

LOW-TEMPERATURE FUEL CELLS

1- PROTON EXCHANGE MEMBRANE FUEL CELLS (PEMFCs)

The PEMFCs were developed originally by General Electric in the 1960s for NASA's space explorations. Over the years, these fuel cells have been known under various names, such as:

- *proton exchange membrane*
- *ion exchange membrane*
- *solid polymer electrolyte*
- or simply, *polymer electrolyte*.

They use hydrogen as fuel, oxygen or air as oxidant, and a solid polymer membrane as electrolyte.

Design Characteristics

The core of the PEMFC design consists of a proton conducting membrane (the electrolyte), located between two platinum-impregnated porous electrodes. Teflon gaskets and current collectors are added to these components to complete a single fuel cell unit. The core of the fuel cell is usually less than a millimeter thick and is referred to as the **membrane-electrode assembly (MEA)**. Depending on the mode of fabrication, MEA can include either the membrane along with the catalyst layers only, or the whole ensemble of the previously mentioned components plus the carbon electrodes. **Figure 1** shows a schematic representation of the PEMFC manufactured by Ballard Power Systems.

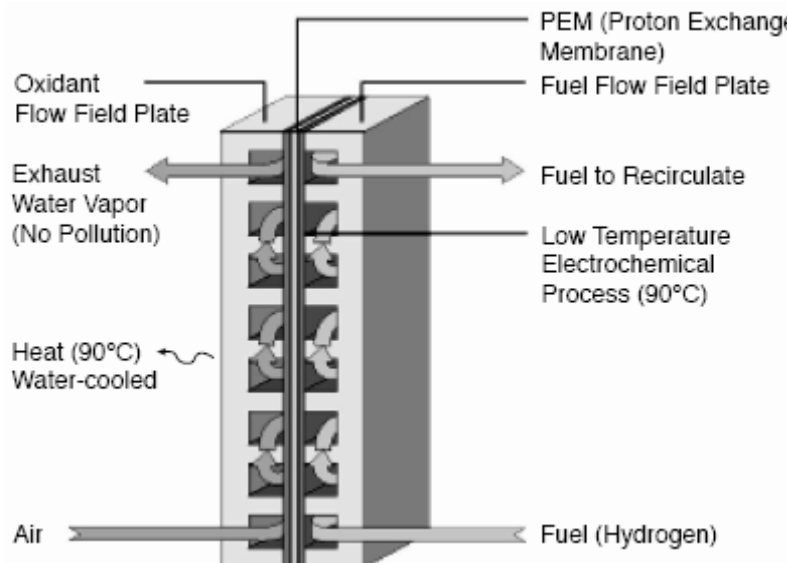


Figure 1: PEMFC, Ballard Power systems (From Ballard Power Systems, How the Ballard® fuel cell works).

A general view of the cell hardware and its cross section are presented in **Figure 2**.

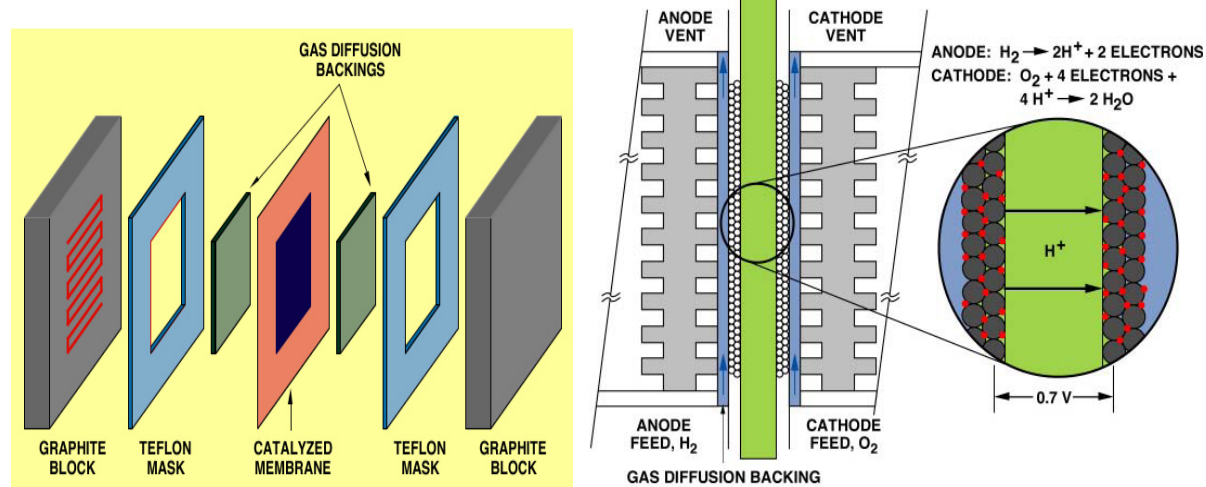


Figure 2: PEMFC design.

Electrolyte (membrane)

Various electrolyte materials have been developed over the years for use in PEMFC, and there is still extensive ongoing research focused on improving the materials currently used or finding new solutions. Currently, the thickness of the membrane is approximately 50–175 μm , and recent developments show that stable operation conditions can be obtained with membranes only 10–25 μm thick.

Most of the membranes used to date in PEMFC have a fluorocarbon-polymerbased structure to which sulfonic acid groups are attached. The key characteristic of these materials is that, although the acid molecules are fixed to the polymer, the protons on these acid groups are free to travel through the membrane. The most well known are the Nafion[®] membranes, which have been developed by DuPont over more than three decades. These types of membranes are thin, nonreinforced films based on the Nafion[®] resin, a perfluorinated polymer. The structure of the Nafion membranes is given in **Figure 3**.

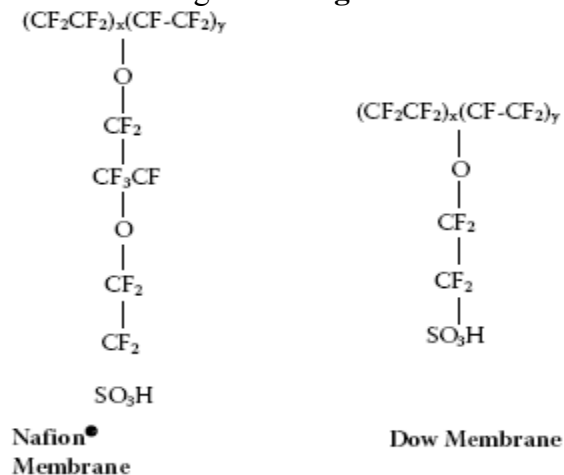


Figure 3: Structural characteristics of PEMFC membranes.



This type of membrane is usually prepared by modifying a basic polymer (polyethylene) through a process called *perfluorination*, where the hydrogen is substituted with fluorine. The modified polymer is the polytetrafluoroethylene (PTFE) or Teflon. A side chain of sulphonic acid HSO_3 is then added to PTFE through the “sulphonation” process. The end of the chain is an SO_3^- ion, and the HSO_3 group is ionically bonded. The resulting structure combines strong hydrophobic properties of the fluorocarbon polymer backbone with strong hydrophilic properties of the terminal sulfonic acid function. It is an excellent proton conductor, durable (owing to strong bonds between the fluorine and carbon) and shows good chemical resistance.

Tests showed that the PEMFC performance levels improved with the membrane developed by Dow Chemical. Although this membrane remains a perfluorosulfonic acid membrane, its structure is characterized by a shorter side chain and thus a lower equivalent weight compared to Nafion®. Conductivity and hydrophilic properties are slightly enhanced, and durability is still maintained. The Dow membrane was tested in 1987–1988 at Ballard Power Systems, and the results showed significant increases in PEMFC performance levels (**Figure 4**).

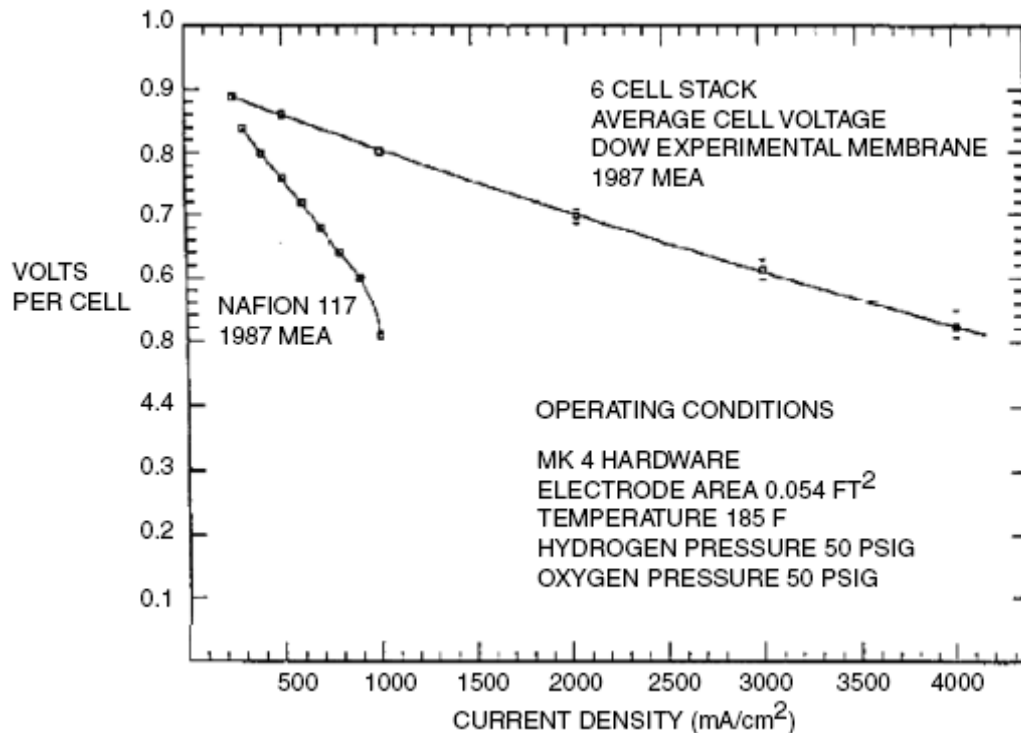


Figure 4: PEMFC performance using Nafion® and Dow membranes.

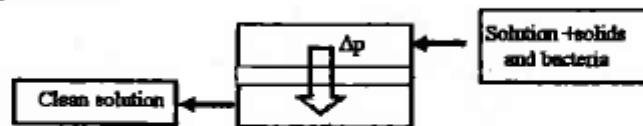
Ion exchange membranes

What is a membrane?

- Separator between two liquids
Thin liquid film or more often organic polymer, ceramic or other inorganic material
- Natural membranes; animals & plants
- Synthetic membranes: 50 years,
Chemical technology, biotechnology and environmental engineering
- Classified according to driving force
Pressure difference, Concentration difference and Potential difference

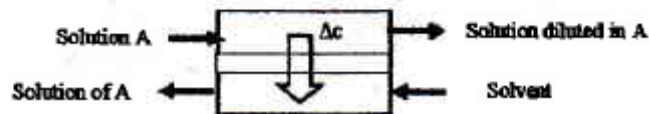
- ΔP

– Microfiltration, ultrafiltration, reverse osmosis, gas separation:



- Δc

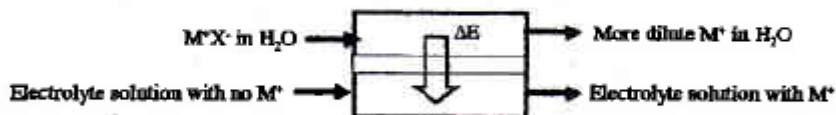
– Dialysis



and

- ΔE

– electrolysis, electro-dialysis, electrochemical process



Ideal separation:

High selectivity and fast rate

Ion selective membranes

- Designed to pass selectively either cations or anions:
Cationic allow positive ions
Anionic allow negative ions

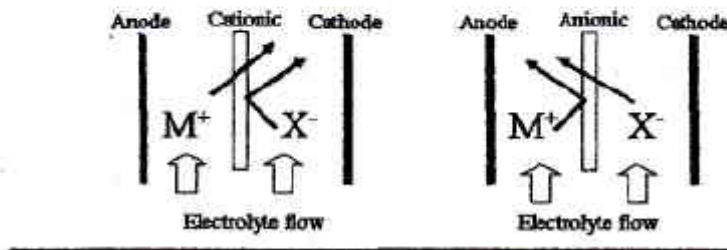
Cation membrane contains strongly acidic group $R-SO^{-3}$ with negatively electric field so that ions with positive charge can be attracted and pass through the membrane. Anion membrane

contains strongly basic group $R-CH_2N^+(CH_3)_3$ with positive electric field so that ions with negative charge can be attracted and pass through the membrane.

- Manufactured from organic polymers
 - a) Styrene/divinylbenzene, high degree of cross linking
 - b) Copolymers of perfluorinated alkene; linear polymers

Ion selective membranes

- Mass transport occurs mainly by migration due ΔE
- Diffusion if Δc is large
- Rate of migration (ionic flux) depends on magnitude of ΔE and properties of ionic polymer: $\text{mol m}^2 \text{ s}^{-1}$



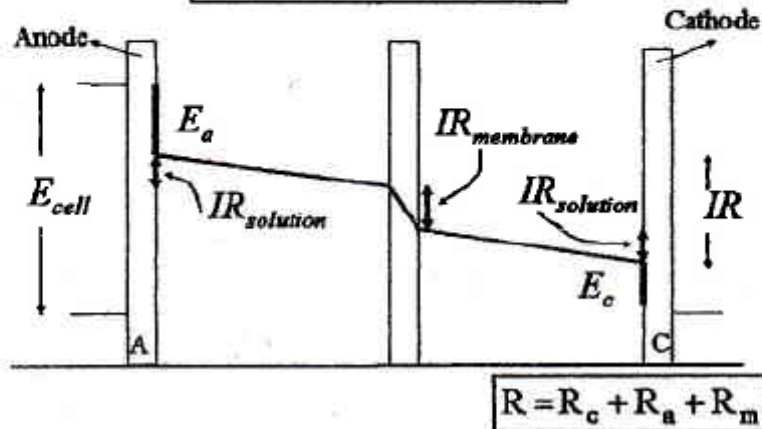
Flux and electrical charge

- Electrical charge transported by the ions through the membrane
- Transport rates: $\frac{\text{mol}}{\text{cm}^2 \text{ s}^{-1}}$
- Electrical flux:
 - Flux in the electrode = $\frac{I}{z_1 F A} = \frac{j}{z_1 F A}$ considering $\Delta E = RI$
 - or:
$$\text{Flux}_1 = \frac{\Delta E}{z_1 F R_A}$$

- ΔE is the potential drop across the membrane
- R_A is the membrane area resistance $R_A = R_m A / \text{ohm cm}^2$

Cell Voltage Components vs. Distance

$$E_{\text{cell}} = E_c - E_a - IR$$



Area resistance

- R_A related to ionic conductivity κ , of the membrane polymer, and its thickness L :

$$R_A = \frac{L}{\kappa}$$

- Transport number: fraction of the total charge carried through the membrane by a particular ion:
 - In a completely cation selective membrane: $t_+ = 1$; $\sum t_- = 0$
 - Typical values are 0.8 to 0.9



Example

- What is the conductivity of an electrolyte solution if the resistance was $1000\ \Omega$ measured in a cell with parallel electrodes of 1 cm^2 separated by 1 cm ?

$$R_A = \frac{L}{\kappa}$$

$$\kappa = \frac{L}{R_A} = \frac{L}{R A} = \frac{0.01\text{ m}}{(1000\ \Omega)(0.0001\text{ m}^2)} = 0.1\ \Omega^{-1}\text{m}^{-1} = 0.1\ \text{Sm}^{-1}$$

Characterisation of ion exchange membranes

- Water content:

$$C_w^m = (W_h - W_d) \rho_m / W_h M_w$$

C_w^m = concentration of water in the membrane,

W_h = weight wet membrane,

W_d = weight dry membrane,

ρ_m = the density of wet membrane

M_w = molar mass of water (18 g mol^{-1})

- Membrane porosity τ :

$$\tau = \Delta V / (1 + \Delta V)$$

$$\Delta V = (W_h - W_d) \rho_d / \rho_w W_d$$

ΔV = volume increase due to absorption of water per unit of dry membrane volume,

W_h = weight of wet membrane,

W_d = dry membrane weight,

ρ_d = density of dry membrane,

ρ_w = density of water,



Membrane ion exchange capacities

- Back titration, equilibrated (6 h) 1 mol L⁻¹ NaOH or HCl
 - -SO₃⁻ with 0.1 mol L⁻¹ NaOH,
 - -R₄N⁺ with 0.1 mol L⁻¹ HCl,

$$E_c = ab / w$$

- E_c = ion exchange capacity,
 - a = burette reading of acid, base or AgCl, dm⁻³
 - b = concentration of acid base or AgCl, mol dm⁻³
 - w = weight of the dry membrane
-

Permselectivity

- Measures how easy the counter ion migration occurs through the ion exchange membrane

$$P_s = (t_i^m - t_i) / (1 - t_i)$$

- P_s = permselectivity,
 - t_i^m = transport number of the counter ion in the membrane
 - t_i = transport number of the counter ion in solution
-



Porous Backing Layer

The polymer membrane is sandwiched between two sheets of porous backing media (also referred to as gas diffusion layers (**GDL**) or current collectors). The functions of the backing layer are to:

- 1- act as a gas diffuser
- 2- provide mechanical support
- 3- provide an electrical pathway for electrons
- 4- channel product water away from the electrodes.

The backing layer is typically carbon-based, and may be in cloth form, a non-woven pressed carbon fiber configuration, or simply a felt-like material. The layer incorporates a hydrophobic material, such as polytetrafluoroethylene. The function of polytetrafluoroethylene is to prevent water from “pooling” within the pore volume of the backing layer so that gases freely contact the catalyst sites. Furthermore, it facilitates product water removal on the cathode as it creates a non-wetting surface within the passages of the backing material.

Product water is removed by two mechanisms:

- 1- transport of liquid water through the porous bipolar plate into the coolant
- 2- evaporation into the reactant gas streams.

The cell is similar in basic design to other PEFCs with membrane, catalysts, substrates, and bipolar plate components. However, there is a difference in construction and composition of the bipolar plate: it is made of porous graphite. During operation, the pores are filled with liquid water that communicates directly with the coolant stream. Product water flows from the cathode through the pores into the coolant stream (a small pressure gradient between reactant and the coolant stream is needed). The water in the coolant stream is then routed to a reservoir. Removal of water by the porous membrane results in the reactant flow stream being free of any obstructions (liquid water). The flooded pores serve a second purpose of supplying water to the incoming reactant gases and humidifying those gases. This prevents drying of the membrane, a common failure mode, particularly at the anode. Control of the amount of area used to humidify the inlet gases has eliminated the need to pre-humidify the reactant gases.

Reasons for removing the water through the porous plate are:

- 1- there is less water in the spent reactant streams
- 2- this approach reduces parasitic power needs of the oxidant exhaust condenser
- 3- the cell can operate at high utilizations that further reduce water in the reactant streams
- 4- higher temperatures can be used with higher utilizations so that the radiator can be smaller
- 5- the control system is simplified.

In fact, in-stack water conservation is even more important in arid climates, where there may exist a significant challenge to achieve water balance at the system level without supplying water or refrigerating the exhaust stream.

Hand-in-hand with water management goes the thermal management of the stack. Temperatures within the stack must be kept within a narrow range in order to avoid local dehydration and hotspots as well as local dead zones. This is particularly challenging when one recognizes the narrow temperature zone and the relatively small temperature difference between the cell operating temperature and the ambient temperature.



Electrode-Catalyst Layer

In intimate contact with the membrane and the backing layer is the catalyst layer. This catalyst layer, integral with its binder, forms the electrode. The catalyst and binder electrode structure is applied either to the membrane or to the backing layer. In either case, the degree of intimacy of the catalyst particles and the membrane is critical for optimal proton mobility. The binder performs multiple functions. In one case, it “fixes” the catalyst particles within a layered structure, while a second function is to contribute to the overall architecture of the electrode. This architecture has a direct bearing on performance.

There are two schools of thought on the electrode composition, in particular, the binder. In the original hydrophobic, porous, gaseous electrodes developed by Union Carbide and later advanced by General Electric, the Dow Chemical Company, and others, the binder was polytetrafluoroethylene: a non-wetting component within the electrode itself. The second school of electrode science developed a hydrophillic electrode in which the binder was perfluorosulfonic acid. The driver for this development was to enhance the membrane/catalyst contact to minimize the platinum loading requirements. In most state-of-the-art PEFC membrane electrode assemblies (MEAs), the catalyst is largely embedded in a solution of electrolyte monomer, which provides high solubility for protons as well as oxygen, and thus effective use of the platinum catalyst surface.

The catalyst is platinum-based for both the anode and cathode. To promote hydrogen oxidation, the anode uses either pure platinum metal catalyst or, as is common in most modern PEFC catalysts, a supported platinum catalyst, typically on carbon or graphite for pure hydrogen feed streams. For other fuels, such as reformat (containing H_2 , CO_2 , CO , and N_2), the desired catalyst is an alloy of platinum containing ruthenium. Oxygen reduction at the cathode may use either the platinum metal or the supported catalyst.

Because of the expense of the platinum catalyst, there have been numerous efforts to minimize the use of platinum in the catalyst layer. The platinum particle size has been extensively optimized, and general agreement is that a ~ 3.5 nm particle size on suitable carbon support is close to optimal: the activity per unit mass of platinum is near optimal under these conditions. In parallel, there have been numerous efforts to substitute other materials for platinum. Most of these attempts focused either on gold or on platinum alloys (usually with transition metals). So far, these efforts have not demonstrated a decisive cost advantage over pure platinum catalysts.

Typically, electrodes can be cast as thin films and transferred to the membrane or applied directly to the membrane. Alternatively, the catalyst-electrode layer may be deposited onto the gas diffusion layer (GDL), then bonded to the membrane. Low platinum loading electrodes (≤ 1.0 mg Pt/cm² total on the anode and the cathode) are regularly used, and have performed as well as earlier, higher platinum loading electrodes (2.0 to 4.0 mg Pt/cm²).

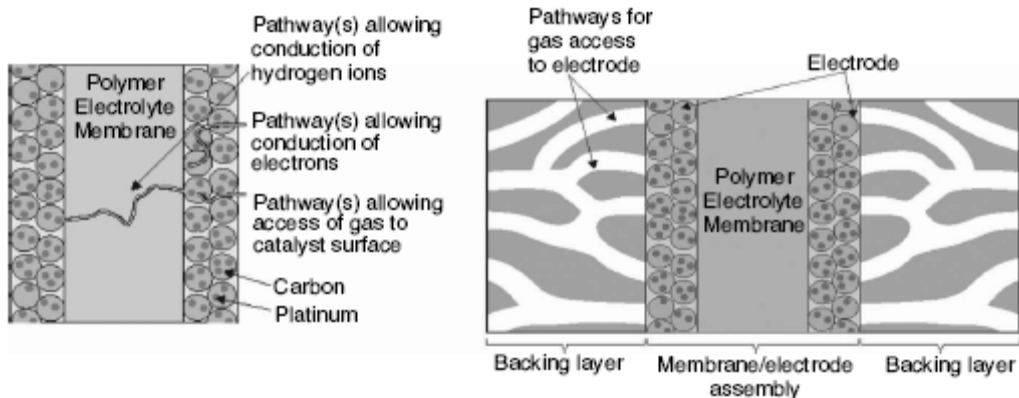
Electrodes

The anode and cathode have an identical structure, consisting of two layers in close contact with each other and with the membrane. The roles of the electrodes in operation of the fuel cell are summarized in **Table 1**.

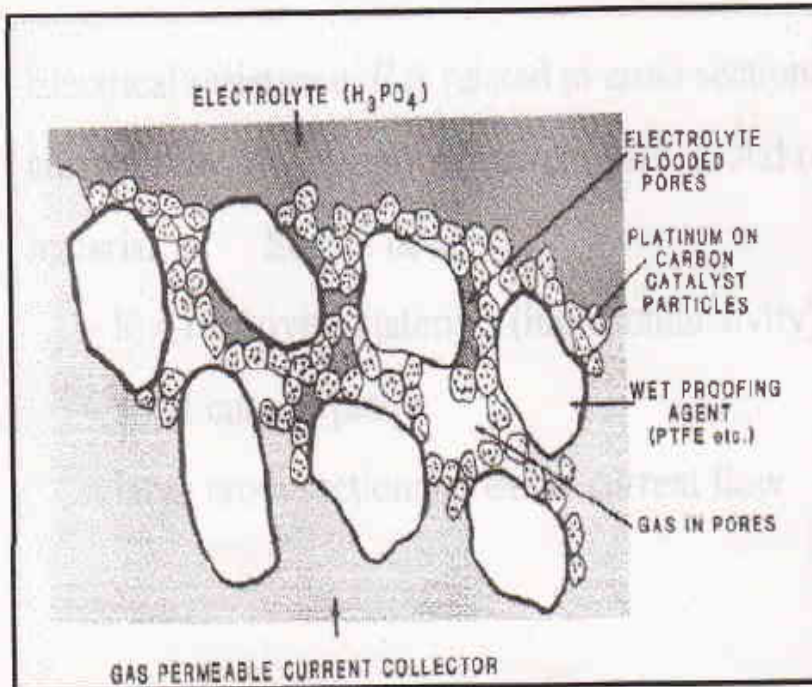
Table 1: Roles of Electrodes in PEMFC Operation

Electrode	Layer	Role
Anode	Catalyst	Catalysis of anode reaction Proton conduction into membrane Electron conduction into gas-diffusion layer Water transport Heat transport
	Gas diffusion	Fuel supply and distribution (hydrogen/fuel gas) Electron conduction Heat removal from reaction zone Water supply (vapor) into electrocatalyst
Cathode	Catalyst	Catalysis of cathode reaction Oxygen transport to reaction sites Proton conduction from membrane to reaction sites Electron conduction from gas-diffusion layer to reaction zone Water removal from reactive zone into gas-diffusion layer Heat generation/removal
	Gas diffusion	Oxidant supply and distribution (air/oxygen) Electron conduction towards reaction zone Heat removal Water transport (liquid/vapor)

The layer situated adjacent to the membrane is the ***catalyst layer***, which provides the area where the electrochemical reactions occur (**Figure 2**). It is a platinum carbon composite film, about 5–10 μm thick, used to increase the reaction rates. Because of the high cost of platinum, sustained technological efforts were focused on reduction of the platinum load, originally about 4 mg Pt/cm^2 , but currently almost 0.2 mg Pt/cm^2 and even lower values, with high performance levels. Typically, carbon paper is used when a compact design of fuel cells is desired; the most used brand is Toray[®] paper. However, if only a simple assembly is preferred, carbon cloth is sufficient. Thickness of the backing layer is typically between 100 and 300 μm . **Figure 5** shows details of the MEA structure with the catalyst and backing layers.


Figure 5: MEA structure design details.

Gas Diffusion Electrode Structure (Gas/C/Pt/PTFE/electrolyte)



TEM of
nanoparticles of Pt/C

Transmission
electron
micrograph



Important Properties of Electrode Materials

- **Moderate costs**
 - e.g, Low loadings ($0.02\text{-}0.4\text{ mg cm}^{-2}$) of Pt catalyst
- **Mechanical, thermal and chemical stability**
 - Adequate lifetime (several years?) and minimal degradation.
- **Effective electrocatalysts**
 - Low overpotential for the desired reaction
 - Selective for the desired reaction
 - Freedom from poisoning (e.g., by adsorbed CO)
- **High electrical and thermal conductivity**
 - Good current distribution, low ohmic losses, good heat transfer.

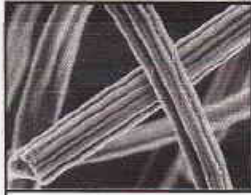
Resistivity of Selected Electrode Materials

Electrical resistance, R is related to cross sectional area for current flow, A_{xs} , length of current path, L and resistivity of material, ρ : So, we need:

- low resistivity materials (high conductivity)
- short current path
- large cross sectional area for current flow

$$R = \frac{\rho \cdot L}{A_{xs}}$$

Copper	1.56 $\mu\text{ohm cm}$	Busbars/feeders
Aluminium	2.45 $\mu\text{ohm cm}$	Busbars/feeders
Nickel	6.10 $\mu\text{ohm cm}$	Electrodes
Platinum	9.80 $\mu\text{ohm cm}$	Electrode coatings
Titanium	43.1 $\mu\text{ohm cm}$	Electrodes
Carbon	600-800 $\mu\text{ohm cm}$	(Bipolar) Electrodes



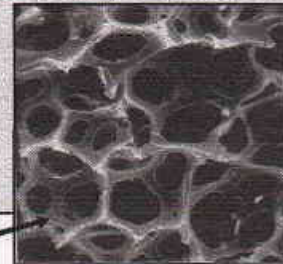
Features of Porous, 3-Dimensional Electrodes

- High surface area (and mass transport)
 - $10\text{-}500\text{ cm}^2\text{ cm}^{-3}$
- Controlled porosity
 - $5\text{-}98\%$ volume
- Mediocre conductivity
 - *can give rise to poor current-distribution*
- Difficulty in making connections
 - *especially in monopolar cells*

felts



foams



Special Problems with Electrodes

Chemical stability:

corrosion, passivation, hydride formation...

Mechanical stability

high stresses, poor adhesion of coatings

Poisoning

irreversible adsorption and film formation

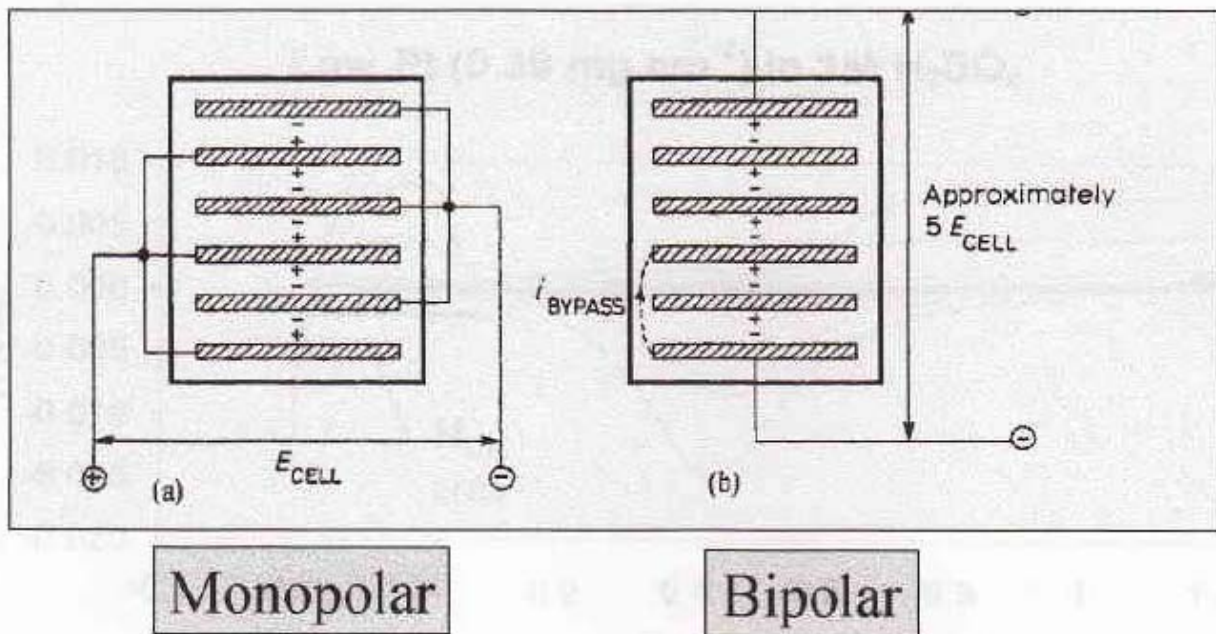
Time-dependent performance

all of the above!

Teflon Masks and Current Collectors

The single-cell structure is completed by two Teflon masks and two high-density graphite plates. The Teflon masks are gaskets that confine the gas flow to the active area, providing an effective seal along the periphery of the membrane. The graphite plates are current collectors, and they also contain gas flow fields at the same time. In a fuel cell stack, the current collector plates contain gas flow fields on both sides, and they become *bipolar plates*.

Monopolar and Bipolar Electrical Connections



Operation Characteristics

Hydrogen gas is supplied to the anode, where it dissociates into hydrogen atoms in the presence of the platinum catalyst. The atoms further split into protons and electrons, which travel separate ways from the anode to the cathode. Protons are conducted through the electrolyte membrane, and electrons are forced to go via an external circuit to the cathode, producing electricity. Oxygen is supplied to the cathode, where a reduction process occurs and water and heat are created as byproducts. **Figure 6** shows an illustration of the PEMFC principle of operation.

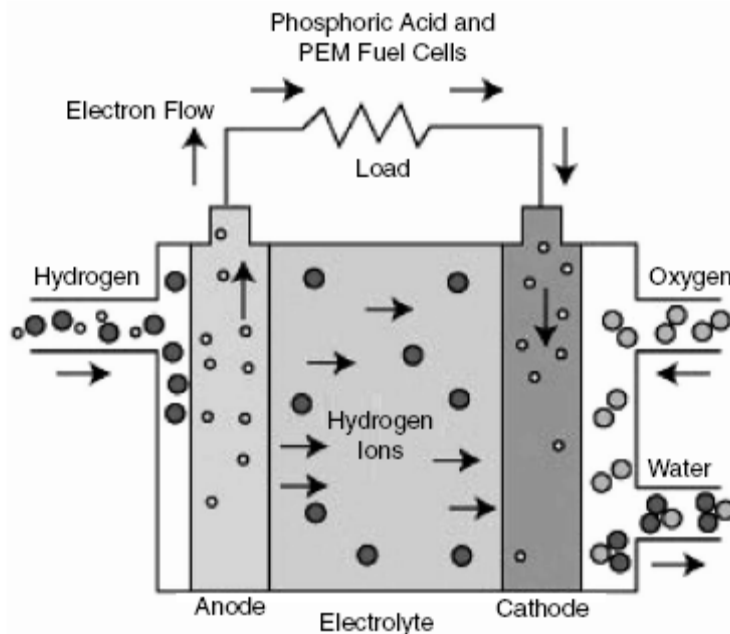
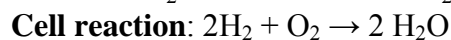
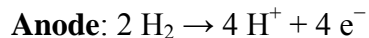


Figure 6: PEMFC and PAFC operation principle.

The basic reactions for the PEMFC are:



Continuous research efforts over the years have led to significant improvements in the performance levels of the PEMFC (**Figure 7**).

The typical output is approximately 0.7 V per cell unit, and the power density is usually higher compared to other fuel cells, which translates into a smaller size of the fuel cell stack. For transport applications, Asia Pacific Fuel Technologies produces 3-kW 64-cell stacks, which are 25 cm high and have an active area of 150 cm². The Mark 902 fuel cell module produced by Ballard Power Systems has the dimensions of 80.5 × 7.5 × 25.0 cm and yields an 85-kW rated net output. The NexaTM power module, Ballard's first volume-produced PEMFC designed to be integrated into stationary and portable applications, is 56 × 25 × 33 cm, with a rated net output of 1200 W.

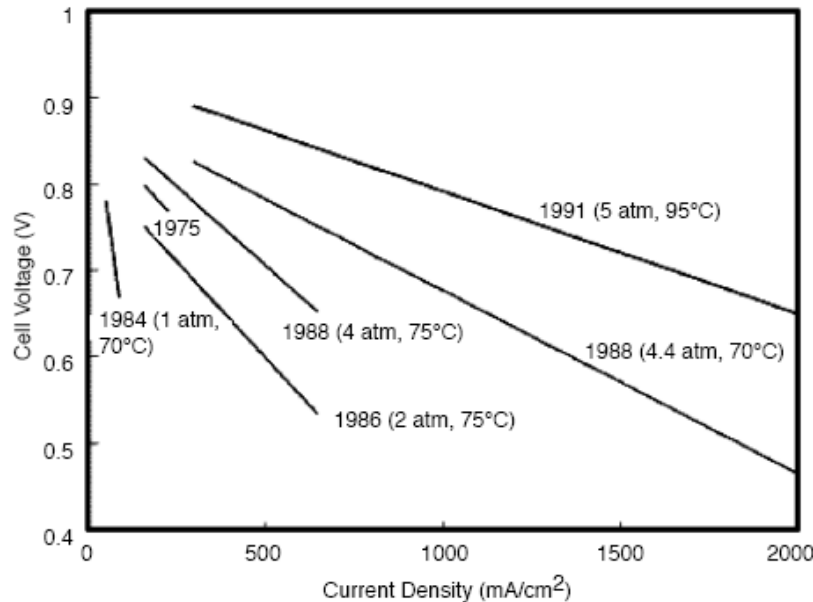


Figure 7: PEMFC performances.

The low operating temperature of a PEFC has both advantages and disadvantages. Low temperature operation is advantageous because the cell can start from ambient conditions quickly, especially when pure hydrogen fuel is available. It is a disadvantage in carbon monoxide-containing fuel streams, because carbon will attack the platinum catalyst sites, masking the catalytic activity and reducing cell performance. The effect is reversible by flowing a CO-free gas over the electrode. To minimize CO poisoning, operating temperatures must be greater than 120 °C, at which point there is a reduction in chemisorption and electrooxidation.

Due to CO affecting the anode, only a few ppm of CO can be tolerated at 80 °C.

Because reformed and shifted hydrocarbons contain about one percent CO, a mechanism to eliminate CO in the fuel gas is needed. This can be accomplished with preferential oxidation (PROX) that selectively oxidizes CO over H₂ using a precious metal catalyst. The low operating temperature also means that little, if any, heat is available from the fuel cell for endothermic reforming.

As this discussion suggests, there is a considerable advantage at the stack level to the use of pure hydrogen rather than reformat, but in most PEFC applications this must be traded off against the challenges in storing hydrogen and the limited availability of hydrogen. Although considerable effort has been expended to develop liquid-fueled PEFC for transportation applications, most believe that on-board storage of hydrogen will be necessary for practical vehicles.

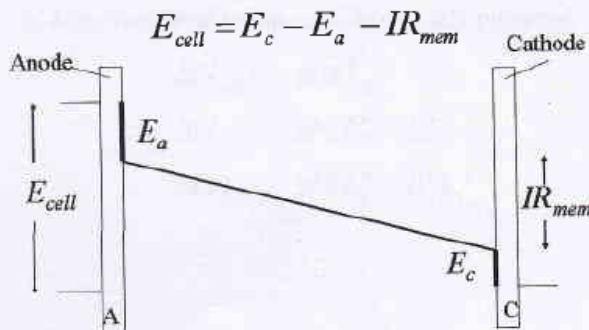
To overcome the challenges of operating on reformat, attempts have been made to develop so-called high-temperature PEFC, which would operate in the 120 °C to 160°C range. New or modified ion exchange membranes would be needed to allow this, because Nafion dehydrates rapidly at such temperatures unless high (greater than 10 bar) pressures are applied. One candidate material is polybenzimidazole (PBI). The higher operating temperature eliminates CO poisoning by eliminating CO occlusion of the platinum sites. Also, this operating regime



provides higher quality heat for possible use in stationary combined heat/power (CHP) applications. Because PBI requires significantly lower water content to facilitate proton transport, an additional benefit is that water management is dramatically simplified. However, to achieve acceptable ionic conductivity, the membrane must be impregnated with phosphoric acid, which is apparently not very tightly bound to the polymer backbone. As a result, similar precautions are necessary as in a PAFC (avoiding liquid water, corrosion protection). The conductivity of PBI can approach the target of 10 S/cm set for high temperature membranes.

Other approaches to high-temperature membranes are based on the modification of Nafion. Reports indicate that some of the modified materials achieve conductivities close to that of Nafion 112, while allowing operation up to 120 °C at low hydration levels. Both temperature and pressure significantly influence cell performance. Present cells operate at 80 °C over a range of 0.0010 to 1.0 MPa (~0.1 to 150 psig). Nominally, 0.285 MPa (25 psig) is used for some transportation applications although some developers pursue ambient pressure technology. Using appropriate current collectors and supporting structure, polymer electrolyte fuel cells and electrolysis cells should be capable of operating at pressures up to 3000 psi and differential pressures up to 500 psi.

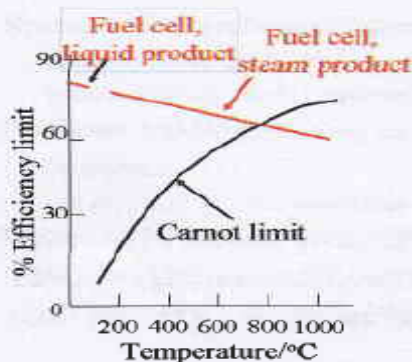
Cell Voltage Components vs. Distance through Cell: PEM Cell



Sources of Energy Loss in a PEM Cell (must be reduced)

- Charge transfer overpotential, η_{ct}
- Mass transport overpotential, η_{mt}
- Ohmic drop, IR
- Utilisation of gases (engineering)
- Fuel cross over ($H_{2(anode)} + O_{2(cathode)} = H_2O$)
- Internal leakage (or shunt or bypass) currents

Energy Efficiency vs. Temperature for H_2/O_2 Cells

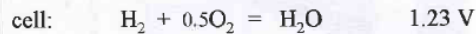
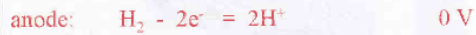
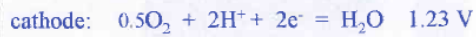


- This is a **thermodynamic treatment only**.
- Kinetics leads to a trend of increasing cell voltage at higher temperature.
- Waste heat is more easily extracted from high temperature cells.
- Heat engines can have a higher efficiency than fuel cells, at high T.



Standard Cell Potential for Self-Driving (Spontaneous) Reactions

Water formation (*galvanic cell*) E^0 vs. SHE



Spontaneous combustion
reaction

$$\Delta G_{\text{cell}} = -ve$$

Gibbs Free Energy Change and Cell Potential

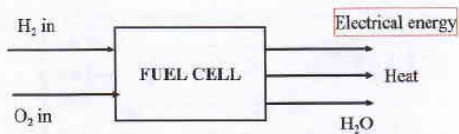
The Gibbs free energy change for the cell reaction is directly related to the equilibrium cell potential

$$\Delta G_{\text{cell}} = -zFE_{\text{cell}}^e$$

$$\Delta G_{\text{cell}} = -zF(E_R^e - E_L^e)$$

$$\Delta G_{\text{cell}} = -zF(E_c^e - E_a^e)$$

Energy Balance over a Fuel Cell



(Mass balance, heat balance and momentum balance)

Energy Efficiency

The maximum thermodynamic efficiency (%):

$$= 100 \left(\frac{\Delta G_{\text{cell}}}{\Delta H_{\text{cell}}} \right)$$

$$= 100 \left(\frac{-zFE_{\text{cell}}}{\Delta H_{\text{cell}}} \right)$$

Important Engineering Aspects of PEM Cells

- **MEA materials**
 - *structure and composition (previously considered)*
- **Water management**
 - *manifolding and temperature profiles*
- **The method of cooling**
 - *flow direction and path*
- **The strategy for electrical connections**
 - *bipolar plates normally preferred*
- **Operating conditions**
 - *temperature, pressure, etc.*
- **Composition of reactants**
 - *pure hydrogen?; oxygen or air, etc.*

Water Management in PEM Cells

- Membrane needs sufficient water for conductivity.
- But too much water floods MEA pores.
- A careful balance is needed!
- An ideal strategy (is difficult to achieve)
 - water formed at the cathode
 - oxygen blown over it dries out excess water
 - water back diffuses through to the anode
 - system operates at constant hydration

Electrochemical Engineering Laboratory

EC
a

Water Movements in a PEM Cell

- Water movement is complex
- H^+ ions carry water via membrane
- Water moves from anode to cathode
- 1-3 mol H_2O per mol of H^+
- Tends to dry out the anode side
- High temp. (>50 C) dehydrates
- Need to humidify air and hydrogen gas streams
- Water profile must be correct over entire stack

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Water Control in a PEM Cell

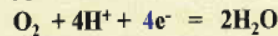
- Electrochemical water production at anode
 - proportional to current
- Electroosmotic drag of water
 - proportional to current
- Water evaporation
 - predict by relative humidity calculations
- Back diffusion of water from cathode to anode
 - depend on membrane thickness and RH each side
- External humidification of the cell
 - is usually controlled via the air feed

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Oxygen Feed Rate in a PEM Cell

Oxygen reduction :



From Faraday's Laws, the molar rate of O_2 use is:

$$\frac{dn}{dt} = \frac{N \cdot I}{4F} \quad [mol \cdot s^{-1}]$$

no. of the
electrons

N = number of cells in the stack
 I = current
 n = amount
 t = time

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Oxygen Feed Rate in a PEM Cell

If each cell operates at the same potential, E_{cell}
And current, I , the power output of the stack is:

$$P = N \cdot E_{cell} \cdot I \quad [W]$$

$$\frac{dn}{dt} = \frac{P}{4F \cdot E_{cell}} \quad [mol \cdot s^{-1}]$$

If pure oxygen is fed to the cell, then the mass
flow rate of oxygen is:

$$\frac{dw_{O_2}}{dt} = \frac{M_{O_2} \cdot P}{4F \cdot E_{cell}} \quad [kg \cdot s^{-1}]$$

$$M_{O_2} = \text{molar mass of oxygen} = 0.032 \text{ kg mol}^{-1}$$



If air is used, rather than pure oxygen, then the molar proportion of air to oxygen is 0.21.

The mass air feed rate becomes

$$\frac{dw_{air}}{dt} = \frac{M_{air} \cdot P}{(0.21)(4)E_{cell} \cdot F} \quad [\text{kg s}^{-1}]$$

In practice, the air feed needs to be more than the stoichiometric mass of O_2 to avoid depletion.

If the stoichiometric coefficient is λ , air feed rate:

$$\frac{dw_{air}}{dt} = \frac{\lambda \cdot M_{air} \cdot P}{(0.21)(4)E_{cell} \cdot F} \quad [\text{kg s}^{-1}]$$

E.g., if $\lambda = 2$, $M_{air} = 0.0290 \text{ kg mol}^{-1}$, $P = 1 \text{ W cm}^{-2}$, $E_{cell} = 0.65 \text{ V}$, $F = 96485 \text{ C mol}^{-1}$, and air feed rate:

$$\frac{dw}{dt} \approx 1.1 \times 10^{-6} \text{ kg s}^{-1} \approx 4.0 \times 10^{-3} \text{ kg h}^{-1} \approx 12.1 \text{ m}^3 \text{ h}^{-1}$$

Reaction Engineering Aspects

- **Large positive cell voltage**
 - low polarisation - good electrocatalysts
 - low ohmic drops - in MEAs and rest of cell
- **Uniform reaction rate across cell stack**
 - bipolar mode of electrical connection
 - uniform membrane and electrode conductivity
 - conductive current collectors
- **Good heat transfer**
 - effective water removal
 - conductive flow field plates

Important Figures of Merit for (Ptbased) Fuel Cell Electrodes

- Specific electrochemical area, ECA ($>5 \times 10^6 \text{ cm}^2 \text{ g}^{-1}$) (usually based on hydrogen adsorption from a cv in H_2SO_4 where $210 \mu\text{C cm}^{-2}$ is equivalent to 1 cm^2).
- Platinum loading ($<0.1 \text{ mg cm}^{-2}$)
- Utilization (>0.1) (the fraction of area available to the reaction).
- Effective Pt surface area, EPSA ($<200 \text{ cm}^2 \text{ cm}^{-2} \text{ Pt}$)

$$\text{EPSA} = (\text{Utilization})(\text{Loading})(\text{ECA})$$

$$(\text{cm}^2 \text{ cm}^{-2} \text{ Pt}) = (\text{g cm}^{-2})(\text{cm}^2 \text{ g}^{-1})$$
- Specific surface area ($\text{cm}^2 \text{ g}^{-1} \text{ Pt}$) (surface area per unit mass of electrocatalyst).
- Mass activity ($\text{mA mg}^{-1} \text{ Pt}$) (current density per unit mass of Pt).
- Specific activity ($\mu\text{A cm}^{-2} \text{ Pt}$) (current density per unit EPSA).



PEFC Applications

1- Transportation Applications

The focus for PEFC applications of PEFC today is on prime power for cars and light trucks. PEFC is the only type of fuel cell considered for prime motive power in on-road vehicles (as opposed to auxiliary power units (APU) power, for which SOFC is also being developed). PEFC systems fueled by hydrogen, methanol, and gasoline have been integrated into light duty vehicles by at least twelve different carmakers. Early prototypes of fuel cell vehicles (Honda and Toyota) have been released to controlled customer groups in Japan and the U.S. However, all automakers agree that the widespread application of PEFC to transportation will not occur until well into the next decade:

- Volume and weight of fuel cell systems must be further reduced
- Life and reliability of PEFC systems must be improved
- PEFC systems must be made more robust in order to be operable under the entire range of environmental conditions expected of vehicles
- Additional technology development is required to achieve the necessary cost reductions
- A hydrogen infrastructure, and the accompanying safety codes and standards must be developed.

2- Stationary Applications

Several developers are also developing PEFC systems for stationary applications. These efforts are aimed at very small-scale distributed generation (~1 to 10 kW AC). The vast majority of systems are designed for operation on natural gas or propane. Hundreds of demonstration units have been sited in programs in the U.S., Europe, and Japan. Typical performance characteristics are given by Plug Power. Considerable progress has been made in system integration and in achieving stand-alone operation. System efficiency typically ranges from 25 to 32 percent (based on the lower heating value LHV). By recovering the waste heat from the cooling water, the overall thermal efficiency can be raised to about 80 percent, but the water temperature (about 50 to 70 °C) is rather modest for many CHP applications. System operating life has been extended to about 8,000 hrs for a single system with a single stack, with degradation of about 5 percent per 1,000 hours.

(Many) Challenges for PEM Fuel Cells

- Improved electrocatalysis
- Lower catalyst loadings
- Improved lifetimes for electrode structures
- Better tolerance to poisons (e.g., CO)
- Lower crossover to the other electrode
- Improved membranes
- Better water management/gas distribution

PEFC Systems

PEFC stacks require tight control of fuel and air feed quality, humidity level, and temperature for sustained high-performance operation. To provide this, PEFC stacks must be incorporated in a sophisticated system. Naturally, the architecture of these systems depends strongly on whether they are fueled by hydrogen or by a hydrocarbon fuel.

1- Direct Hydrogen PEFC Systems

Direct hydrogen PEFC systems require extensive thermal and water management to ensure that the PEFC stack operates under the desired design conditions (**Figure 8**). Key components are heat exchangers, humidifiers, and condensers. To understand the challenge of designing such a system, contrast the operating conditions of a PEFC stack (60 °C to 80 °C and 40 to 100 percent RH) with the environment such systems must work in. Automotive design standards require that engines to operate at temperatures up to 60 °C (start in a sunny spot). Thus, very little driving temperature difference will be available between the PEFC cooling medium and the ambient, requiring a large radiator surface area. If such conditions occur in an arid region, significant amounts of water are lost from the exhaust unless sophisticated water recovery systems (such as sorbent wheels or refrigerated systems) are used.

A key part of the direct hydrogen PEFC system is the hydrogen storage tank. A wide range of hydrogen storage methods is being considered (compressed hydrogen storage, liquid storage, storage in metal hydrides, and chemical storage). Each of these options offers distinct advantages, but also represents a compromise between energy density, weight, impact on energy efficiency, and cost. Special safety considerations must be made in all cases. As a consequence, the size and weight of the balance of plant components for these systems are important factors in the overall power system weight and volume. Automotive fuel cell developers have made tremendous strides in reducing the volume of direct hydrogen PEFC systems. Nevertheless, significant additional volume and weight reduction are required to match the power density of internal combustion engines.

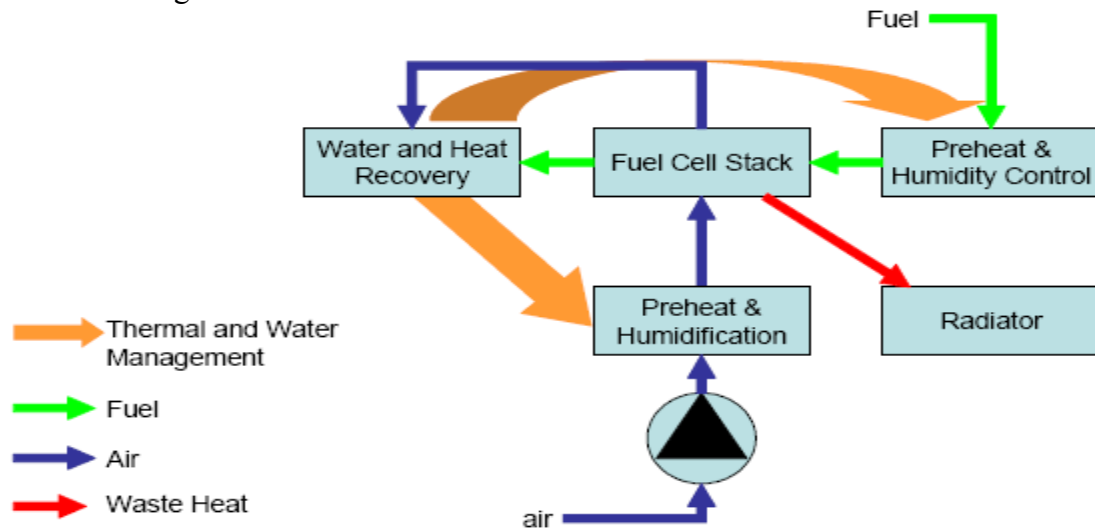


Figure 8: Typical Process Flow Diagram Showing Major Components of Direct Hydrogen PEFC System.

2- Reformer-Based PEFC Systems

Reformer-based PEFC systems avoid the complexities and compromises of hydrogen storage, but instead the system must be designed to handle hydrocarbon fuels (similar considerations apply for alcohol fuels). This requires four major additional unit operations (**Figure 9**), collectively referred to as fuel processing:

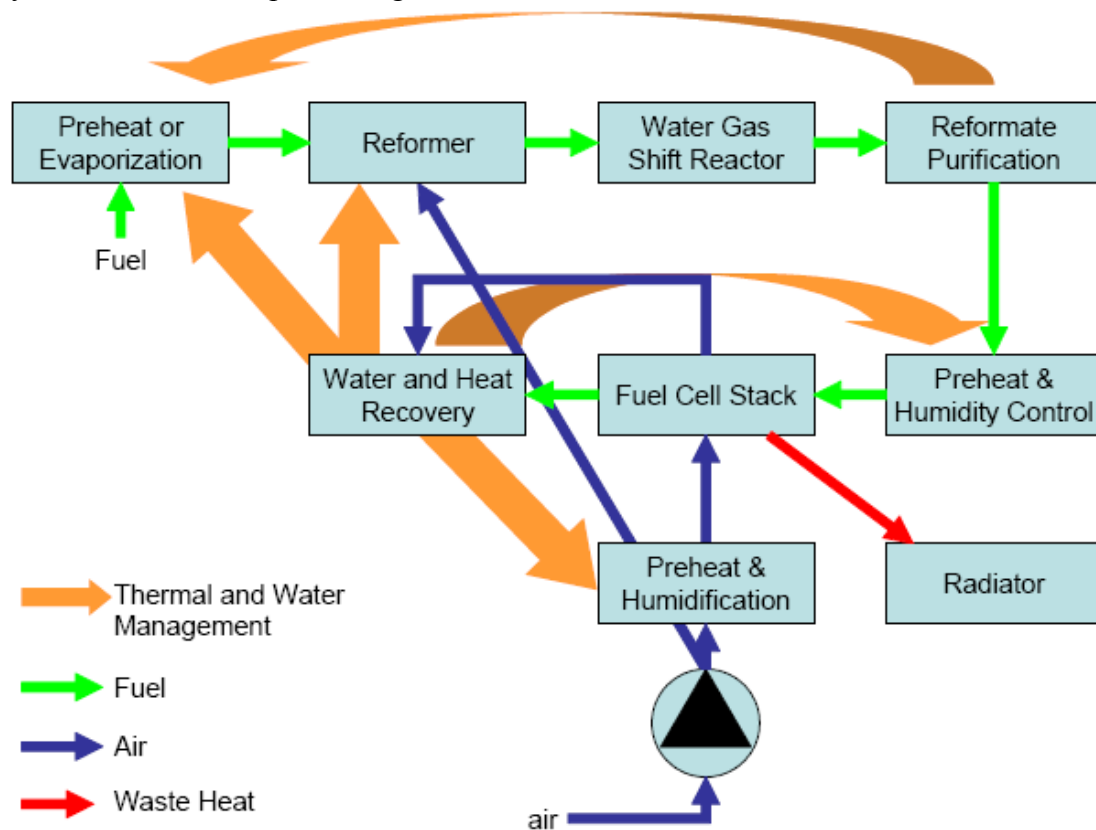


Figure 9: Schematic of Major Unit Operations Typical of Reformer-Based PEFC Systems.

