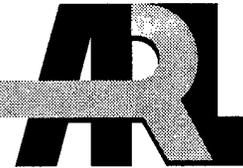


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# An Overview of Hydrogen Generation and Storage for Low-Temperature PEM Fuel Cells

Charles W. Walker, Jr., Rhongzhong Jiang, and Deryn Chu

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## An Overview of Hydrogen Generation and Storage for Low-Temperature PEM Fuel Cells

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## Abstract

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Successful deployment of man-portable, low-temperature proton exchange membrane (PEM) fuel cells depends on finding a suitable hydrogen fuel that is easily stored and transported, inexpensive, readily available, safe, and practical for use in light and compact vessels. Because storage of hydrogen as a compressed gas in metal cylinders is inefficient and heavy, many alternative methods to store hydrogen have been investigated. This report lists several technologies for the storage and generation of hydrogen and provides brief descriptions.

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# 1. Introduction

Based on operating temperature alone, proton exchange membrane (PEM) fuel cells are the most likely technology to be used for small-scale portable power (PEM 80 °C, phosphoric acid 200 °C, molten carbonate 650 °C, and solid oxide 1100 °C). In addition, PEM cells have several other attractive characteristics such as light weight, relatively low cost, low volume, simple sealing and mechanical design, low corrosion, good cell/stack life, and fast start-up time. Drawbacks include the use of platinum catalysts that are costly and easily poisoned by carbon monoxide, and cells are sensitive to changes in temperature and gas pressure. Fuel generation and storage are the most serious technical challenges enabling these small systems to be practical to use. Efficient storage of hydrogen fuel (gravimetric and volumetric) that adds minimal complexity and cost to the system must be available for small PEM fuel cells to be successful.

The U.S. Army is most interested in using its logistic fuels (diesel and JP8) for which the supply, storage, and transportation infrastructure is already in place. Although large-scale hydrocarbon reforming technology is available, the challenge for small systems is in miniaturizing all the component parts of the system (pumps, blowers, regulators, heat exchangers, reactors, valves, etc) and in identifying efficient catalysts that are inexpensive and tolerant to feed stock impurities such as sulfur compounds. Multifuel processing technology has been demonstrated but is not yet an available or "proven" technology and may take many years to mature. The interim solutions have been to research direct methanol fuel cells and to develop convenient methods for hydrogen storage. Several approaches to the storage and delivery of hydrogen are discussed.

## 2. Gaseous Hydrogen

On a weight basis, the storage of gas in steel cylinders is very inefficient. Because of the weight of steel cylinders, only about 1 percent by weight is hydrogen (even less in small-size cylinders) [1,2]. Compressed gas at very high pressure deviates from the ideal gas law, yielding only about 82 percent of the hydrogen calculated for room temperature and the commonly used pressure of 175 atm (approximately 2600 psi) [1]. Increasing pressure causes further deviation and requires the cylinder wall thickness to be increased. A pressure vessel at low temperature or 80 K (the temperature of liquid nitrogen) can increase storage by a factor of 3.5 compared to ambient temperature [2].

The weight percent of hydrogen stored can be tripled if a composite pressure vessel is used [1]. A compressed hydrogen gas system offered by Structural Composites Industries comprises an aluminum-lined carbon filament wound tank that withstands pressures to 3000 psi. A burst disk rated to 3707 psi prevents tank overpressure. The package weight of 2.93 lb has a capacity of 235 Wh of hydrogen.

Thiokol Corporation (Brigham City, UT) is developing conformable (noncylindrical) high-pressure storage tanks for more efficient onboard fuel packaging than is possible with cylinders. Carbon composite plastic-lined tanks with burst pressures up to 13,750 psi have been achieved.

### 3. Liquid Hydrogen

Liquid H<sub>2</sub> is 800 times more dense than the gas [2]. "Slush hydrogen," which is 50 percent solid and 50 percent liquid hydrogen, is formed at the triple point temperature of 13.8 K and is 15 percent more dense than liquid hydrogen [2]. This is not a man-portable option.

### 4. Cryoadsorbed Hydrogen

High-surface-area materials such as activated carbon can store hydrogen at pressures of about 60 atm at liquid nitrogen temperatures and above, 77 to 150 K [1]. Good storage based on weight and volume is achieved, but this is not a feasible solution for man-portable applications.

