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:

- **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.

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**Figure 9:** Schematic of Major Unit Operations Typical of Reformer-Based PEFC Systems.
• 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 10.

Figure 10: 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: \( \text{CH}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 \)
- 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 2 shows a comparison of the gas compositions obtained after using different options for the reforming process, using methanol as fuel.

<table>
<thead>
<tr>
<th>Composition (dry gas, %)</th>
<th>Steam Reforming</th>
<th>Partial Oxidation</th>
<th>Autothermal Reforming</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2 )</td>
<td>67</td>
<td>45</td>
<td>55</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>22</td>
<td>20</td>
<td>22</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>-</td>
<td>22</td>
<td>21</td>
</tr>
<tr>
<td>( \text{CO} )</td>
<td>-</td>
<td>-</td>
<td>2</td>
</tr>
</tbody>
</table>

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 \( \text{CO}_2 \), a significant contributor to the environment pollution. To eliminate this, various other technologies are being developed as potential solutions for “\( \text{CO}_2\)-free” hydrogen production from fossil fuels, such as the **pyrolytic cracking** of natural gas:

\( \text{CH}_4 \rightarrow \text{C} + 2 \text{H}_2 \)

- **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 3** 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 °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 3: Hydrogen Storage Properties of Metal Hydrides

<table>
<thead>
<tr>
<th>Metal Hydride System</th>
<th>Mg/MgH₂</th>
<th>Ti/TiH₂</th>
<th>V/VH₂</th>
<th>Mg₂Ni/Mg₂NiH₆</th>
<th>FeTi/FeTiH₄</th>
<th>LaNi₅/LaNi₅H₆</th>
<th>LH₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen content as mass fraction (%)</td>
<td>7.7</td>
<td>4.0</td>
<td>2.1</td>
<td>3.2</td>
<td>1.8</td>
<td>1.4</td>
<td>100.0</td>
</tr>
<tr>
<td>Hydrogen content by volume (kg/m³)</td>
<td>0.101</td>
<td>0.15</td>
<td>0.09</td>
<td>0.08</td>
<td>0.096</td>
<td>0.09</td>
<td>0.077</td>
</tr>
<tr>
<td>Energy content (based on HHV) (MJ/kg)</td>
<td>9.9</td>
<td>5.7</td>
<td>3.0</td>
<td>4.5</td>
<td>2.5</td>
<td>1.95</td>
<td>143.0</td>
</tr>
<tr>
<td>Energy content (based on LHV) (MJ/kg)</td>
<td>8.4</td>
<td>4.8</td>
<td>2.5</td>
<td>3.8</td>
<td>2.1</td>
<td>1.6</td>
<td>120.0</td>
</tr>
<tr>
<td>Heat of reaction (kJ/Nm³)</td>
<td>3360</td>
<td>5600</td>
<td>—</td>
<td>2800</td>
<td>1330</td>
<td>1340</td>
<td>—</td>
</tr>
<tr>
<td>Heat of reaction (kJ/mol)</td>
<td>76.3</td>
<td>127.2</td>
<td>—</td>
<td>63.6</td>
<td>30.2</td>
<td>30.4</td>
<td>—</td>
</tr>
<tr>
<td>Heat of reaction (as fraction of HHV) (%)</td>
<td>26.7</td>
<td>44.5</td>
<td>—</td>
<td>22.2</td>
<td>10.6</td>
<td>10.6</td>
<td>—</td>
</tr>
<tr>
<td>Heat of reaction (as fraction of LHV) (%)</td>
<td>31.6</td>
<td>52.6</td>
<td>—</td>
<td>26.3</td>
<td>12.5</td>
<td>12.6</td>
<td>—</td>
</tr>
</tbody>
</table>