- Fuel preheat and vaporization. Necessary to prepare the fuel to meet the reformer's feed requirements. Often, this unit operation is physically integrated with the reformer.
- Reformer. This unit chemically converts hydrocarbon or alcohol to synthesis gas (a mixture of hydrogen and carbon monoxide). The two most practical oxidants are steam and air. If air is used, the reformer is referred to as a partial oxidation (POX) reformer; if steam is used, a steam reformer (SR), and if a mix of air and steam is used, an autothermal reformer (ATR). The choice of reformer type depends on a number of factors. Typically, POX reformers are smaller, cheaper, respond faster, and are suitable for a wide range of fuels. Steam reformers enable a higher system efficiency. ATRs and catalytic POX reformers (CPOX) share some of the advantages of each type.



- Water Gas Shift Reactor (WGSR). The WGSR reacts carbon monoxide with water vapor to form hydrogen and carbon dioxide. This reactor is critical in PEFC systems (as well as PAFC), since the stack is unable to convert carbon monoxide.
- Reformate purification. This is necessary because the PEFC stacks are sensitive to even trace concentrations of contaminants. Especially CO and sulfur are problematic species, and must be reduced to levels of around 10 and 1 ppm or less, respectively. Sulfur removal is, in actuality, done upstream in the process (just before or just after the reformer), but CO removal must be done just prior to stack entry.

A number of approaches can be used to purify reformate fuel (including pressure swing adsorption, membrane separation, methanation, and selective oxidation). Selective or preferential oxidation (PROX) is usually the preferred method for CO removal in the relatively small fuel cell systems because of the parasitic system loads and energy required by other methods. In selective oxidation, the reformed fuel is mixed with air or oxygen either before the fuel is fed to the cell or within the stack itself. Current selective oxidation technology can reduce CO levels to <10 ppm. Another approach involves the use of a selective oxidation catalyst that is placed between the fuel stream inlet and the anode catalyst. Since the stack cannot tolerate even 10 ppm, air is usually bled into the anode directly to manage CO. Research to find approaches and materials that better tolerate impurities in the fuel continues today.

These unit operations add weight and volume, and reduce the efficiency of the system (fuel processor “efficiencies” typically range from 75 to 90 percent, but similar losses occur in the production of hydrogen from fossil fuels). In addition to the unit operations however, it is important to realize that their presence also impacts the size, performance, and cost of the fuel cell stack:

- The hydrogen in the anode feed of reformate-based systems is typically diluted with CO₂ and (in case of POX or ATR) nitrogen. As a consequence, the hydrogen mole fraction at the anode inlet is rarely higher than 0.3 (vs. 75 percent in the case of a direct hydrogen system). This decreases the ideal potential of the cells and increases the concentration-related losses.
- The presence of trace CO and sulfur and large quantities of CO₂ affects the performance of the anode electro-catalyst. As a consequence, more platinum must be used (typically 0.4 to 1 mg/cm² more), and even then the power density is typically 30 to 40 percent lower than with hydrogen-based systems.

The choice between a direct hydrogen and a reformate-based system depend on the application. For light duty vehicles, most experts now prefer direct hydrogen systems, while for stationary applications natural gas reformer-based PEFC systems are favored.

3- Direct Methanol Fuel Cell Systems

Specially optimized PEFCs can be fed with methanol (or fuels with similar chemical structure), creating a so-called direct methanol fuel cell (DMFC). Conceptually, this could lead to a very simple system with a fuel that has a relatively high energy density and is a liquid under ambient conditions. Performance levels achieved with a DMFC using air is now in the range of 180 to 250 mA/cm² but because cell voltages typically range between 0.25 to 0.4 V, the power



density ranges between 40 to 100 mW/cm². This low cell voltage is caused by a few common problems with the DMFC, several of which result from the cross-over of neutral methanol from the anode to the cathode side:

- High anode overpotential has been shown to be caused by absorption of partial decomposition products of methanol (e.g. CO)
- High cathode overpotential, caused by poisoning of the cathode electro-catalyst by cross-over methanol and its decomposition products

This performance still requires platinum loadings that are almost ten times higher (around 3 to 5 mg/cm²) than needed in high-performance direct hydrogen PEFC. When feeding concentrated methanol directly, the cross-over can be as high as 30 to 50 percent compared with the amount oxidized electrochemically. If the concentration is reduced, the cross-over is reduced but so is the current density (due to reduced activity of the reactants). Obviously, the methanol crossed over is lost, affecting efficiency and hence the heat generation. Research has focused on finding more advanced electrolyte materials to combat fuel crossover and more active anode catalysts to promote methanol oxidation.

Other developers have focused on miniaturizing the balance of plant components necessary to control water balance and minimize methanol loss or even developing reformer-based portable systems.

Another, less-well-reported disadvantage is that a large amount of water is transported across the membrane (has an aqueous methanol solution on one side and air on the other). This transport must be mitigated by sometimes complex water recovery systems that detract significantly from the conceptual simplicity of the DMFC. These limitations bar DMFCs from application in automobiles or stationary applications until the cross-over is reduced by at least an order of magnitude. Some developers are focusing on membranes and MEAs that reduce water crossover. Despite the challenges mentioned, there is significant interest in DMFCs for portable power applications in the 1 W to 1 kW capacity range.

Improvements in solid polymer electrolyte materials have extended the operating temperature of direct methanol PEFCs from 60 °C to almost 100°C. Electro-catalyst developments have focused on materials with higher activity. Researchers at the University of Newcastle upon Tyne have reported over 200 mA/cm² at 0.3 V at 80 °C with platinum/ruthenium electrodes having platinum loading of 3.0 mg/cm². The Jet Propulsion Laboratory in the U.S. has reported over 100 mA/cm² at 0.4 V at 60°C with platinum loading of 0.5 mg/cm². Recent work at Johnson Matthey has clearly shown that platinum/ruthenium materials possess substantially higher activity than platinum alone.

All fuel cells exhibit kinetic losses that cause the electrode reactions to deviate from their theoretical ideal. This is particularly true for a direct methanol PEFC. Eliminating the need for a fuel reformer, however, makes methanol and air PEFCs an attractive alternative to PEFCs that require pure hydrogen as a fuel. The minimum performance goal for direct methanol PEFC commercialization is approximately 200 mW/cm² at 0.5 to 0.6 V.

Developers in the U.S., Japan, and Europe have developed impressively integrated DMFC systems. Although energy density must still improve to broadly compete with state-of-the-art lithium-ion batteries in consumer applications, several developers have announced products for niche consumer or industrial applications within the next few years. If successful, this could represent the earliest commercialization of fuel cells beyond space applications.

HYDROGEN PRODUCTION AND STORAGE

1- HYDROGEN PRODUCTION

Fuel cells operate with hydrogen-rich fuels, and either direct hydrogen or reformed fuels are typically used. Currently, industrial production of hydrogen is designed to accommodate the required supply for producing ammonia, which is largely used in agriculture as fertilizer and in oil refineries to produce automotive fuels. A number of methods can be used to obtain hydrogen, as illustrated in **Figure A**.

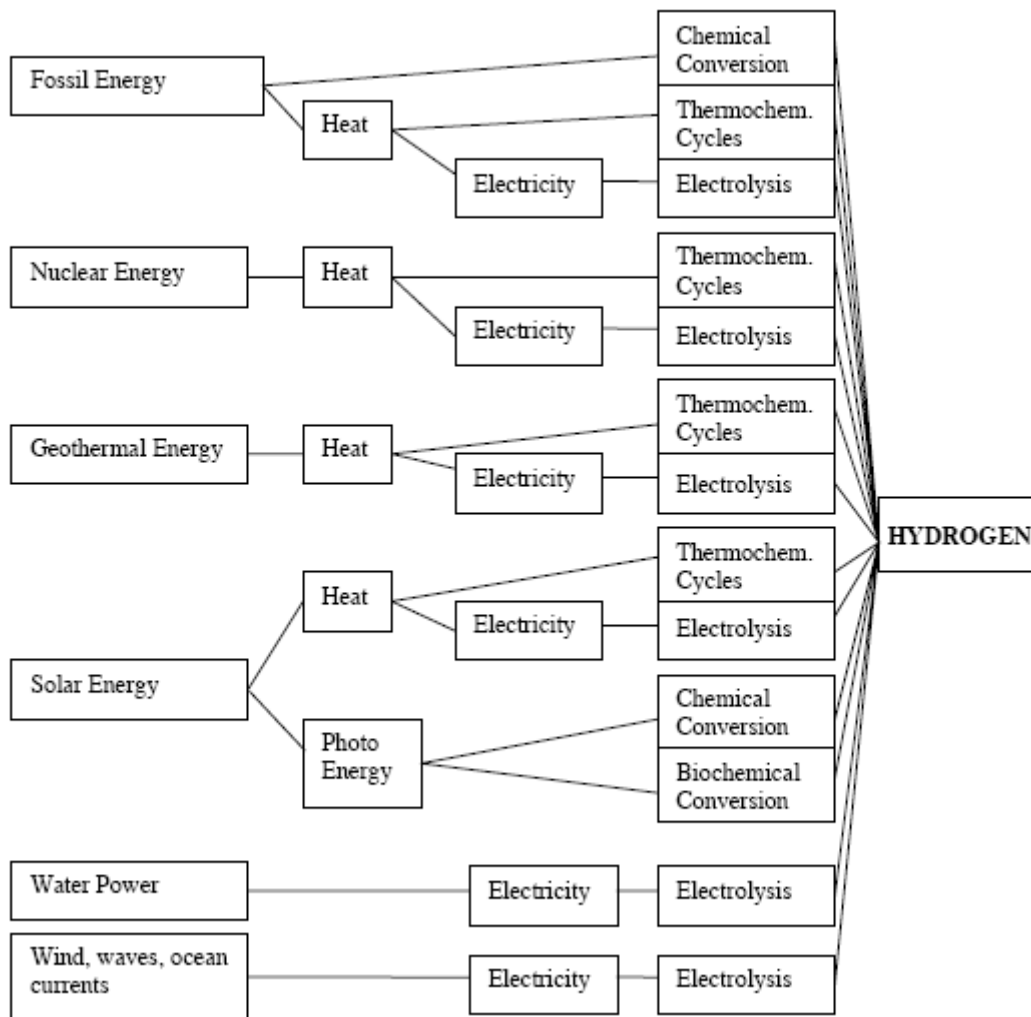


Figure A: Hydrogen production sources.

- **Fossil Fuels**

Hydrogen is extracted from fossil fuels through various techniques, such as steam reforming, partial oxidation (or a combination of them), and gasification.

Steam reforming is a well-established technology, which uses natural gas as feedstock. This process takes place at temperatures between 750 and 1000°C. Methane reacts with water over a



catalyst (usually nickel, supported by alumina) and produces the hydrogen-rich gas that is further used by fuel cells. The overall process takes place in two steps:

- Steam reforming: $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3 \text{H}_2$
- Shift reaction: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$

Methanol is also used for producing hydrogen, and the reaction takes place at temperatures between 200 and 300°C, the catalyst being made of copper, supported by zinc oxide:

- Steam reforming: $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3 \text{H}_2$
- Shift reaction: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$

Partial oxidation is typically used to process heavy oil fractions; the exothermic reaction in this case does not require the presence of a catalyst. If applied to natural gas or methane, presence of a catalyst becomes necessary. The following reactions for methane are given as an example:

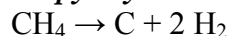
- Partial oxidation: $\text{CH}_4 + 1/2 \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$
- Shift reaction: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$

The advantage of steam reforming technology is that its output has the highest hydrogen concentration compared to other technologies based on fossil fuel. However, it does not offer fast start-up and dynamic response. Partial oxidation, on the other hand, produces only low concentrations of hydrogen combined with a fast start-up and dynamic response. A natural question is thus, what would happen if we try to combine both these technologies, using the advantages of each of them? This combination is known as **autothermal reforming**, and efforts have been made to develop various reformers, such as the HotSpot fuel processor developed by Johnson Matthey. **Table A** shows a comparison of the gas compositions obtained after using different options for the reforming process, using methanol as fuel.

Table A: Gas Composition of Reformer Outputs

Composition (dry gas, %)	Steam Reforming	Partial Oxidation	Autothermal Reforming
H ₂	67	45	55
CO ₂	22	20	22
N ₂	—	22	21
CO	—	—	2

The third technology, **coal gasification**, is achieved through coal reaction with oxygen and steam at high temperatures, and uses all types of coals for the process. A disadvantage common to all these technologies is that one of the by-products of the reforming reactions is CO₂, a significant contributor to the environment pollution. To eliminate this, various other technologies are being developed as potential solutions for “CO₂-free” hydrogen production from fossil fuels, such as the **pyrolytic cracking** of natural gas:



• Water Electrolysis

Another way of obtaining hydrogen is through water electrolysis. This technology is based on decomposition of water into hydrogen and oxygen with the help of electricity. Although its development began with the 19th century, water electrolysis has never reached the level of large-scale production because it uses electricity as input, and this has a direct impact on the overall



cost of producing hydrogen. Costs associated with this technology are considerably higher than for obtaining hydrogen directly from the fossil fuels. The contribution of water electrolysis technology to the total production of hydrogen represents only about 0.5%.

- **Other Sources**

Nuclear or renewable energies are also considered potentially “CO₂-free” sources of hydrogen production.

Several forms of energy can be used to make hydrogen:

- **Thermal:** Thermal decomposition of water into hydrogen and oxygen occurs at temperatures around 2,500 °C. The process isn't attractive because few materials can withstand that temperature. In the plasma arc process, water is heated to 5,000 °C by an electric field resulting in the cracking products H, H₂, O, O₂, OH, HO₂, and H₂O. A fraction of 50 percent by volume of H and H₂ is possible. The plasma gases are quenched with a cryogenic liquid to prevent the gases from recombining. This process consumes a lot of energy and is very expensive to operate.
- **Thermochemical:** Today, hydrogen is produced mainly from natural gas by steam methane reforming. Steam methane reforming (SMR) is not only the most common, but is also the least expensive method of producing hydrogen; almost 48 percent of the world's hydrogen is produced from SMR.
- **Electrochemical:** Water electrolysis passes a direct current between two electrodes in water. The water is made more conductive by adding an electrolyte such as potassium hydroxide. Hydrogen gathers around the negative electrode (cathode) and oxygen gathers around the positive electrode (anode). The gases are collected separately.
- **Photoelectrochemical:** Sunlight (photons) provides the source of energy for this process. Photons interact with dissolved chemicals to produce activated species, which in turn deactivate by releasing hydrogen from water. This is solar-powered electrolysis.
- **Photobiological:** Sunlight provides the source of energy for this process. Living organisms, such as green algae, make enzymes. The pigment of algae absorbs solar energy, and the enzyme in the cell acts as a catalyst to split the water molecules.

Promising technologies related to production, infrastructure, and utilization of hydrogen are:

- Production of hydrogen from coal National Renewable Energy Laboratory (NETL).
- Thermal-plasma/quench process for converting methane to hydrogen, with solid carbon produced as a by-product Idaho National Engineering and Environmental Laboratory (INEEL).
- Biotechnology processes for production of hydrogen from carbon-containing waste and renewable resources (INEEL).
- Photoconversion production uses either biological organisms (bacteria or algae) or semiconductors to absorb sunlight, split water, and produce hydrogen (NREL).
- Thermochemical production uses heat to produce hydrogen from biomass and solid waste (NREL).
- Low-pressure storage of hydrogen in the use of metal ion intercalated graphite fibers as a medium (INEEL).



- Fleet and fueling systems engineering analysis of hydrogen-powered buses and supporting fueling stations (INEEL).
- Safety and risk assessment of hydrogen as transportation fuel (INEEL).
- Demonstration of hydrogen-powered vehicles and related transportation system infrastructure, including hydrogen production, storage, and fueling.
- Demonstration of hydrogen-fueled, small-scale power generation for local (distributed) electricity production.
- Since hydrogen can neither be seen nor smelled, as an added safety precaution for hydrogen-fueled vehicles, hydrogen sensors are being developed. To detect hydrogen, a very thin sensor that reacts to hydrogen by changing colors is applied to the end of a fiber optic cable. The sensors can be placed throughout the vehicle to relay information on leak detection to a central control panel (NREL).

2- HYDROGEN STORAGE

Hydrogen storage represents one of the difficult issues associated with operation of the fuel cell systems. This is because hydrogen is characterized by low energy density and high specific energy.

The four most common methods for storing hydrogen are:

- **Compressed gas in pressure vessels:** New materials have allowed pressure vessels and storage tanks to be constructed that can store hydrogen at extremely high pressures.
- **Hydrogen absorbing materials:**
 1. Metals (pure and alloyed) can combine with hydrogen to make a metal hydride. The hydride releases hydrogen when heated. Hydrogen stored in hydrides under pressure has a very high energy density. **Table B** shows the characteristics of a number of metal hydride systems.
 2. Hydrogen molecules that have been absorbed on charcoal can approach the storage density of liquid hydrogen.
 3. Small glass spheres (microspheres), carbon nanotubes, and fullerenes can hold hydrogen if it is induced at high pressure and temperature. The hydrogen is held captive in the solid matrix when the temperature lowers. Hydrogen can be released by heating the solid.
- **Liquid storage:** Hydrogen can be converted into a liquid by reducing the temperature to $-253\text{ }^{\circ}\text{C}$. This can save cost in transportation, but requires additional energy and cost to keep the hydrogen at the low temperature. Refrigerating hydrogen in liquid form uses the equivalent of 25 to 30 percent of its energy content. A concern of storing liquid hydrogen is minimizing loss of liquid hydrogen by evaporation.
- **Underground storage in depleted oil and natural gas reservoirs, aquifers, and salt cavities:** For underground storage of hydrogen, a large cavern of porous rock with an impermeable caprock above it would be needed to contain the gas. As much as 50 percent of the hydrogen pumped into the formation would remain in the formation.



Table B: Hydrogen Storage Properties of Metal Hydrides

Metal Hydride System	Mg/MgH ₂	Ti/TiH ₂	V/VH ₂	Mg ₂ Ni/ Mg ₂ NiH ₄	FeTi/ FeTiH _{1.95}	LaNi ₅ / LaNi ₅ H _{5.9}	LH ₂
Hydrogen content as mass fraction (%)	7.7	4.0	2.1	3.2	1.8	1.4	100.0
Hydrogen content by volume (kg/dm ³)	0.101	0.15	0.09	0.08	0.096	0.09	0.077
Energy content (based on HHV) (MJ/kg)	9.9	5.7	3.0	4.5	2.5	1.95	143.0
Energy content (based on LHV) (MJ/kg)	8.4	4.8	2.5	3.8	2.1	1.6	120.0
Heat of reaction (kJ/Nm ³)	3360	5600	—	2800	1330	1340	—
Heat of reaction (kJ/mol)	76.3	127.2	—	63.6	30.2	30.4	—
Heat of reaction (as fraction of HHV) (%)	26.7	44.5	—	22.2	10.6	10.6	—
Heat of reaction (as fraction of LHV) (%)	31.6	52.6	—	26.3	12.5	12.6	—

2- ALKALINE FUEL CELLS (AFCs)

The development of the AFC started almost seven decades ago, when researchers started to realize that hydrogen fuel cells with alkaline electrolytes can be used in commercial applications. The first notable solution was the high-power-density AFC developed by Sir Francis Bacon, with an output of 0.6 V at 1.11 A/cm² current density and 240°C operating temperature. AFCs have been used by NASA on their space explorations during the 1960s and 1970s.

The AFCs utilize potassium hydroxide (KOH) as an electrolyte of variable concentration, either in aqueous solution or stabilized matrix form. The KOH concentration varies with the operating temperature, increasing from 35 wt% for low temperatures (<120 °C) to about 85 wt% for high temperatures (~260 °C). The electrolyte is contained in a porous asbestos matrix, and the catalysts are typically made of nickel (Ni) and silver (Ag). Noble metals, metal oxides, or spinels are also considered among the materials used to fabricate the catalysts.

Hydrogen and oxygen are supplied to the electrodes similarly to PEMFCs. The KOH electrolyte is extremely sensitive to potential poisoning with CO or reaction with CO₂ and, thus, only pure hydrogen and oxygen can be used as reactants for the electrochemical processes. The carrier in this case is the hydroxyl ion (OH⁻), which travels from the cathode to the anode, where it combines with H₂ and creates water and electrons (**Figure 10**).

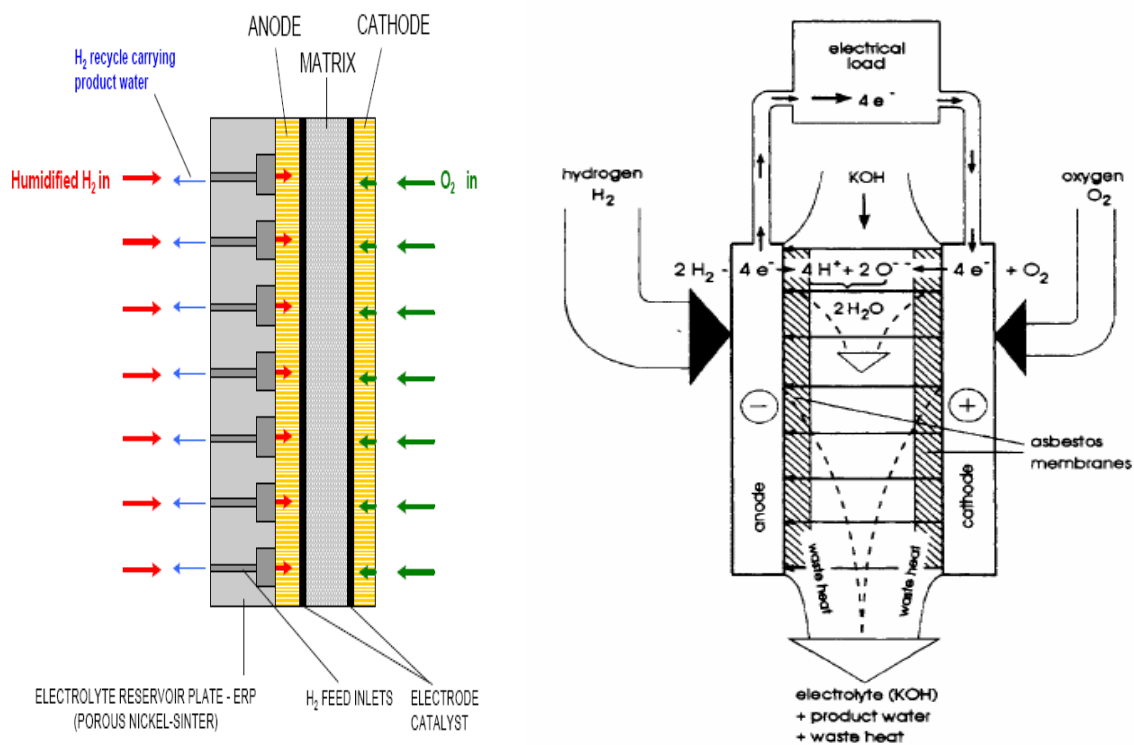
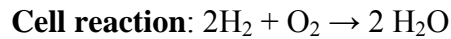
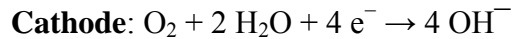


Figure 10: AFC operation principle **Immobilized Electrolyte** (left) and **Circulating Electrolyte** (right).

If the electrolyte is in a solution form, it mixes up with the water created at the anode. To ensure proper operation of the fuel cell unit, it is required that water be continuously removed from the electrolyte. Electrons formed at the anode are conducted to the external circuit to create the



electrical output and then forced to the cathode, closing the circuit. The basic electrochemical reactions for the AFC are:



Hydroxyl ions, OH^- , are the conducting species in the electrolyte. Since KOH has the highest conductance among the alkaline hydroxides, it is the preferred electrolyte.

The kinetics of O_2 reduction in alkaline electrolytes are more favorable than in phosphoric acid electrolyte. Consider a Pt cathode (0.25 mg/cm^2) in 30 percent KOH at 70°C and in 96 percent phosphoric acid at 165°C . The cathode potentials (vs. RHE - Reversible Hydrogen Electrode) at 100 mA/cm^2 in these two electrolytes are 0.868 and 0.730 V, respectively, according to data reported by Appleby. Various explanations have been advanced for the higher O_2 reduction rates in alkaline electrolytes. The practical consequence of the higher performance of Pt cathodes in alkaline electrolytes is that AFCs are capable of higher efficiencies than PAFCs at a given current density, or higher power densities at the same efficiency. The efficiency of AFCs fueled by pure H_2 is about 60 percent higher heating value (HHV), and that of PAFCs is about 50 percent HHV.

Due to its high performance, particularly for motive power, the majority of the AFCs developers use circulating electrolytes with an external, commercial type soda-lime absorber that promises to resolve the problem of CO_2 in the air stream. The quantity of CO_2 can be limited to a small amount with a circulating electrolyte, versus a continual build-up with an immobilized electrolyte. Life expectancy increases ($\sim 5,000$ hour life is ample for personal automobile engine life) because the cell is nearly inactive when switched off. Hence, only the true operating hours count for the total lifetime. During normal operation, the electrolyte circulates continuously, which has several advantages over an immobilized system:

1. no drying-out of the cell occurs because the water content of the caustic electrolyte remains quite constant everywhere inside the stack
2. heat management by dedicated heat exchanger compartments in the stack becomes unnecessary - the electrolyte itself works as a cooling liquid inside each cell
3. accumulated impurities, such as carbonates, are concentrated in the circulating stream and can easily be removed (comparable to a function of oil in today's gasoline engines)
4. the OH^- concentration gradient is highly diminished
5. the electrolyte prevents the build-up of gas bubbles between electrodes and electrolyte as they are washed away.

Other attributes are that the alkaline cell could have high reactivity without the need for noble metal catalysts on the cell electrodes; this represents a cost savings. Additionally, the radiator of the alkaline cell system should be smaller than the radiator in the competitive PEFC system because of higher alkaline cell temperature and its higher performance.

In stacks using circulating electrolytes, parasitic currents might occur. All cells are connected via the electrolyte stream to all other cells, producing high voltages between the electrodes. Parasitic current not only lowers the stack performance, but can also harm the electrodes. Fortunately, this issue can be resolved easily by using a special electrode frame design with long, narrow electrolyte channels.



Some developers have investigated a direct methanol alkaline cell to circumnavigate hydrocarbon fuel separator issues. These cells exhibit a reduced performance, and have not been as thoroughly investigated as the hydrogen-fueled cells.

The unusual economics for remote power applications (i.e., space, undersea, and military applications) result in the cell itself not being strongly constrained by cost. The consumer and industrial markets, however, require the development of low-cost components if the AFC is to successfully compete with alternative technologies. Much of the recent interest in AFCs for mobile and stationary terrestrial applications has addressed the development of low-cost cell components. In this regard, carbon-based porous electrodes play a prominent role. It remains to be demonstrated whether alkaline cells will prove commercially viable for the transportation sector.

Owing to the fact that only pure fuel or oxidant can be used in operation, the AFC is used for specialized applications. Space explorations, military use, and research are among the few areas in which these fuel cells are utilized. Efforts are being made to broaden the spectrum of terrestrial daily applications. Tests and demonstrations have shown that AFC hybrid vehicles are potential technological solutions for the near future in transportation. In the 1970s, an AFC-based hybrid vehicle was tested for 3 years, using liquid hydrogen and oxygen, and KOH liquid electrolyte. The improved version of this vehicle was tested again in 1998, using a system consisting of AFC and rechargeable alkaline manganese dioxide-zinc (RAMTM) batteries. The operating lifetime of these AFCs is anticipated to be about 4000 h, and the mass production cost is expected to become comparable to the cost of the currently used heat engines (\$50 to \$100 per kW).

Cell Components

The electrodes contain high loadings of noble metals: 80 percent Pt – 20 percent Pd anodes are loaded at 10 mg/cm² on Ag-plated Ni screen; 90 percent Au – 10 percent Pt cathodes are loaded at 20 mg/cm² on Ag plated Ni screen. Both are bonded with PTFE to achieve high performance at the lower temperature of 85 to 95 °C. A wide variety of materials (e.g., potassium titanate, ceria, asbestos, zirconium phosphate gel) have been used in the micro-porous separators for AFCs. The electrolyte is 35 percent KOH and is replenished via a reservoir on the anode side. Gold-plated magnesium is used for the bipolar plates.

A typical configuration, Apollo uses carbonbased plastic-bonded gas diffusion electrodes with a current collector (nickel) inside. Due to the ease of preparation, the electrodes in present stacks use noble metals loaded to less than 0.5mg/cm². The 0.3 cm thick cells are stacked in a monopolar order and are commonly connected in series via edge connectors. Neither membranes nor bipolar plates are needed. The stacks operate at 75 °C, using a 9N KOH electrolyte. The gases are fed at ambient pressure; either pure hydrogen or cracked ammonia is used. Lifetime testing has not been finished, but is >1,000 hours at intermittent operation (a few hours per day). Several types of catalysts are used or are being considered for the electrodes:

- noble metals (expensive but simple, and acceptable for low volume stack preparation)
- “classic” non-noble metals (silver for the cathode and Raney nickel for the anode)
- spinels and perovskites (often referred to as alternative catalysts, these are being developed because they cost less than the noble metal catalysts).



Development Components

Immobilized electrolyte AFCs, used mostly in space or closed environments, and circulating electrolyte AFCs, used for terrestrial application, face separate and unique development challenges.

H₂/O₂ alkaline technology using immobilized electrolytes is considered to be fully developed. Confidence in the present cell technology is best represented by the fact that there is no back-up electric power on the Space Shuttle Orbiter. Further improvement of the present H₂/O₂ design is not considered to be cost effective with one exception: maintenance cost can be decreased directly by increasing the cell stack life of the Orbiter power plant.

The life-limiting event in the present Orbiter cell is KOH corrosion of the cell frame (cell support). Present stack life is 2,600 hours. The cell stacks have demonstrated capability to reach this life in 110 flights and a total of ~87,000 hours in the Orbiter (July 2002). Present practice is to refurbish the power unit at 2,600 hours by installing a new stack, and cleaning and inspecting the balance of equipment. The stack life is being improved to 5,000 hours by elongating the path length associated with KOH-induced corrosion of the cell frame. A 10 cell short stack has demonstrated the new 5,000 hours concept. The concept is now being qualified in a complete power plant, presently being tested.

Electrode development in circulating electrolyte AFCs has concentrated on:

1. multi-layered structures with porosity characteristics optimized for flow of liquid electrolytes and gases (H₂ and air)
2. catalyst development.

Another area for concern is the instability of PTFE, which causes weeping of the electrodes. Most developers use noble metal catalysts; some use non-noble catalysts. Spinel and perovskites are being developed in an attempt to lower the cost of the electrodes. Development of low-cost manufacturing processes includes powder mixing and pressing of carbon-based electrodes, sedimentation and spraying, and high-temperature sintering.

AFC electrolyte development has been restricted to KOH water solutions with concentrations ranging from 6 to 12N. Still, use of less expensive NaOH has been considered. Minimal cost advantages appear to be far outweighed by performance reductions due to wetting angle and lower conductivity. However, NaOH as an electrolyte increases the lifetime of electrodes when CO₂ is present, because sodium carbonate, although less soluble than potassium carbonate, forms much smaller crystals, which do not harm the carbon pores.

Other approaches to increasing life and reducing weight and cost include investigating epoxy resins, polysulfone and ABS (acrylonitrile-butadiene-styrene). Framing techniques under development include injection molding, filter pressing, and welding.

Immobilized electrolyte AFCs are highly sensitive to carbon dioxide (CO₂). Non-hydrocarbon hydrogen fuel or pure H₂ can be fed directly to the anode. For example, a carbon-free fuel gas such as cracked ammonia (25 percent N₂, 75 percent H₂, and residual NH₃) can be fed directly to the cell. Due to the high diffusion rate of hydrogen compared to nitrogen, only a very small decrease in potential is observed with hydrogen content greater than 25 percent (at medium current densities). Gas purification is necessary when H₂ is produced from carbon-containing fuel sources (e.g., methanol, gasoline, propane and others). There are many approaches to separate CO₂ from gaseous or liquid streams. Physical separation and chemical separation are the most common methods used. However, CO₂ removal by these methods requires more than



one process step to reduce the CO_2 to the limits required by the fuel cell. Two additional methods include cryogenic separation and biological fixation. If liquid hydrogen is used as the fuel for the alkaline fuel cell, a system of heat exchangers can be used to condense the CO_2 out of the air for the oxidant stream. This technique has a potential weight advantage over the sodalime scrubber. Low-temperature distillation is commonly used for the liquefaction of CO_2 from high purity sources. A new, potentially efficient technique that is being investigated uses capillary condensation to separate gases by selective wicking. Biological separation is promising, but must overcome the challenge of reactivation after shutdown periods. Another promising CO_2 separation method is membrane separation. This has the advantages of being compact, no moving parts, and the potential for high energy efficiency. Polymer membranes transport gases by solution diffusion, and typically have a low gas flux and are subject to degradation. These membranes are relatively expensive. The main drawbacks of membrane separation are the significant pressure differential that may be required across the membrane and its high cost. The need for a high pressure gradient can be eliminated by using a membrane in which a potential is applied over the membrane. This approach is sometimes referred to as the “sacrificial cell” technique. Another approach is to use a membrane with steam reforming of liquid fuels. Little additional energy is needed to pressurize the liquid fuel and water to the pressure required for separation. Alkaline cell developers continue to investigate CO_2 separation methods that show economic promise. However, circulating electrolyte is the technology of choice for terrestrial applications.

Performance

Performance of AFCs since 1960 has undergone many changes, as evident in the performance data in **Figure 11**. H_2 /air performance is shown as solid lines, and H_2 / O_2 performance is shown as dashed lines. The early AFCs operated at relatively high temperature and pressure to meet the requirements for space applications. More recently, a major focus of the technology is for terrestrial applications in which low-cost components operating at near-ambient temperature and pressure with air as the oxidant are desirable. This shift in fuel cell operating conditions resulted in the lower performance shown in Figure 11. The figure shows, using dotted lines, H_2 / O_2 performance for: (1) the Orbiter with immobilized electrolyte, and (2) a circulating electrolyte cell.

1- Effect of Pressure

AFCs experience the typical enhanced performance with an increase in cell operating pressure. **Figure 12** plots the increase in reversible e.m.f. (electromotive force) of alkaline cells with pressure over a wide range of temperatures. The actual increase in cell open circuit voltage is somewhat less than shown because of the greater gas solubility with increasing pressure that produces higher parasitic current.

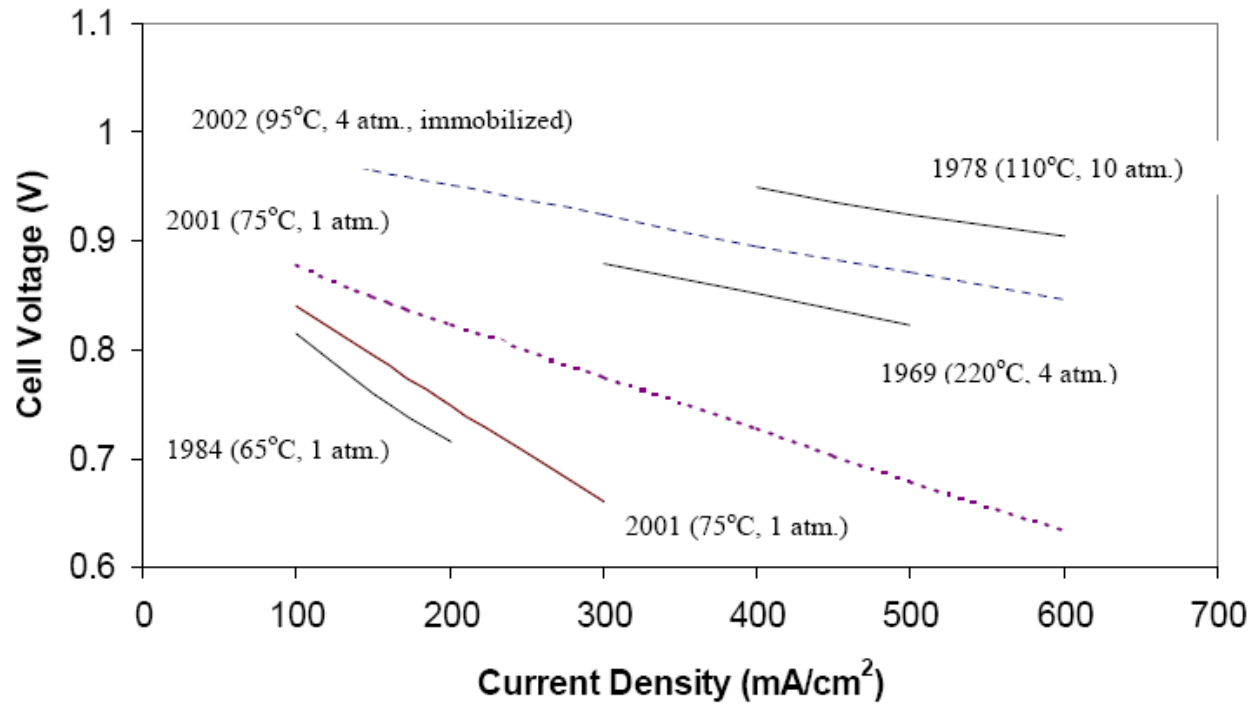


Figure 11: Evolutionary Changes in the Performance of AFCs.

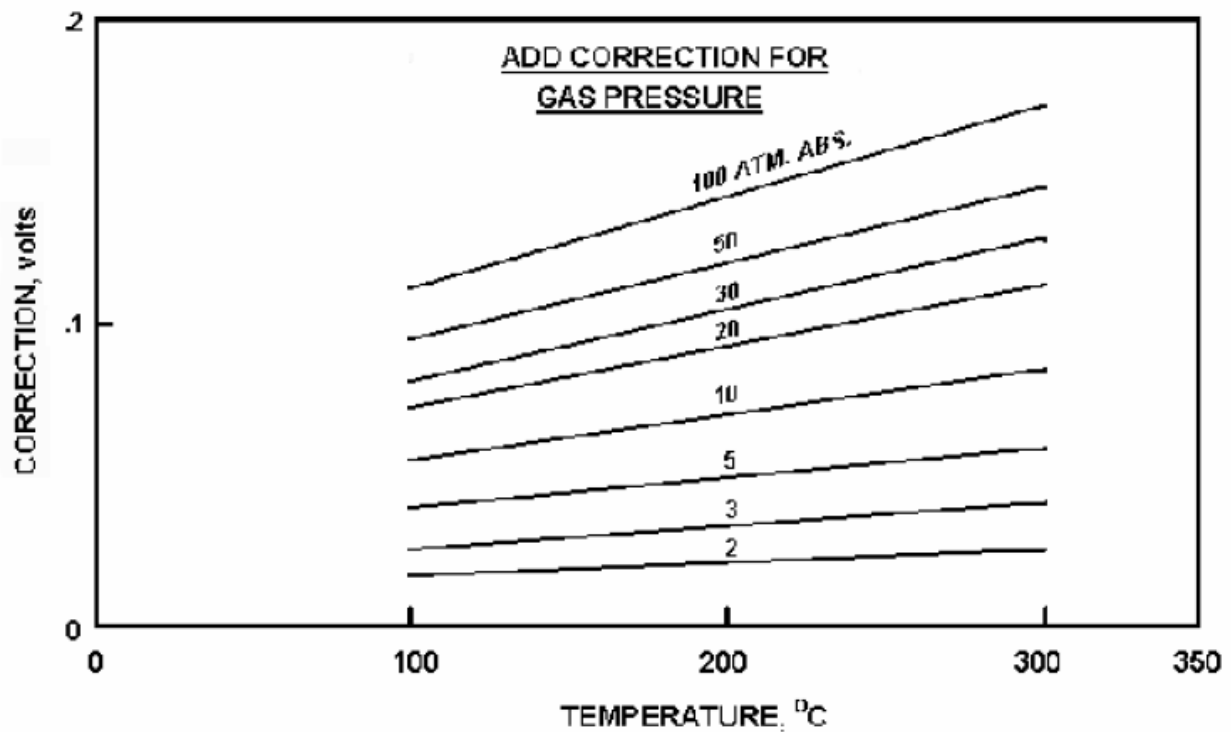


Figure 12: Reversible Voltage of the Hydrogen-Oxygen Cell.



At an operating temperature (T), the change in voltage (ΔV_P) as a function of pressure (P) can be expressed fairly accurately using the expression:

$$\Delta V_P \text{ (mV)} = 0.15T \text{ (}^\circ\text{K)} \log(P_2/P_1)$$

over the entire range of pressures and temperatures shown in Figure 12. In this expression, P_2 is the desired performance pressure and P_1 is the reference pressure at which performance is known. To achieve faster kinetics, operating temperatures greater than 100 °C, accompanied by higher pressures, are used. Spacecraft fuel cells have operated for over 5,000 hours at 200 °C at 5 atm achieving HHV efficiencies exceeding 60 percent. It should be noted that a pressure increase beyond about 5 atm produces improvements that are usually outweighed by a significant weight increase required to sustain the higher operating pressure. For space applications, weight is critical. Also, this increase in performance can only be realized in applications where compressed gases are available (such as in space vehicles or submarines). In all other cases, compressors are needed. Compressors are not only noisy, but incur parasitic power that lowers the system efficiency. An increase of overall efficiency when using compressors in simple cycles is very unlikely.

2- Effect of Temperature

The reversible cell potential for a fuel cell consuming H_2 and O_2 decreases by 49 mV under standard conditions in which the reaction product is water vapor.

However, as is the case in PAFCs, an increase in temperature improves cell performance because activation polarization, mass transfer polarization, and ohmic losses are reduced.

The improvement in performance with cell temperature of catalyzed carbon-based (0.5 mg Pt/cm²) porous cathodes is illustrated in **Figure 13**. As expected, the electrode potential at a given current density decreases at lower temperatures, and the decrease is more significant at higher current densities. In the temperature range of 60 to 90 °C, the cathode performance increases by about 0.5 mV/°C at 50 to 150 mA/cm².

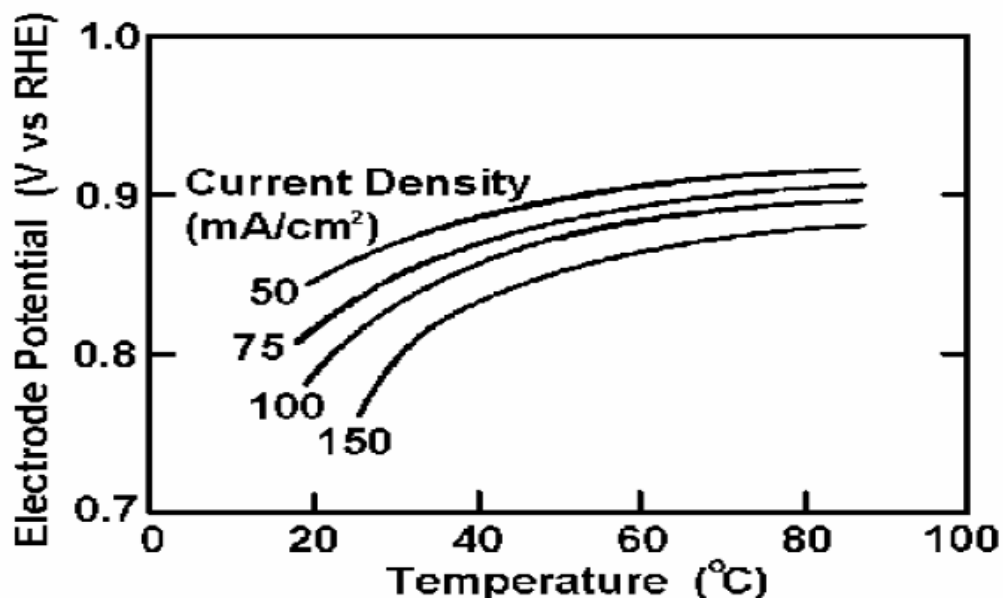


Figure 13: Influence of Temperature on O_2 , (air) Reduction in 12 N KOH.



Early data indicated a temperature coefficient for AFCs operating between 50 to 70 °C of about 3 mV/°C at 50 mA/cm², and cells with higher polarization had higher temperature coefficients under load. Later measurements by McBreen, et al. on H₂/air single cells (289 cm² active area, carbon-based Pd anode and Pt cathode) with 50 percent KOH showed that the temperature coefficient above 60 °C was considerably lower than that obtained at lower temperatures, as shown in **Figure 14**.

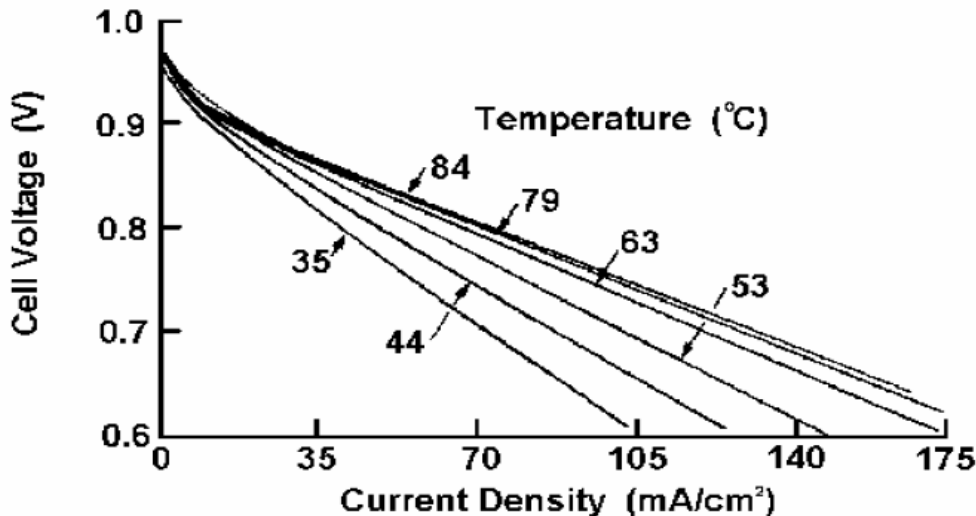


Figure 14: Influence of Temperature on the AFC Cell Voltage.

The McBreen data suggest the following expressions for evaluating the change in voltage (ΔV_T) as a function of temperature (T) at 100 mA/cm²:

$$\Delta V_t \text{ (mV)} = 4.0 (T_2 - T_1) \quad \text{for } T < 63 \text{ } ^\circ\text{C}$$

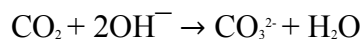
or

$$\Delta V_t \text{ (mV)} = 0.7 (T_2 - T_1) \quad \text{for } T > 63 \text{ } ^\circ\text{C}$$

Alkaline cells exhibit reasonable performance when operating at low temperatures (room temperature up to about 70 °C). This is because the conductivity of KOH solutions is relatively high at low temperatures. For instance, an alkaline fuel cell designed to operate at 70 °C will reduce to only half power level when its operating temperature is reduced to room temperature.

3- Effect of Impurities

Carbon dioxide was the only impurity of concern in the data surveyed. AFCs with immobilized electrolytes suffer a considerable performance loss with reformed fuels containing CO₂ and from the presence of CO₂ in air (typically ~350 ppm CO₂ in ambient air). The negative impact of CO₂ arises from its reaction with OH⁻.



producing the following effects:

1. reduced OH⁻ concentration, interfering with kinetics



2. electrolyte viscosity increase, resulting in lower diffusion rate and lower limiting currents
3. precipitation of carbonate salts in the porous electrode, reducing mass transport
4. reduced oxygen solubility
5. reduced electrolyte conductivity.

In the case of circulating liquid electrolytes, the situation is not as critical, but is still significant. The influence of CO_2 on air cathodes (0.2 mg Pt/cm^2 supported on carbon black) in 6N KOH at 50°C can be ascertained by analysis of the performance data presented in **Figure 15**.

To obtain these data, the electrodes were operated continuously at 32 mA/cm^2 , and current-voltage performance curves were periodically measured. Performance in both CO_2 -free air and CO_2 -containing air showed evidence of degradation with time. However, with CO_2 -free air the performance remained much more constant after 2,000 to 3,000 hours of operation. Later tests, however, showed that this drop in performance was caused purely by mechanical destruction of the carbon pores by carbonate crystals. Improved electrodes can withstand even high amounts of CO_2 (5 percent) over many thousands of hours, as proven recently by DLR (Deutsches Zentrum fuer Luft- und Raumfahrt).

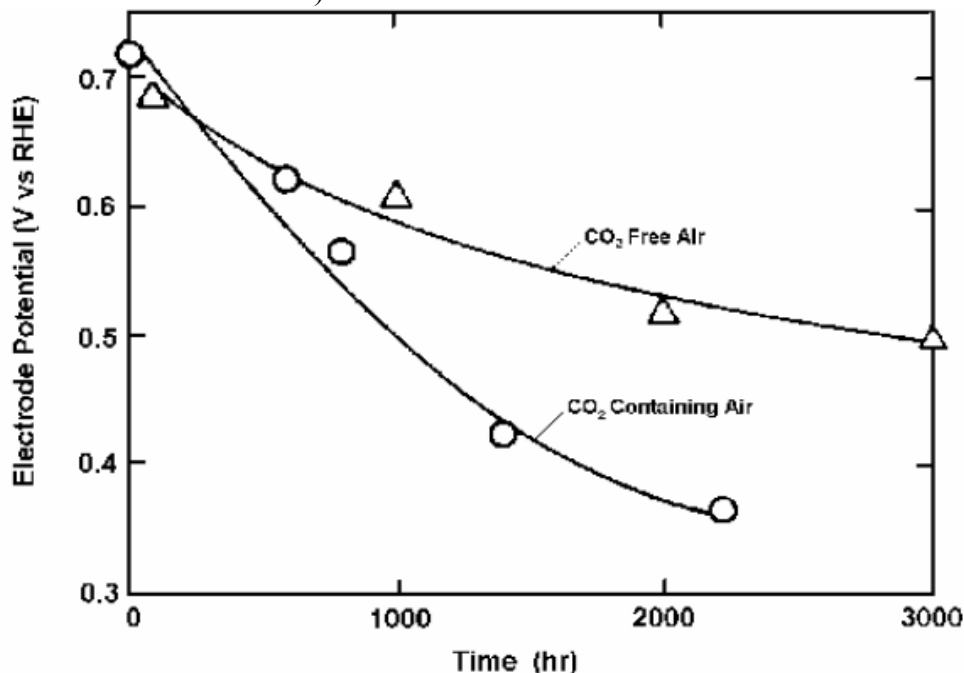


Figure 15: Degradation in AFC Electrode Potential with CO_2 Containing and CO_2 -free air.

High concentrations of KOH are also detrimental to the life of O_2 electrodes operating with CO_2 -containing air, but operating the electrode at higher temperature is beneficial because it increases the solubility of CO_2 in the electrolyte. Hence, modifying the operating conditions can prolong electrode life. Extensive studies by Kordesch, et al. indicate that the operational life of air electrodes (PTFE-bonded carbon electrodes on porous nickel substrates) with CO_2 -containing air in 9N KOH at 65°C ranges from 1,600 to 3,400 hours at a current density of 65 mA/cm^2 . The life of these electrodes with CO_2 -free air tested under similar conditions ranged from 4,000 to 5,500 hours. It was reported that a lifetime of 15,000 hours was achieved with AFCs, with failure caused at that time by corrosion of the cell frames.



4- Effects of Current Density

As in the case with PAFCs, voltage obtained from an AFC is affected by ohmic, activation, and concentration losses. **Figure 16** presents data obtained in the 1960s that summarizes these effects, excluding electrolyte ohmic (iR) losses, for a catalyzed reaction (0.5 to 2.0 mg noble metal/cm²) with carbon-based porous electrodes for H₂ oxidation and O₂ reduction in 9N KOH at 55 to 60 °C. The electrode technology was similar to that employed in the fabrication of PAFC electrodes.

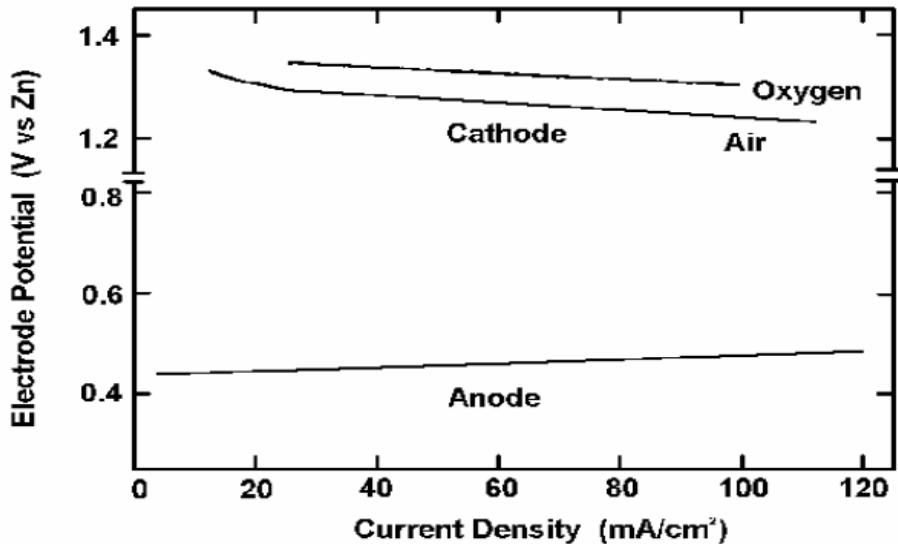


Figure 16: iR -Free Electrode Performance with O₂ and Air in 9 N KOH at 55 to 60°C. Catalyzed (0.5 mg Pt/cm² Cathode, 0.5 mg Pt-Rh/cm² Anode) Carbon-based Porous Electrodes.

The results in Figure 16 yield the following current density equations for cells operating in 9N KOH at 55 to 60 °C:

$$\Delta V_J \text{ (mV)} = -0.18\Delta J \quad \text{for } J = 40 \text{ to } 100 \text{ mA/cm}^2 \text{ operating in O}_2$$

or

$$\Delta V_J \text{ (mV)} = -0.31\Delta J \quad \text{for } J = 40 \text{ to } 100 \text{ mA/cm}^2 \text{ operating in air}$$

where J is in mA/cm². The performance of a single cell with supported noble metal electrocatalyst (0.5 mg Pt-Rh/cm² anode, 0.5 mg Pt/cm² cathode) in 12N KOH at 65°C is shown in **Figure 17**. These results, reported in 1986, are comparable to those obtained in 1965. The iR -free electrode potentials (vs. RHE) at 100 mA/cm² in Figure 17 are 0.9 V with O₂ and 0.85 V with air. One major difference between the early cathodes and the cathodes in current use is that the limiting current for O₂ reduction from air has been improved (i.e., 100 to 200 mA/cm² improved to >250 mA/cm²).

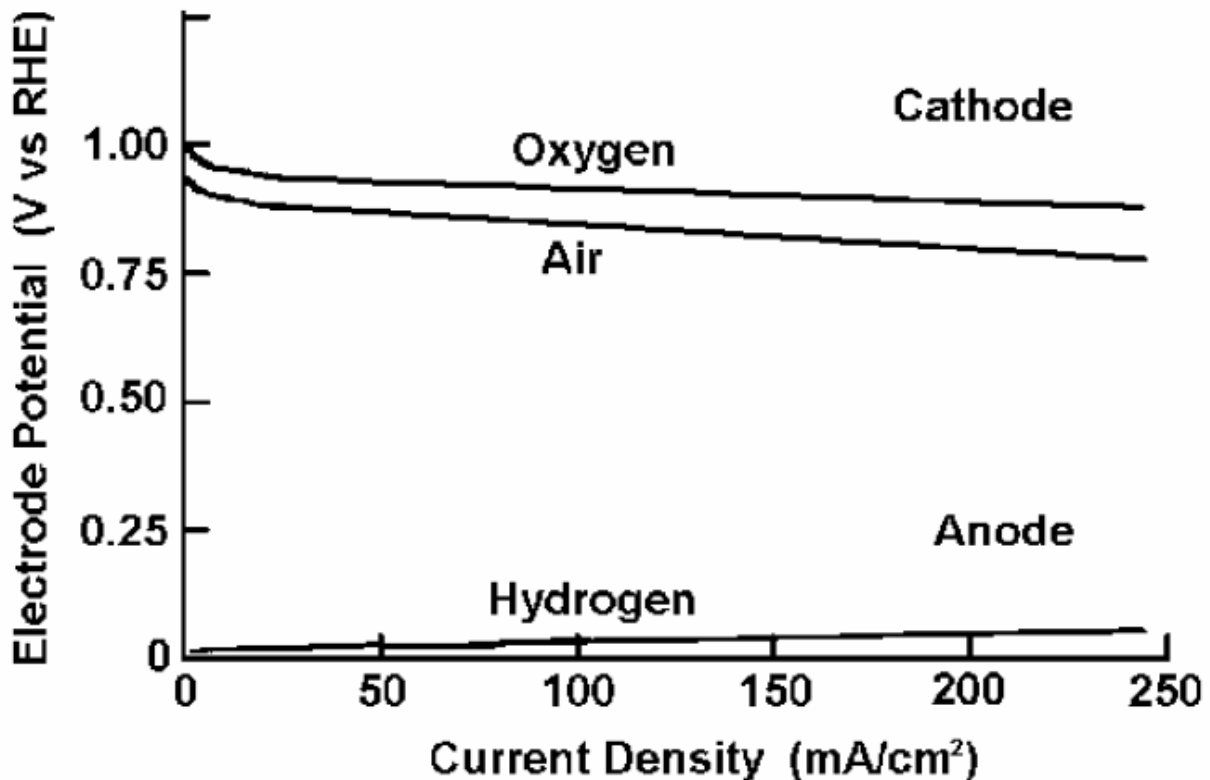


Figure 17: iR Free Electrode Performance with O₂ and Air in 12N KOH at 65 °C. Catalyzed (0.5 mg Pt/cm² Cathode, 0.5 mg Pt-Rh/cm² Anode), Carbon-based Porous Electrodes.

These results yield the following equations for cells operating in 12N KOH at 65°C:

$$\Delta V_J \text{ (mV)} = -0.25\Delta J \quad \text{for } J = 50 \text{ to } 200 \text{ mA/cm}^2 \text{ operating in O}_2$$

or

$$\Delta V_J \text{ (mV)} = -0.47\Delta J \quad \text{for } J = 50 \text{ to } 200 \text{ mA/cm}^2 \text{ operating in air.}$$

5- Effects of Cell Life

The United Technologies Corporation (UTC) Fuel Cells H₂/O₂ alkaline technology exhibits a degradation of ~25 mV/1,000 hours. AFC cell stacks have demonstrated sufficiently stable operation for at least 5,000 hours, with degradation rates of 20 mV per 1,000 hours or less. Siemens reported a total of >8,000 operating hours with approximately 20 units. For large scale utility applications, economics demand operating times exceeding 40,000 hours, which presents perhaps the most significant obstacle to commercialization of AFC devices for stationary electric power generation.

3- PHOSPHORIC ACID FUEL CELLS (PAFCs)

The phosphoric acid fuel cell (PAFC) was the first fuel cell technology to be commercialized. The number of units built exceeds any other fuel cell technology, with over 85 MW of demonstrators that have been tested, are being tested, or are being fabricated worldwide. Most of the plants are in 50 to 200 kW capacity range, but large plants of 1 MW and 5 MW have been built. The largest plant operated to date achieved 11 MW of grid quality ac power.

Figure 18 depicts the operating configuration of the phosphoric acid cell.

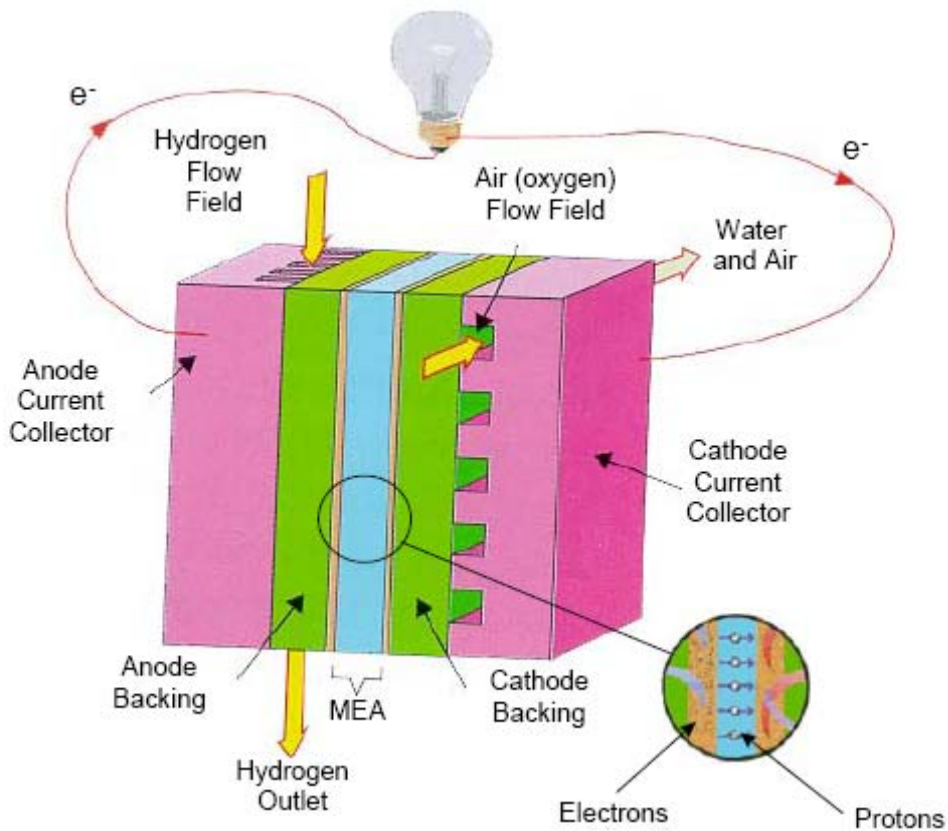
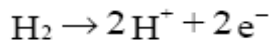
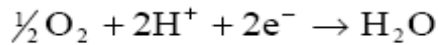


Figure 18: Principles of Operation of Phosphoric Acid Fuel Cell.

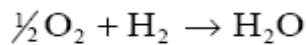
The electrochemical reactions occurring in PAFCs are:



at the anode, and



at the cathode. The overall cell reaction is



The electrochemical reactions occur on highly dispersed electro-catalyst particles supported on carbon black. Platinum (Pt) or Pt alloys are used as the catalyst at both electrodes.

The PAFC have a similar design with the PEMFC. The electrolyte used for PAFC is concentrated phosphoric acid (H_3PO_4), allowing operation at temperatures higher than the PEMFC (i.e., over 100°C). This electrolyte is contained in a silicon carbide matrix, and catalysts are typically made of Pt.

Cell Components

There have been only minor changes in cell design in recent years. The major U.S. manufacturer, UTC Fuel Cells, has concentrated on improving cell stability and life, and in improving the reliability of system components at reduced cost.

Technological advances of the components of this type of fuel cells have been extensively documented over the last 40 years, and a brief summary is presented in **Table 2**.

Table 2: PAFC Component Characteristics

Component	Ca.1965	Ca.1975	Current status
Anode	PTFE-bonded Pt black	PTFE-bonded Pt/C Vulcan XC-72	PTFE-bonded Pt/C Vulcan XC-72
	9 mg Pt/cm ²	0.25 mg Pt/cm ²	0.1 mg Pt/cm ²
Cathode	PTFE-bonded Pt black	PTFE-bonded Pt/C Vulcan XC-72	PTFE-bonded Pt/C Vulcan XC-72
	9 mg Pt /cm ²	0.5 mg Pt/cm ²	0.5 mg Pt/cm ²
Electrode Support	Ta mesh screen	Carbon paper	Carbon paper
Electrolyte Support	Glass fiber paper	PTFE-bonded SIC	PTFE-bonded SIC
Electrolyte	85% H_3PO_4	95% H_3PO_4	100% H_3PO_4

The operating temperatures and acid concentrations of PAFCs have increased to achieve higher cell performance; temperatures of about 200°C and acid concentrations of 100 % H_3PO_4 are commonly used today. Although the present practice is to operate at atmospheric pressure, the operating pressure of PAFCs surpassed 8 atm in the 11 MW electric utility demonstration plant, confirming an increase in power plant efficiency. However, a number of issues remain whether to design and operate PAFC units at atmospheric vs. pressurized conditions.

Primarily, small, multi-kW PAFC power units that were the focus of initial commercial



applications led to atmospheric pressure operation. Although pressurization increased efficiency (lower fuel cost), it complicated the power unit - resulting in higher capital cost. The economic trade-off favored simpler, atmospheric operation for early commercial units.

Another important issue, independent of power unit size, is that pressure promotes corrosion. Phosphoric acid electrolyte (H_3PO_4) produces a vapor. This vapor, which forms over the electrolyte, is corrosive to cell locations other than the active cell area. These cell locations are at a mixed voltage (open circuit and cell voltage), that can be over $\sim 0.8\text{V}/\text{cell}$. That is the limit above which corrosion occurs (active area limited to operation under $\sim 0.8\text{ V}/\text{cell}$). An increase in cell total pressure causes the partial pressure of the H_3PO_4 vapor to increase, causing increased corrosion in the cell. Cell temperature must also be increased with pressurized conditions to produce steam for the steam reformer.

Carbon black and graphite were sufficiently stable to replace the more expensive gold-plated tantalum cell hardware used at the time. The use of high-surface area graphite to support Pt permitted a dramatic reduction in Pt loading without sacrificing electrode performance. It was reported that **"without graphite, a reasonably inexpensive acid fuel cell would be impossible, since no other material combines the necessary properties of electronic conductivity, good corrosion resistance, low density, surface properties (especially in high area form) and, above all, low cost"**. However, carbon corrosion and Pt dissolution become an issue at cell voltages above $\sim 0.8\text{ V}$. Consequently, low current densities at cell voltage above 0.8 V and hot idle at open circuit potential should be avoided.

The porous electrodes contain a mixture of electro-catalyst supported on carbon black and a polymeric binder, usually PTFE (30 to 50 wt %). The PTFE binds the carbon black particles together to form an integral, but porous, structure that is supported on a porous graphite substrate. The graphite structure serves as a support for the electro-catalyst layer, as well as the current collector. A typical graphite structure used in PAFCs has an initial porosity of about 90 %, which is reduced to about 60 % by impregnation with 40 wt % PTFE. This wet-proof graphite structure contains macropores of 3 to 50 μm diameter (median pore diameter of about 12.5 μm) and micropores with a median pore diameter of about 34 Å for gas permeability. The composite structure, consisting of a carbon black/PTFE layer on the graphite substrate, forms a stable, three-phase interface in the fuel cell, with H_3PO_4 electrolyte on one side (electro-catalyst side) and the reactant gas environment on the other.

A bipolar plate separates the individual cells and electrically connects them in series in a fuel cell stack. In some designs, the bipolar plate also contains gas channels that feed the reactant gases to the porous electrodes and remove the reaction products and inerts. Bipolar plates made from graphite resin mixtures that are carbonized at low temperature ($\sim 900^\circ\text{C}$) are not suitable because of their rapid degradation in PAFC operating environments. However, corrosion stability is improved by heat treatment to $2,700^\circ\text{C}$, i.e., the corrosion current is reduced by two orders of magnitude at 0.8 V in 97 % H_3PO_4 at 190°C and 4.8 atm. The all-graphite bipolar plates are sufficiently corrosion-resistant for a projected life of 40,000 hours in PAFCs, but they are still relatively costly to produce.

A typical PAFC stack contains cells connected in series to obtain the practical voltage level desired for the load. In such an arrangement, individual cells are stacked with bipolar plates between the cells. The bipolar plates used in early PAFCs consisted of a single piece of graphite



with gas channels machined on either side to direct the flow of fuel and oxidant. Currently, both bipolar plates of the previous design and new designs consisting of several components are being considered. In the multi-component bipolar plates, a thin impervious plate separates the reactant gases in adjacent cells in the stack, and separate porous plates with ribbed channels are used to direct gas flow. In a cell stack, the impervious plate is subdivided into two parts, and each joins one of the porous plates. The electrolyte vaporizes so that a portion of H_3PO_4 escapes from the cell in the air stream over time. An electrolyte reservoir plate (ERP), made of porous graphite, provides enough electrolyte to achieve a 40,000-hour cell life goal (there is no electrolyte replacement). The ERP also accommodates increases in electrolyte volume due to an increase in H_2O , so the porous graphite electrodes don't flood. These fluctuations in electrolyte volume occur during start-up and during transient operation. The porous structure, which allows rapid gas transport, is also used to store additional acid to replenish the supply lost by evaporation during the cell operating life.

In PAFC stacks, provisions must be included to remove heat generated during cell operation. In practice, heat has been removed by either liquid (two-phase water or a dielectric fluid) or gas (air) coolants that are routed through cooling channels located (usually about every fifth cell) in the cell stack. Liquid cooling requires complex manifolds and connections, but better heat removal is achieved than with air-cooling. The advantage of gas cooling is its simplicity, reliability, and relatively low cost. However, the size of the cell is limited, and the air-cooling passages must be much larger than the liquid-cooling passages.

Development Components

Phosphoric acid electrode/electrolyte technology has reached a level of maturity at which developers commit resources for commercial capacity, multi-unit demonstrations and preprototype installations. UTC Fuel Cells has 25 (200 kW) atmospheric pressure power plants that have operated between 30,000 to 40,000 hours. Most cell parts are graphite, and there has been no electrolyte replacement over the cell life of 40,000 hours. Grid-independent units undergo extensive cycling. Cell components are manufactured at scale and in large quantities, demonstrating confidence that predicted performance will be met. However, further increases in power density and reduced cost are needed to achieve economic competitiveness with other energy technologies, as expressed in the early 1990s. Fuel cell developers continue to address these issues.

In 1992, UTC Fuel Cells' predecessor, International Fuel Cells, completed a government sponsored, advanced water-cooled PAFC development project to improve the performance and reduce the cost of both its atmospheric and pressurized technology for both on-site and utility applications. The project focused on five major activities:

- 1- produce a conceptual design of a large stack with a goal of 0.188 W/cm^2 , 40,000 hour useful life, and a stack cost of less than \$400/kW
- 2- test pressurized Configuration "B" single cells developed in a previous program, but improved with proprietary design advances in substrates, electrolyte reservoir plates, catalysts, seals, and electrolyte matrix to demonstrate the 0.188 W/cm^2 power density goal
- 3- test a pressurized short stack with subscale size, improved component cells, and additional improvements in the integral separators and coolers to confirm the stack design



- 4- test a pressurized short stack of improved full-size cell components, nominal 1 m^2 size, to demonstrate the 0.188 W/cm^2 power density goal
- 5- test an advanced atmospheric "on-site" power unit stack with the improved components.

Several important technology development efforts for which details have been published include catalyst improvements, advanced gas diffusion electrode development, and tests on materials that offer better carbon corrosion protection. Transition metal (e.g., iron, cobalt) organic macrocycles from the families of tetramethoxyphenylporphyrins (TMPP), phthalocyanines (PC), tetraazaannulenes (TAA) and tetraphenylporphyrins (TPP) have been evaluated as O_2 -reduction electro-catalysts in PAFCs. One major problem with these organic macrocycles is their limited chemical stability in hot concentrated phosphoric acid. However, after heat treatment of the organic macrocycle (i.e., CoTAA, CoPC, CoTMPP, FePC, FeTMPP) on carbon at about 500 to 800 °C, the pyrolyzed residue exhibits electro-catalytic activity that, in some instances, is comparable to that of Pt and has promising stability, at least up to about 100 °C. Another successful approach for enhancing the electro-catalysis of O_2 -reduction is to alloy Pt with transition metals such as Ti, Cr, V, Zr, and Ta. The enhancement in electro-catalytic activity has been explained by a correlation between the optimum nearest-neighbor distance of the elements in the alloy and the bond length in O_2 .

Conventional cathode catalysts comprise either platinum or platinum alloys supported on conducting carbon black at 10 wt % platinum. Present platinum loadings on the anode and cathode are 0.1 mg/cm^2 and 0.5 mg/cm^2 , respectively. It has been suggested by Ito, et al., that the amount of platinum may have been reduced to the extent that it might be cost effective to increase the amount of platinum loading on the cathode. However, a problem exists in that fuel cell stack developers have not experienced satisfactory performance improvements when increasing the platinum loading. Johnson Matthey Technology Centre (J-M) presented data that resulted in improved performance nearly in direct proportion to that expected based on the increase in platinum. Initial tests by J-M confirmed previous results - that using platinum alloy catalyst with a 10 wt % net platinum loading improves performance. Platinum/nickel alloy catalysts yielded a 49 wt % increase in specific activity over pure platinum. This translated into a 39 mV improvement in the air electrode performance at 200 mA/cm^2 .

Johnson Matthey then determined that the platinum loading in the alloyed catalyst could be increased up to 30 wt % while retaining the same amount of platinum without any decrease in specific activity or performance; the amount of nickel, hence the total amount of alloyed catalyst, decreased. Next, J-M researchers increased the amount of platinum from 10 to 30 wt % while keeping the same nickel catalyst loading. The total amount of alloyed catalyst increased in this case. Results showed an additional 36 wt % increase in specific activity, which provided another 41 mV increase at 200 mA/cm^2 . The ideal voltage increase would have been 46 mV for this increase in platinum. Thus, the performance increase obtained experimentally was nearly in direct proportion to the theoretical amount expected. The type of carbon support did not seem to be a major factor, based on using several typical supports during the tests.

The anode of a phosphoric acid fuel cell is subject to a reduction in performance when even low amounts of contaminants are preferentially absorbed on the noble catalysts. Yet, hydrogen-rich fuel gases, other than pure hydrogen, are produced with contaminant levels well in excess of the anode's tolerance limit. Of particular concern are CO, COS, and H_2S in the fuel gas. The fuel



stream in a state-of-the-art PAFC anode, operating at approximately 200 °C, must contain 1 vol % or less of CO, less than 50 ppmv of COS plus H₂S, and less than 20 ppmv of H₂S. Current practice is to place COS and H₂S cleanup systems and CO shift converters prior to the cell (normally in the fuel processor before reforming) to reduce the fuel stream contaminant levels to the required amounts. Giner, Inc. performed experiments to develop a contaminant tolerant node catalyst in order to reduce or eliminate the cleanup equipment. An anode catalyst, G87A-17-2, was identified that resulted in only a 24 mV loss from reference when exposed to a 75 % H₂, 1 % CO, 24 % CO₂, 80 ppm H₂S gas mixture at 190 °C, 85 % fuel utilization, and 200 mA/cm². A baseline anode experienced a 36 mV loss from the reference at the same conditions. At 9.2 atm pressure, the anode loss was only 19 mV at 190 °C and 17 mV at 210 °C (compared with pure H₂) with a gas of 71 % H₂, 5 % CO, 24 % CO₂, and 200 ppm H₂S. Economic studies comparing the tradeoff between decreased cell performance with increased savings in plant cost showed no advantage when the new anode catalyst was used with gas containing 1 % CO/200 ppm H₂S. A \$7/kW increase resulted with the 5 % CO gas (compared to a 1 % CO gas) at a 50 MW size. Some savings would result by eliminating the low temperature shift converter. The real value of the catalyst may be its ability to tolerate excessive CO and H₂S concentrations during fuel processor upsets, and to simplify the system by eliminating equipment.

As previously mentioned, state-of-the-art gas diffusion electrodes are configured to provide an electrolyte network and a gas network formed with the mixture of carbon black and PTFE. In the electrodes, carbon black agglomerates, consisting of small primary particles 0.02 to 0.04 μm, are mixed with much larger PTFE particles of ~0.3 μm. The carbon black surface may not be covered completely by the PTFE because of the large size of conventional PTFE particles. The space in the agglomerates or the space between the agglomerates and PTFE may act as gas networks at the initial stage of operation, but fill with electrolyte eventually because of the small contact angle of carbon black, uncovered with PTFE, to electrolyte (<90°), resulting in the degradation of cell performance. Attempts to solve this flooding problem by increasing the PTFE content have not been successful because of the offset in performance resulting from the reduction of catalyst utilization. Higher performance and longer lifetime of electrodes are intrinsically at odds, and there is a limit to the improvement in performance over life by optimizing PTFE content in the state-of-the-art electrode structures. Watanabe, et al. proposed preparing an electrode utilizing 100 % of catalyst clusters, where the functions of gas diffusion electrodes were allotted completely to a hydrophilic, catalyzed carbon black and a wet-proofed carbon black. The former worked as a fine electrolyte network, and the latter worked as a gas-supplying network in a reaction layer. Higher utilization of catalyst clusters and longer life at the reaction layer were expected, compared to state-of-the-art electrodes consisting of the uniform mixture of catalyzed carbon black and PTFE particles. The iR-free electrode potentials for the reduction of oxygen and air at 200 mA/cm² on the advanced electrode were 10 mV higher than those of the conventional electrode.

There is a trade-off between high power density and cell life performance. One of the major causes of declining cell performance over its life is that electrode flooding and drying, caused by migration of phosphoric acid between the matrix and the electrodes, occurs during cell load cycling. Researchers at Fuji Electric addressed two approaches to improve cell life performance while keeping power density high. In one, the wettability of the cathode and anode were optimized, and in the other a heat treatment was applied to the carbon support for the cathode



catalyst. During tests, it was observed that a cell with low cathode wettability and high anode wettability was more than 50 mV higher than a cell with the reverse wetting conditions after 40 start/stop cycles.

The use of carbon black with large surface area to improve platinum dispersion on supports was investigated as a method to increase the power density of a cell. However, some large surface area carbon blacks are fairly corrosive in hot potassium acid, resulting in a loss of catalytic activity. The corrosivity of the carbon support affects both the rate of catalyst loss and electrode flooding and, in turn, the life performance of a cell. Furnace black has been heat treated at high temperature by Fuji Electric to increase its resistance to corrosion. It was found that corrosion could be reduced and cell life performance improved by heat treating carbon supports at high temperature, at least to around 3,000 °C.

More recently, UTC Fuel Cells cites improvements to achieve 40,000 hour cell life through better cell temperature control, increasing H_3PO_4 inventory, and incorporating electrolyte reservoir plates in the cell stack.

**Cell Performance**

Cell performance for any fuel cell is a function of pressure, temperature, reactant gas composition, and fuel utilization. In addition, performance can be adversely affected by impurities in both the fuel and oxidant gases.

The major polarization occurs at the cathode, and furthermore, the polarization is greater with air than with pure oxygen because of dilution of the reactant. The anode exhibits very low polarization on pure H_2 , and increases when CO is present in the fuel gas. The ohmic (iR) loss in PAFCs is also relatively small, amounting to about 12 mV at 100 mA/cm^2 .

Typical PAFCs will generally operate in the range of 100 to 400 mA/cm^2 at 600 to 800 mV/cell. Voltage and power constraints arise from increased corrosion of platinum and carbon components at cell potentials above approximately 800 mV.

1- Effect of Pressure

Even though pressure operation is not being pursued, it is still of interest for possible future development. It is well known that an increase in the cell operating pressure enhances the performance of PAFCs. The theoretical change in voltage (ΔV_P) as a function of pressure (P) is expressed as:

$$\Delta V_P (\text{mV}) = \frac{(3)(2.3 RT)}{2F} \log \frac{P_2}{P_1}$$

$$\text{where } \frac{3(2.3 RT)}{2F} = 138 \text{ mV at } 190^\circ\text{C (374 } ^\circ\text{F)}$$

where P_1 and P_2 are different cell pressures.

Experimental data reported that the effect of pressure on cell performance at 190°C and 323 mA/cm^2 is correlated by the equation:

$$\Delta V_P (\text{mV}) = 146 \log \frac{P_2}{P_1}$$

for a temperature range of $177^\circ\text{C} < T < 218^\circ\text{C}$ and a pressure range of $1 \text{ atm} < P < 10 \text{ atm}$.

The improvement in cell performance at higher pressure and high current density can be attributed to a lower diffusion polarization at the cathode and an increase in the reversible cell potential. In addition, pressurization decreases activation polarization at the cathode because of the increased oxygen and water partial pressures. If the partial pressure of water is allowed to increase, a lower acid concentration will result. This will increase ionic conductivity and bring about a higher exchange current density. The net outcome is a reduction in ohmic losses.

2- Effect of Temperature

An increase in temperature has a beneficial effect on cell performance because activation polarization, mass transfer polarization, and ohmic losses are reduced.

The kinetics for the reduction of oxygen on Pt improves as the cell temperature increases. At a mid-range operating load ($\sim 250 \text{ mA/cm}^2$), the voltage gain (ΔV_T) with increasing temperature of pure H_2 and air is correlated by:



$$\Delta V_T \text{ (mV)} = 1.15 (T_2 - T_1) \text{ (}^\circ\text{C)}$$

for a temperature range of $180^\circ\text{C} < T < 250^\circ\text{C}$.

Although temperature has only a minimal effect on the H_2 oxidation reaction at the anode, it is important in terms of the amount of CO that can be absorbed by the anode. **Figure 19** shows that increasing the cell temperature results in increased anode tolerance to CO absorption. A strong temperature effect was also observed using simulated coal gas. Below 200°C , the cell voltage drop was significant. Experimental data suggest that the effect of contaminants is not additive, indicating that there is an interaction between CO and H_2S . Increasing temperature increases performance, but elevated temperature also increases catalyst sintering, component corrosion, electrolyte degradation, and evaporation. UTC Fuel Cells operates its phosphoric acid cells at 207°C , which is a compromise that allows reasonable performance at a life of 40,000 hours.

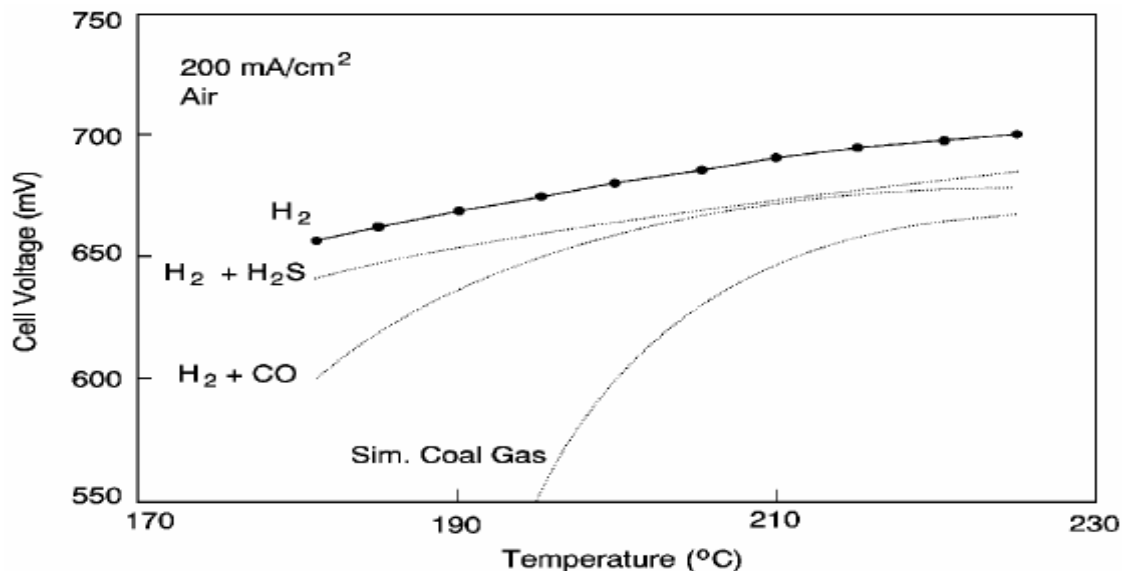


Figure 19: Effect of Temperature: Ultra-High Surface Area Pt Catalyst.

3- Effect of Reactant Gas Composition and Utilization

Increasing reactant gas utilization or decreasing inlet concentration results in decreased cell performance due to increased concentration polarization and Nernst losses. These effects are related to the partial pressures of reactant gases and are discussed below.

Oxidant: The oxidant composition and utilization are parameters that affect the cathode performance, air, which contains $\sim 21\%$ O_2 , is the obvious oxidant for terrestrial application PAFCs. The use of air with $\sim 21\%$ O_2 instead of pure O_2 results in a decrease in the current density of about a factor of three at constant electrode potential. The polarization at the cathode increases with an increase in O_2 utilization.

Based on experimental data, the voltage loss due to a change in oxidant utilization can be described by:



$$\Delta V_{\text{Cathode}} (\text{mV}) = 148 \log \frac{(\bar{P}_{\text{O}_2})_2}{(\bar{P}_{\text{O}_2})_1} \quad 0.04 \leq \frac{\bar{P}_{\text{O}_2}}{\bar{P}_{\text{Total}}} \leq 0.20$$

$$\Delta V_{\text{Cathode}} (\text{mV}) = 96 \log \frac{(\bar{P}_{\text{O}_2})_2}{(\bar{P}_{\text{O}_2})_1} \quad 0.20 < \frac{\bar{P}_{\text{O}_2}}{\bar{P}_{\text{Total}}} < 1.00$$

where \bar{P}_{O_2} is the average partial pressure of O_2 .

The first equation will generally apply to fuel cells using air as the oxidant and the second equation for fuel cells using an O_2 -enriched oxidant.

Fuel: Hydrogen for PAFC power plants will typically be produced from conversion of a wide variety of primary fuels such as CH_4 (e.g., natural gas), petroleum products (e.g., naphtha), coal liquids (e.g., CH_3OH), or coal gases. Besides H_2 , CO and CO_2 are also produced during conversion of these fuels (unreacted hydrocarbons are also present). These reformed fuels contain low levels of CO (after steam reforming and shift conversion reactions in the fuel processor) that cause anode CO absorption in PAFCs. The CO_2 and unreacted hydrocarbons (e.g., CH_4) are electrochemically inert and act as diluents. Because the anode reaction is nearly reversible, the fuel composition and hydrogen utilization generally do not strongly influence cell performance. The voltage change due to a change in the partial pressure of hydrogen (which can result from a change in either the fuel composition or utilization) can be described by:

$$\Delta V_{\text{Anode}} (\text{mV}) = 55 \log \frac{(\bar{P}_{\text{H}_2})_2}{(\bar{P}_{\text{H}_2})_1}$$

where \bar{P}_{H_2} is the average partial pressure of H_2 .

At 190°C , the presence of 10 % CO_2 in H_2 should cause a voltage loss of about 2 mV. Thus, diluents in low concentrations are not expected to have a major effect on electrode performance; however, relative to the total anode polarization (i.e., 3 mV/100 mA/cm²), the effects are large. It

has been reported that with pure H_2 , the cell voltage at 215 mA/cm² remains nearly constant at H_2 utilizations up to 90 %, and then it decreases sharply at H_2 utilizations above this value. Low utilizations, particularly oxygen utilization, yield high performance. Low utilizations, however, result in poor fuel use. Optimization of this parameter is required. State-of-the-art utilizations are on the order of 85 % and 50 % for the fuel and oxidant, respectively.

4- Effect of Impurities

The concentrations of impurities entering the PAFC are very low relative to diluents and reactant gases, but their impact on performance is significant. Some impurities (e.g., sulfur compounds) originate from fuel gas entering the fuel processor and are carried into the fuel cell with the



reformed fuel, whereas others (e.g., CO) are produced in the fuel processor.

Carbon Monoxide: The presence of CO in a H₂-rich fuel has a significant effect on anode performance because CO affects Pt electrode catalysts. CO absorption is reported to arise from the dual site replacement of one H₂ molecule by two CO molecules on the Pt surface.

According to this model, the anodic oxidation current at a fixed overpotential, with (i_{CO}) and without (i_{H₂}) CO present, is given as a function of CO coverage (θ_{CO}) by:

$$\frac{i_{CO}}{i_{H_2}} = (1 - \theta_{CO})^2$$

For [CO]/[H₂] = 0.025, θ_{CO} = 0.31 at 190°C

therefore, i_{CO} is about 50 % of i_{H₂}.

Both temperature and CO concentration have a major influence on the oxidation of H₂ on Pt in CO containing fuel gases. Benjamin, et al. derived the following equation for the voltage loss resulting from CO absorption as a function of temperature:

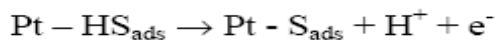
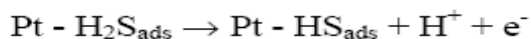
$$\Delta V_{CO} = k(T) ([CO]_2 - [CO]_1)$$

where k(T) is a function of temperature, and [CO]₁ and [CO]₂ are the mole fractions CO in the fuel gas.

Sulfur Containing Compounds: Hydrogen sulfide and carbonyl sulfide (COS) impurities in fuel gases from fuel processors and coal gasifiers can reduce the effectiveness of fuel cell catalysts.

Concentrations of these compounds must also be limited in a power plant's fuel processing section, because the fuel reformer too has catalysts. As a result, sulfur must be removed prior to fuel reforming with the non-sulfur tolerant catalysts now in use in PAFC power plants. It is prudent to be concerned about sulfur effects in the cell, however, because the fuel processor catalyst's tolerance limits may be less than the fuel cell catalyst's or there could be an upset of the fuel processor sulfur guard with sulfur passing through to the cell. The concentration levels of H₂S in an operating PAFC (190 to 210 °C, 9.2 atm, 80 % H₂ utilization, <325 mA/cm²) that can be tolerated by Pt anodes without suffering a destructive loss in performance are <50 ppm (H₂S + COS) or <20 ppm (H₂S). Rapid cell failure occurs with fuel gas containing more than 50 ppm H₂S. Sulfur does not affect the cathode, and the impact of sulfur on the anodes can be re-activated by polarization at high potentials (i.e., operating cathode potentials). A synergistic effect between H₂S and CO negatively impacts cell performance.

Experimental studies by Chin and Howard indicate that H₂S adsorbs on Pt and blocks the active sites for H₂ oxidation. The following electrochemical reactions:

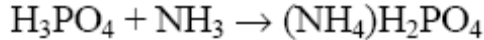


Elemental sulfur (in the last equation) is expected on Pt electrodes only at high anodic potentials; at sufficiently high potentials, sulfur is oxidized to SO₂. The extent of catalyst masking by H₂S



increases with increasing H_2S concentration, electrode potential, and exposure time. The effect of H_2S , however, decreases with increasing cell temperature.

Other Compounds: The effects of other compounds (such as those containing nitrogen) on PAFC performance has been adequately reviewed by Benjamin, et al.. Molecular nitrogen acts as a diluent but other nitrogen compounds (e.g., NH_3 , HCN , NO_x) may not be as innocuous. NH_3 in the fuel or oxidant gases reacts with H_3PO_4 to form a phosphate salt, $(\text{NH}_4)\text{H}_2\text{PO}_4$,



which decreases the rate of O_2 reduction. A concentration of less than 0.2 mol % $(\text{NH}_4)\text{H}_2\text{PO}_4$ must be maintained to avoid unacceptable performance losses. Consequently, the amount of molecular nitrogen must be limited to 4 % because it will react with hydrogen to form NH_3 . The effects of HCN and NO_x on fuel cell performance have not been clearly established.

5- Effects of Current Density

The voltage that can be obtained from a PAFC is reduced by ohmic, activation, and concentration losses that increase with increasing current density. The magnitude of this loss can be approximated by the following equations:

$$\Delta V_J (\text{mV}) = -0.53 \Delta J \quad \text{for } J = 100 \text{ to } 200 \text{ mA/cm}^2$$

$$\Delta V_J (\text{mV}) = -0.39 \Delta J \quad \text{for } J = 200 \text{ to } 650 \text{ mA/cm}^2$$

Similarly, at atmospheric conditions, the magnitude of this loss can be approximated by:

$$\Delta V_J (\text{mV}) = -0.74 \Delta J \quad \text{for } J = 50 \text{ to } 120 \text{ mA/cm}^2$$

$$\Delta V_J (\text{mV}) = -0.45 \Delta J \quad \text{for } J = 120 \text{ to } 215 \text{ mA/cm}^2$$

6- Effects of Cell Life

One of the primary areas of research is in extending cell life. The goal is to maintain the performance of the cell stack during a standard utility application (~40,000 hours). Previous state-of-the-art PAFCs showed the following degradation over time:

$$\Delta V_{\text{lifetime}} (\text{mV}) = -3 \text{ mV/1,000 hours}$$

Assuming that the loss in efficiency is due solely to cell voltage loss, the maximum degradation rate can be determined as:

$$\Delta V_{\text{lifetime}} (\text{mV}) = -2 \text{ mV/1,000 hours}$$