### 5. Direct Fuel

In addition to hydrogen, many other fuels may be used directly in a fuel cell system with minimal processing and complexity. Oxidation of the fuel can usually occur with the use of catalysts and low heating.

#### 5.1 Methanol

Methanol-water solutions can be used "directly" without complex reforming steps. Methanol, which is oxidized to H<sub>2</sub> and CO<sub>2</sub>, is the most attractive alternative fuel, because it is easy to store and transport and the oxidation is accomplished at low temperature (60 °C) with the use of a Pt-Ru catalyst. The intermediate compounds formaldehyde and formate, formed during oxidation of methanol, are also possible fuels. However, CO binds strongly to platinum at temperatures below 150 °C and poisons catalyst activity. In addition, methanol crosses over through the PEM to the cathode, where it is oxidized, and results in lowering cell performance. Current research seeks to find new membranes that prevent methanol crossover and to find more efficient catalysts that are tolerant to carbon monoxide poisoning. Because Pt-Ru still seems to be the preferred catalyst, much of the catalyst work has centered on preparation of nanoparticles to increase surface area (thereby increasing activity) and centered on packaging/dispersion of the catalyst to minimize the mass used per electrode and ensure maximum activity.

## 5.2 Organics

Direct oxidation of other organic substances, such as dimethoxymethane [3], trioxane [3], and trimethoxymethane [3,4], has been proposed and studied. All three substances are derivatives of natural gas and should be readily attainable. Complete oxidation should be easy to accomplish since there are no carbon-to-carbon bonds to resist complete oxidation to carbon dioxide [3]. Dimethoxymethane has a low boiling point of 42.3 °C, which renders this compound undesirable. Trioxane is a solid at room temperature (mp 64 °C), which would be easy to transport but is not useful in a fuel cell at temperatures below 55 °C [3]. Trimethoxymethane (trimethyl orthoformate) is the most attractive of the three, with a higher boiling point (105 °C) and lower toxicity than methanol. Complete oxidation to CO<sub>2</sub> occurs with methanol as an intermediate product. Performance of trimethoxymethane is only slightly lower than that of methanol [3].

## 5.3 Inorganics

Nitrogen-containing fuels include hydrazine (N<sub>2</sub>H<sub>4</sub>), which decomposes easily into H<sub>2</sub> and N<sub>2</sub>, and ammonia (NH<sub>3</sub>), which is oxidized at higher temperatures to N<sub>2</sub> and H<sub>2</sub>O. However, hydrazine is highly toxic and expensive. Ammonia is also toxic and corrosive. In addition, residual ammonia must be removed from the fuel [5]. A portable ammonia cracker (reactor temperature 1050 °C, total system weight just over 15 lb) has been developed to convert enough NH<sub>3</sub> to H<sub>2</sub> and N<sub>2</sub> for a 200-W fuel cell [6].

# 6. Carbon Sorption

Claims that very high quantities of hydrogen can be stored in carbon structures are being reported. Assuming these claims are true, several points must be kept in mind beyond the issues of cost and availability of the materials. First, it is not merely how much hydrogen can be stored that is important but how much can be released (i.e., the reversibly stored quantity). It has also been argued that carbons with high sorbent capacity generally have very high surface areas (m<sup>2</sup> g<sup>-1</sup>), which may be compromised by their fragility and inability to withstand crumbling and powdering under normal shock and vibration [7]. Purity of the source of hydrogen could be critical since carbon readily adsorbs many chemical species, most in preference to hydrogen [7]. Impurities may not completely desorb with the hydrogen and could accumulate over time, thereby decreasing the capacity of the carbon and requiring a periodic regeneration.

## 6.1 Carbon Fullerenes

Fullerenes can be hydrogenated electrochemically or catalytically up to 6 wt %, but require significant heat to release H<sub>2</sub> [5]. Material cost and manufacturing capabilities are critical problems.

## 6.2 Nanotubes

Studies report that extremely high amounts of gaseous hydrogen can be stored in carbon cylinders. In one study, single-wall nanotubes delivered up to 110 mAh/g at quite low discharge rates [8]. However, poor kinetics causes capacity to drop precipitously at higher rates. Other problems include material cost and manufacturing capability.

## 6.3 Graphite Nanofibers

Graphite nanofibers can be prepared by metal-catalyzed decomposition (at 450 to 750 °C) of carbon-containing gases to possess a cross-sectional area between 30 to 500 Å and a length between 10 and 100 μm [9]. The fibers consist of graphite platelets aligned either parallel, perpendicular, or at an angle with respect to the face of the metal particle. Separation distance between layers depends on the type of catalyst, gas, and reaction conditions used. The minimum value possible is 3.35 Å [9], while the diameter of hydrogen is 2.89 Å. Thus, an array of pores ( $\geq 3.35$  Å) is well suited for the sorption of hydrogen.

In high-pressure sorption studies [9], researchers exposed graphite nanofibers to hydrogen at 25 °C under a pressure of 112 atm. Pd powder, LaNi<sub>5</sub>, MnNi<sub>4.5</sub>Al<sub>0.5</sub>, active carbon, and graphite were treated similarly. The nanofibers adsorbed between 50 to 450 times more hydrogen volumetrically (L/g) than these other materials and 15 to 150 times more hydrogen by weight fraction. The stored hydrogen (under pressure) is released by opening a regulating valve. Approximately 70 percent of the hydrogen was released from the nanofibers at room temperature, whereas the Pd and alloy samples released no hydrogen until the temperature was raised to 300 °C.

Up to 50 wt % hydrogen absorption at hundreds of atmospheres over a 24-hr period with 80 percent recovery at room temperature by decreasing the pressure has been claimed but not verified [5]. Vessels capable of withstanding high pressure would be required to use this hydrogen storage technology.

## 7. Zeolites and Glass Spheres

Under high pressure and temperature, hydrogen can be forced into the space inside zeolites or glass microspheres (50 μm) and is trapped upon cooling [1,5]. The amount of stored hydrogen in zeolites is small (0.08 wt %) and requires heat to be released. Glass microspheres theoretically trap up to 40 wt % H<sub>2</sub> (not yet achieved) and also require heat to release the hydrogen [1].

## 8. Natural Gas, Ethane, Propane, and Butane

Steam reforming can be used to convert methane to  $H_2$  and  $CO_2$  and yields the highest percentage of  $H_2$  of any reformer type. This method can also be used for other light hydrocarbons, such as butane and propane. Accomplished at temperatures starting about 760 to 980 °C, hydrogen reformed from natural gas and steam in the presence of a catalyst is endothermic.

Pipeline quality natural gas contains catalyst-poisoning sulfur compounds used as odorants for leak detection. Removal of these compounds requires a zinc oxide (ZnO) sulfur polisher and possibly a hydrodesulfurizer [10]. The ZnO removes mercaptans and disulfides. The hydrodesulfurizer removes thiophane by converting it to  $H_2S$  that is then removed by ZnO. The ZnO operates over a wide range of temperatures, but the minimum bed volume is achieved at 350 to 400 °C.  $H_2S$  can also be removed electrochemically with a porous nickel cathode at 650 °C by reducing it to  $H_2$  and sulfide ion [11]. Partial oxidation (POX) reformers are usually used on liquid fuels that are not suited for steam reformers [10], but may also be used with gaseous fuels.

POX reformers rank second to steam reformers based on hydrogen yield, yielding about 75 percent of the hydrogen produced by steam reforming using gaseous fuels. A POX reformer will oxidize methane to CO and  $H_2$ , which must then undergo the water gas shift reaction ( $CO + H_2O \rightarrow CO_2 + H_2$ ) to reduce CO levels to prevent catalyst poisoning. Two or more processes are often involved [10]. First, a high-temperature stage permits high reaction rates, and then, a low-temperature converter allows a higher conversion. To be used in a proton exchange fuel cell, the CO must also pass through a catalytic oxidizer, since catalysts only tolerate CO concentrations of 50 ppm. The disadvantage of this selective catalytic oxidizer is the occurrence of two competing reactions in which one consumes fuel ( $H_2$ ):



POX reformers that employ liquid fuels (distillate, naphtha, diesel, and heavy fuel oil) use oxygen in the presence of steam with flame temperatures of 1300 to 1500 °C [10]. The size of the equipment used for POX reforming can be reduced if one uses a pressurized (20 to 40 atm) system.

## 9. Reversible Metal Hydride

Hydrogen can be reversibly absorbed within the crystal structure of many metal alloys (e.g., LaNi, FeTi), usually absorbed at lower temperature and released by heating or at reduced pressure. