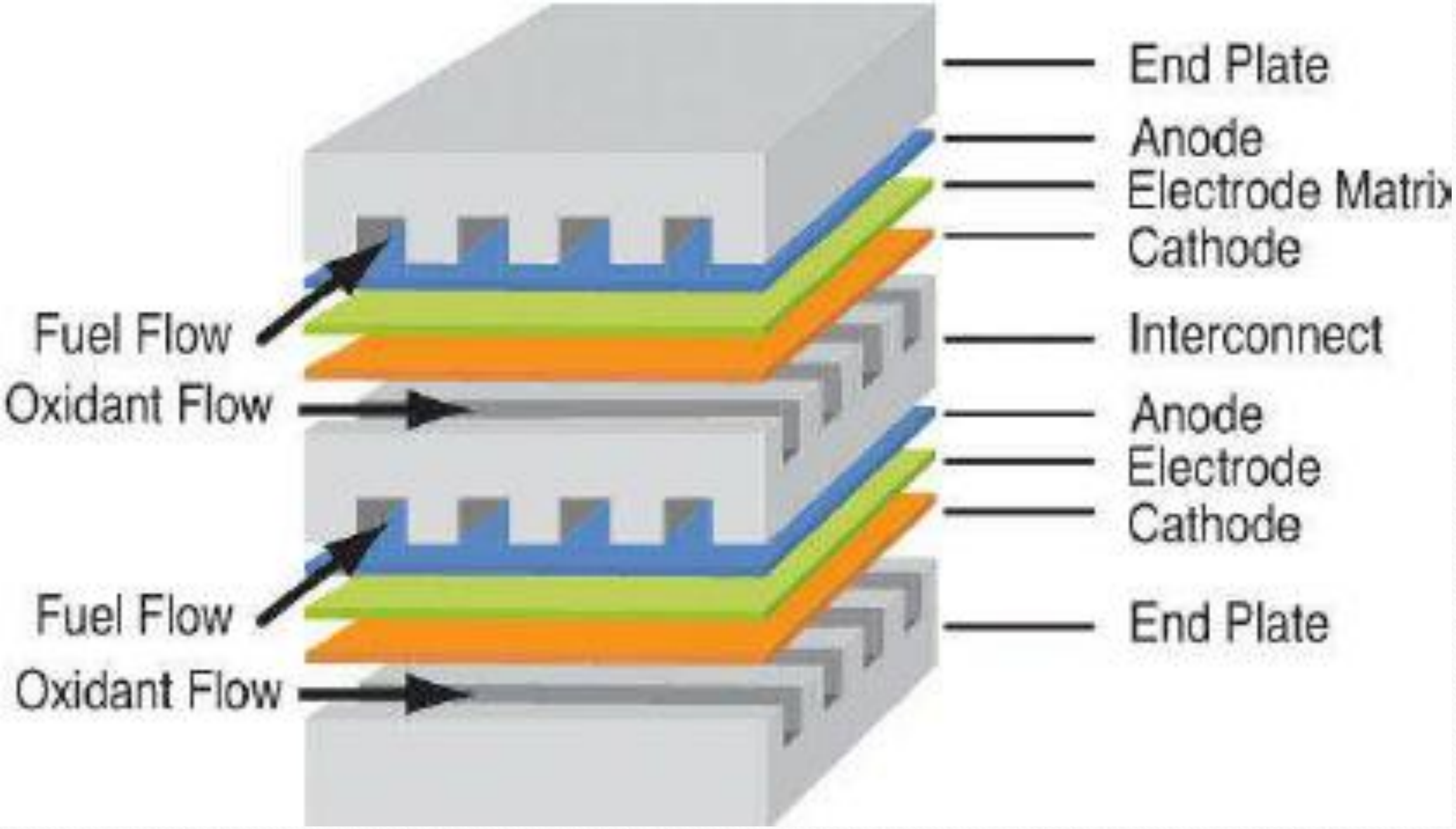
First Fuel Cell

In 1839, William Grove, a British jurist and amateur physicist, first discovered the principle of the fuel cell. Grove utilized four cells, each containing hydrogen and oxygen, to produce electric power which was then used to split the water in the smaller upper cell into hydrogen and oxygen

Individual Fuel Cell



Fuel Cell Stack



Fuel Cell vs. Battery

- In principles, a fuel cell operates like a battery. Unlike a battery, a fuel cell does not run down or requires recharging. It will produce energy in the form of electricity and heat as long as fuel is supplied. While a battery must be replaced (disposed of) or recharged when its active materials are consumed.
- In a fuel cell, the active materials are supplied from an external source, while the active materials are stored inside the battery. In fact, a battery is an energy storage device, and
- The electrode materials of a fuel cell are inert (provide catalytic sites for the active materials to react) and are typically not consumed like the electrodes in a battery.

Fuel Cell vs. Heat Engine

The following points show the differences:-

- Because the intermediate steps of producing heat and mechanical work typical of most conventional power generation methods are avoided, fuel cells are not limited by thermodynamic limitations of heat engines such as the Carnot efficiency, and
- In addition, because combustion is avoided, fuel cells produce power with minimal pollution.

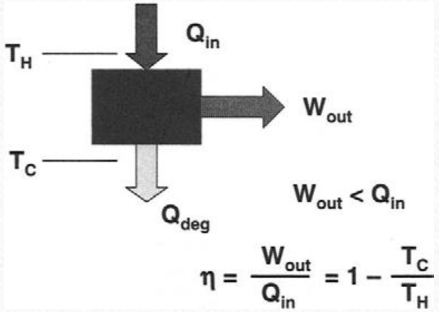
- Note: it is commonly expressed that a fuel cell is more efficient than a heat engine because it is not subject to Carnot Cycle limitations (second law of thermodynamics).
- Comment: this statement is misleading. A more suitable statement for understanding differences between the theoretical efficiencies of fuel cells and heat engines is that if a fuel cell is compared to an equivalent efficiency heat engine, the fuel cell is not limited by temperature as is the heat engine.

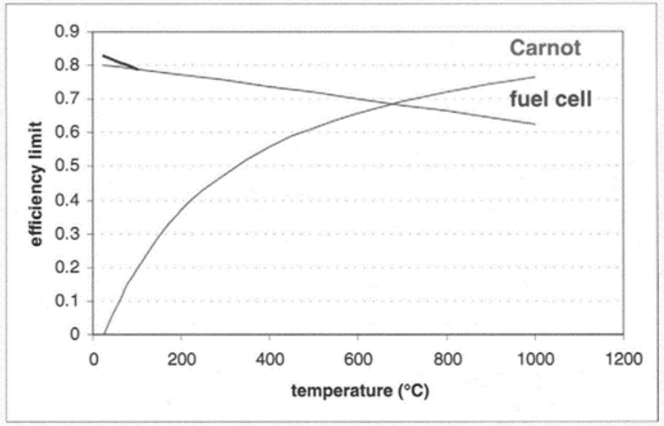
Fuel Cell vs. Heat Engine

Typically, a process of electricity generation from fuels involves several energy conversion steps, namely:

- ✓ combustion of fuel converts chemical energy of fuel into heat,
- ✓ this heat is then used to boil water and generate steam,
- ✓ steam is used to run a turbine in a process that converts thermal energy into mechanical energy, and finally
- ✓ mechanical energy is used to run a generator that generates electricity.

Carnot efficiency is the maximum efficiency that a heat engine may have operating between the two temperatures.





Theoretical Fuel Cell Efficiency

- ✓ The maximum electrical work (Wel) obtainable in a fuel cell operating at constant temperature and pressure is given by the change in Gibbs free energy (ΔG) of the electrochemical reaction:

  $$W_{el} = \Delta G = - n F E$$

  Where n is the number of electrons participating in the reaction, *F* is Faraday's constant (96,487 coulombs/g-mole electron), and E is the ideal potential of the cell.
- ✓ $\Delta G = \Delta H - T \Delta S$
- ✓ For general cell reaction

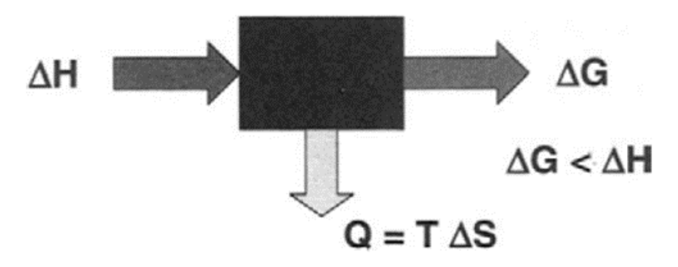
  $$aA + bB = cC + dD$$
- ✓ $\Delta G = \Delta G^o + (RT) \ln [C]^c [D]^d / [A]^a [B]^b$
- ✓ $E = E^o + (RT / nF) \ \ln [A]^a [B]^b / [C]^c [D]^d$

  Nernst equation

The thermal efficiency of an energy conversion device is defined as the amount of useful energy produced relative to the change in stored chemical energy (commonly referred to as thermal energy) that is released when a fuel is reacted with an oxidant.

$$\eta = \text{useful energy} / \Delta H$$

Or $\eta = \Delta G / \Delta H = 237.34 / 286.02 = 83\%$



Classification of Fuel Cells

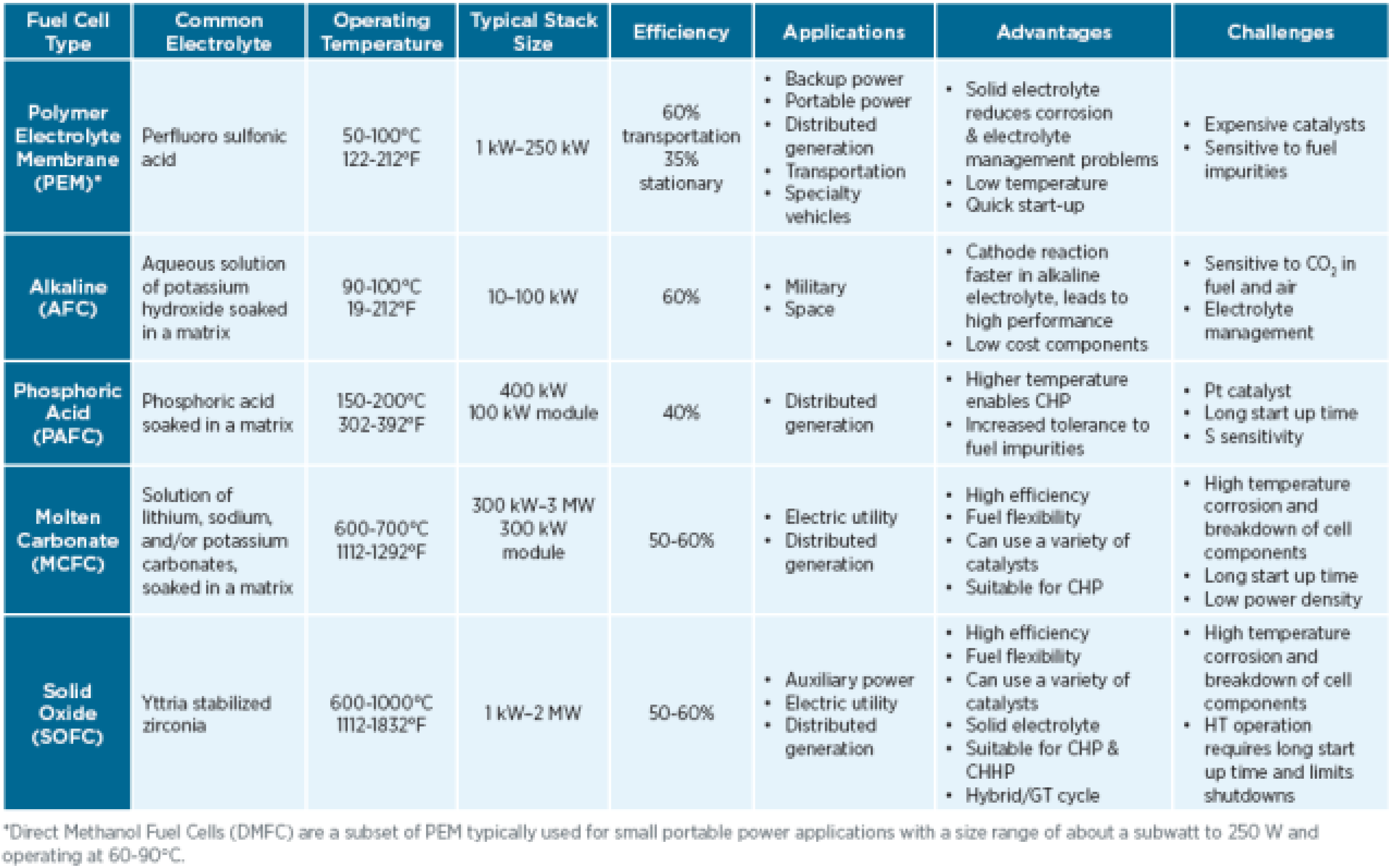
The most common classification of fuel cells is by the type of the electrolyte used in the fuel cell and includes:

Low Temperature Fuel Cells

- Fuel Cell Proton Exchange Membrane (PEFC), (40-80 ^{o}C).
- Alkaline Fuel Cell (AFC), (65-220 ^{o}C).
- Phosphoric Acid Fuel Cell (PAFC), (205 ^{o}C).

High Temperature Fuel Cells

- Molten Carbonate Fuel Cell (MCFC), (650 ^{o}C).
- Solid Oxide Fuel Cell (SOFC), (600-1000 ^{o}C).

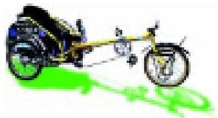


Fuel Cell Type	Common Electrolyte	Operating Temperature	Typical Stack Size	Efficiency	Applications	Advantages	Challenges
Polymer Electrolyte Membrane (PEM)*	Perfluoro sulfonic acid	50-100°C 122-212°F	1 kW–250 kW	60% transportation 35% stationary	• Backup power • Portable power • Distributed generation • Transportation • Specialty vehicles	• Solid electrolyte reduces corrosion & electrolyte management problems • Low temperature • Quick start-up	• Expensive catalysts • Sensitive to fuel impurities
Alkaline (AFC)	Aqueous solution of potassium hydroxide soaked in a matrix	90-100°C 19-212°F	10–100 kW	60%	• Military • Space	• Cathode reaction faster in alkaline electrolyte, leads to high performance • Low cost components	• Sensitive to CO_2 in fuel and air • Electrolyte management
Phosphoric Acid (PAFC)	Phosphoric acid soaked in a matrix	150-200°C 302-392°F	400 kW 100 kW module	40%	• Distributed generation	• Higher temperature enables CHP • Increased tolerance to fuel impurities	• Pt catalyst • Long start up time • S sensitivity
Molten Carbonate (MCFC)	Solution of lithium, sodium, and/or potassium carbonates, soaked in a matrix	600-700°C 1112-1292°F	300 kW–3 MW 300 kW module	50-60%	• Electric utility • Distributed generation	• High efficiency • Fuel flexibility • Can use a variety of catalysts • Suitable for CHP	• High temperature corrosion and breakdown of cell components • Long start up time • Low power density
Solid Oxide (SOFC)	Yttria stabilized zirconia	600-1000°C 1112-1832°F	1 kW–2 MW	50-60%	• Auxiliary power • Electric utility • Distributed generation	• High efficiency • Fuel flexibility • Can use a variety of catalysts • Solid electrolyte • Suitable for CHP & CHHP • Hybrid/GT cycle	• High temperature corrosion and breakdown of cell components • HT operation requires long start up time and limits shutdowns

*Direct Methanol Fuel Cells (DMFC) are a subset of PEM typically used for small portable power applications with a size range of about a subwatt to 250 W and operating at 60-90°C.

Pros – Cons (specific)

- PEMFC:



The first fuel cell powered bicycle to compete in the American Tour-de-Sol. (Courtesy [illegible])

+ Solid electrolyte → excellent resistance to gas crossover

+ working temperature ~80C → short startup time

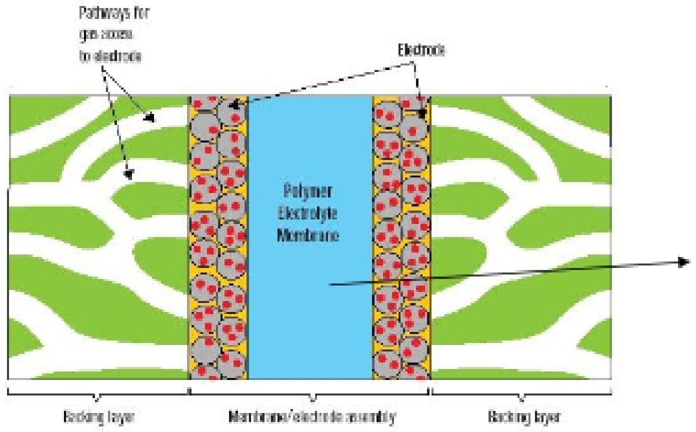
+ can work at high current densities compared to other cells

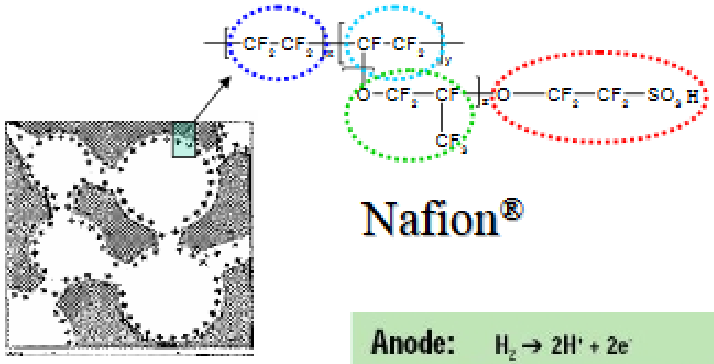
– Low CO tolerance (~ppm level)

– low temperature

– unefficient to use rejected heat for cogeneration of additional power

– difficult heat and water management limit the operating power densities





Nafion®

Anode: $H_2 \rightarrow 2H^+ + 2e^-$

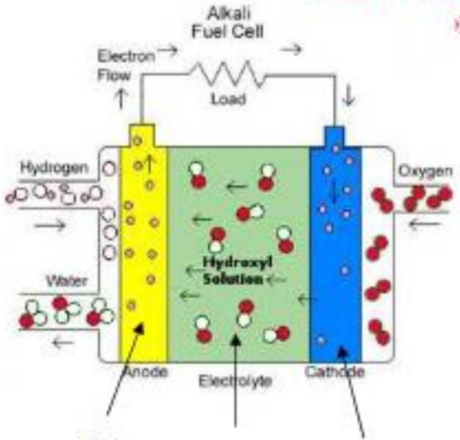
Cathode: $\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$

Cell: $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

Pros – Cons (specific)

- AFC:
  - + Excellent performance on H_2 and O_2 compared to other cells due to active O_2 electrode kinetics (70% efficiency)
  - + relatively low temperatures (~80C)
  - + wide range of possible electrocatalysts
  - – very clean fuel required, since small contaminations dissociate alkaline base,
  - – CO_2 poisoning
  - – significant pressure difference across the membrane is required
  - – large Pt quantity is needed
  - f harsh conditions

ISS



Pt

KOH
in matrix

Pt

Anode: $H_2 + 2(OH)^- \rightarrow 2H_2O + 2e^-$

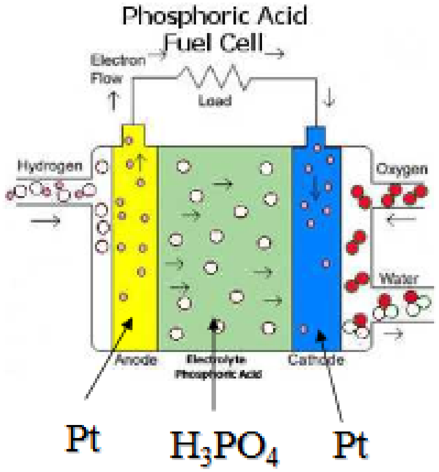
Cathode: $1/2\,O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$

Cell: $H_2 + 1/2\,O_2 \rightarrow H_2O$

Pros – Cons (specific)

- **PAFC:**
  - + CO_2 (of reformed fuel gas stream) resistent electrolyte
  - + low working temperatures (~200C)
  - + water boiling point is not limiting
  - + less complex fuel conversion (no membrane and attendent pressure drop)
  - – lower performance due to slow cathode reaction (37-42%)
  - – fuel from external hydrocarbon reformation
  - – high cost catalysts
  - – harsh conditions
  - – CO poisoning (water gas shift reaction required)

Timesquare



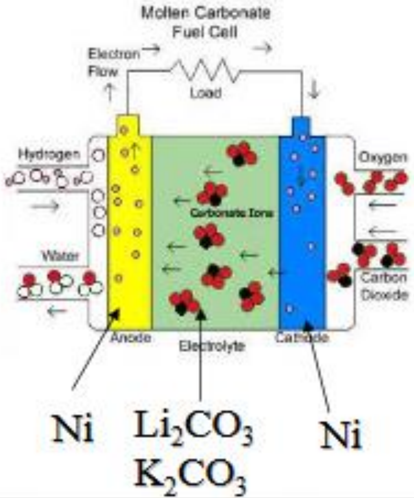
Anode: $H_2 \rightarrow 2H^+ + 2e^-$

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

Cell: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

Pros – Cons (specific)

- **MCFC** :
  - \+ higher temperatures (~650C) less sensitive reactions and less expensive materials
  - \+ Ni as catalyst
  - \+ reforming within the cell
  - \+ CO can directly be used as fuel
  - \+ heat exhaust can be used with external gas turbine (η~80%)
  - – very corrosive and mobile electrolyte
  - – source of CO_2 is required at cathode to form carbonate ions
  - – low sulfur tolerance
  - – high temperatures (~650C)
  - – stainless steel as cell hardware
  - – complex working procedure



Anode: $H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$

Cathode: $\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$

Cell: $H_2 + \frac{1}{2}O_2 + CO_2 \rightarrow H_2O + CO_2$

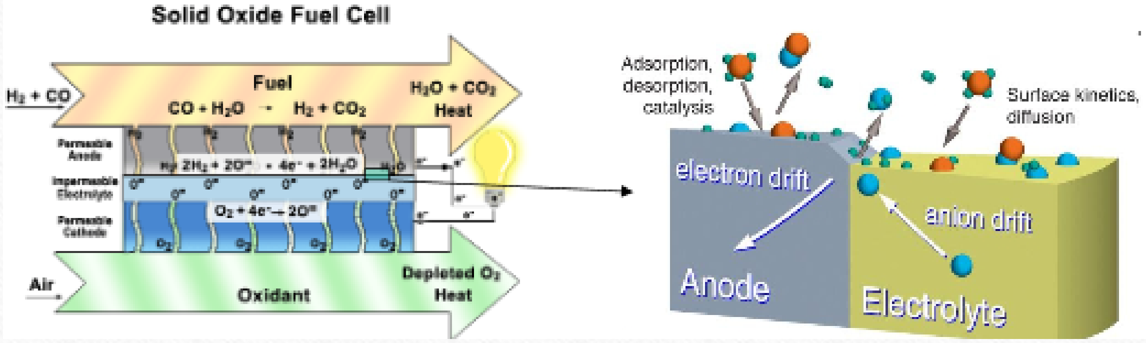
Pros – Cons (specific)

- SOFC

+ ceramic construction
  → no hardware corrosion
  → no gas crossover due to absence of liquid
+ fast kinetics
+ fast kinetics
+ CO is directly usable
+ no CO_2 is required at cathode (as in MCFC)
+ high temperature (~1000C)
  → fuel can be reformed within the cell

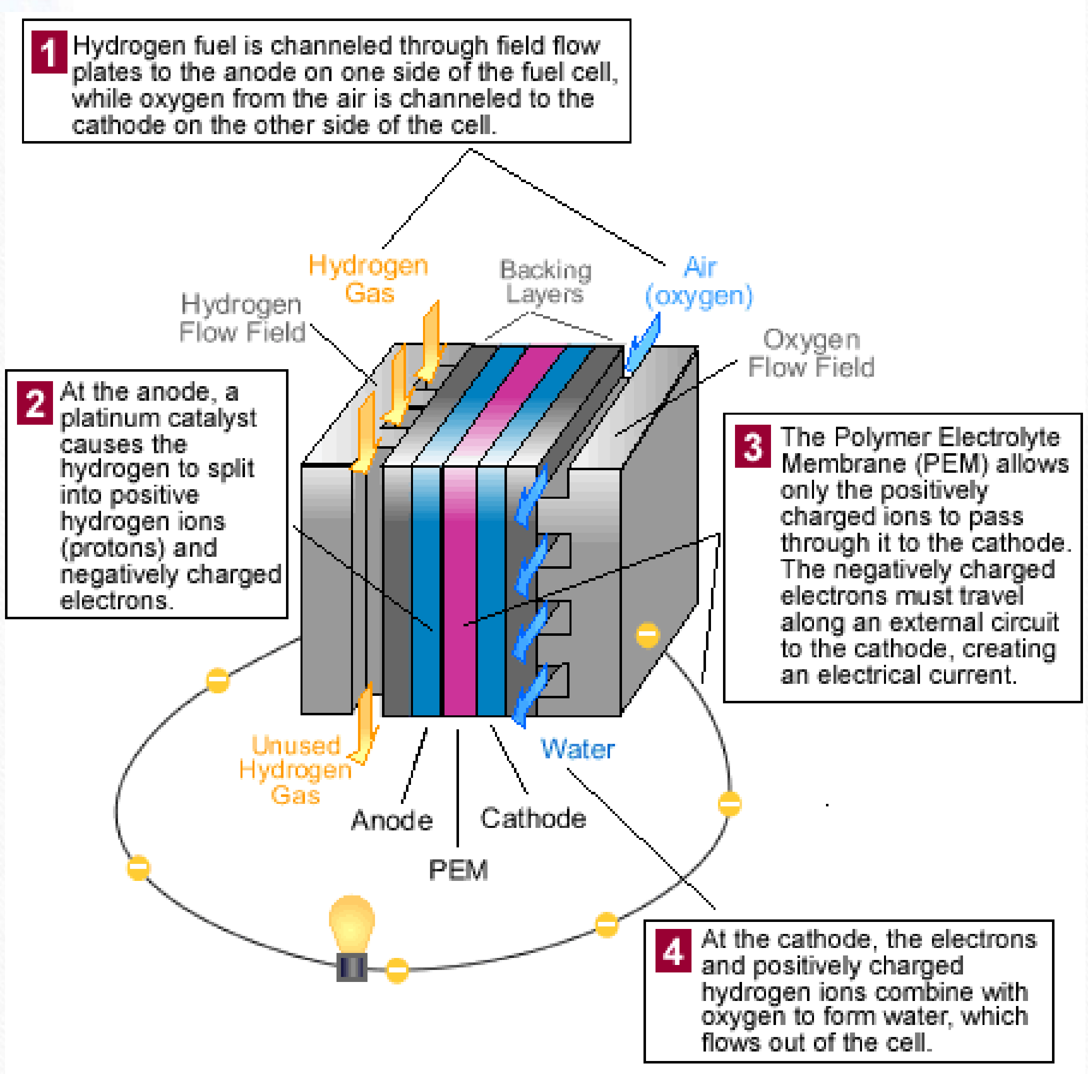
– incoming air has to preheated
– high temperature (~1000C)
  → thermal expansion mismatch
  → sealing between cells is difficult
– constraints on material collection
– difficult fabricate process
– high electrical resistivity in the electrolyte → low performance
– high cost catalysts

Anode: $H_2 + O^{2-} \rightarrow H_2O + 2e^-$
Cathode: $\frac{1}{2} O_2 + 2e^- \rightarrow O^{2-}$
Cell: $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$



Anode: Ni
Cathode: $LaMnO_3$
Electrolyte: YSZ
$ZrO_2[Y_2O_3]$

How does a Fuel Cell work?

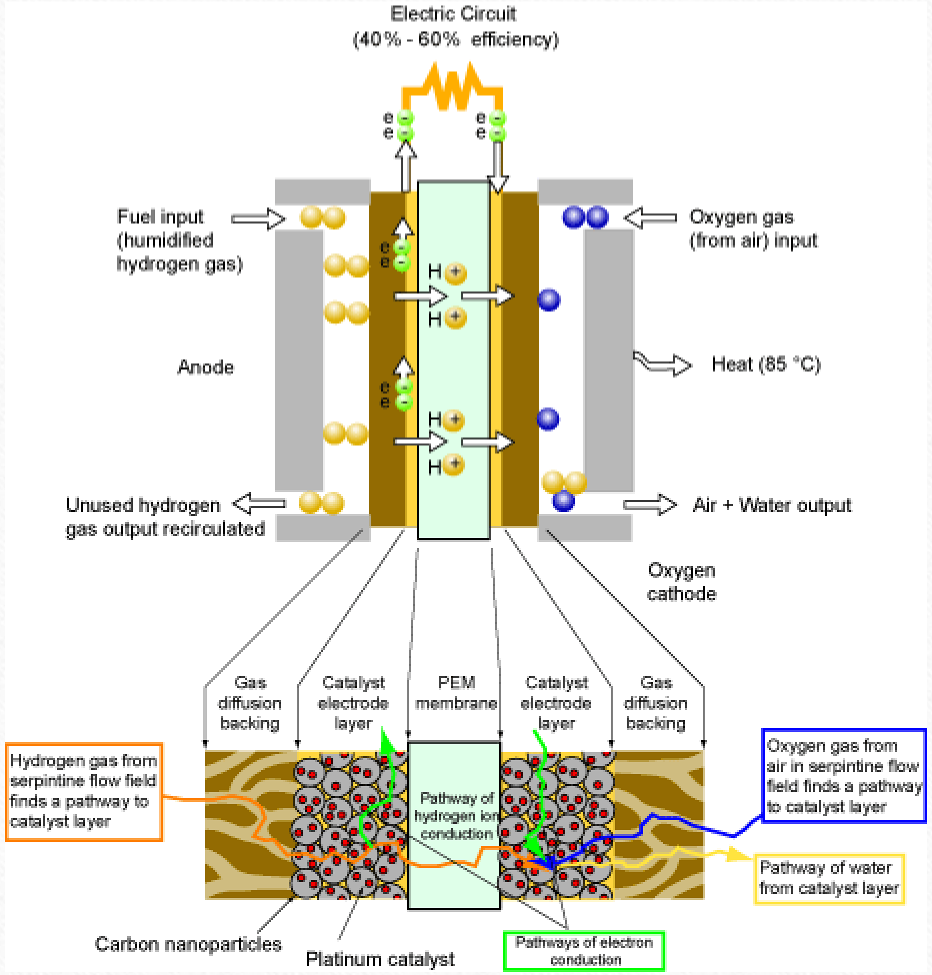


1 Hydrogen fuel is channeled through field flow plates to the anode on one side of the fuel cell, while oxygen from the air is channeled to the cathode on the other side of the cell.

2 At the anode, a platinum catalyst causes the hydrogen to split into positive hydrogen ions (protons) and negatively charged electrons.

3 The Polymer Electrolyte Membrane (PEM) allows only the positively charged ions to pass through it to the cathode. The negatively charged electrons must travel along an external circuit to the cathode, creating an electrical current.

4 At the cathode, the electrons and positively charged hydrogen ions combine with oxygen to form water, which flows out of the cell.



Why gaseous hydrogen has become the fuel of choice for most applications?

- In principles, Hydrogen has become the preferred choice for the most applications for the following reasons:-

✓ Its high reactivity when suitable catalysts are used.

✓ Its ability to be produced chemically from a wide range of fossil and renewable fuels, as well as via electrolysis, and

✓ Its high energy density when stored cryogenically for closed environment applications, such as in space.

- Similarly, the most common oxidant is gaseous oxygen, which is readily and economically available from air and again easily stored in a closed environment.

Why a fuel cell goes "Platinum"?

- In principles the half reactions occurring at each electrode can only occur at a high rate at the surface of the Pt catalyst. Platinum is unique because it is sufficiently reactive in bonding H and O intermediates as required to facilitate the electrode processes, and also capable of effectively releasing the intermediate to form the final product. For example, the anode process requires Pt sites to bond H atoms when the H_2 molecule reacts, and these Pt sites next release the H atoms, as $H^+ + e^-$

$$H_2 + 2Pt = 2\,Pt\text{-}H$$

$$2\,Pt - H = 2\,Pt + 2\,H^+ + 2e^-$$

- This requires optimized bonding to H atoms — not too weak and not too strong — and this is the unique feature of a good catalyst. However, one of the most obstacles that fuel cell commercialization facing is the high cost of Platinum, lowering Pt catalyst levels is an on-going effort.

Why a fuel cell goes "Platinum"? (Continued)

One of the best ways to accomplish this is to construct the catalyst layer with the highest possible surface area. Each electrode consists of porous carbon (C) to which very small Pt particles are bonded. The electrode is somewhat porous so that the gases can diffuse through each electrode to reach the catalyst. Both Pt and C conduct electrons well, so electrons are able to move freely through the electrode. The small size of the Pt particles, about 2 nano-meters in diameter, results in an enormously large total surface area of Pt that is accessible to gas molecules. The total surface presented by this huge number of small particles is very large even when the total mass of Pt used is small. This large Pt surface area allows the electrode reactions to proceed at many Pt surface sites simultaneously. This high dispersion of the catalyst is one key to generating significant electron flow, i.e. current, in a fuel cell.

Fuel Cell Applications

Potential Port & Maritime Fuel Cell Applications

Small material handling

Large material handling

On/off site trucks

Portable, backup, and stationary generators

Shore power

Harbor craft propulsion

Ship auxiliary power (includes LNG-fueled ships)

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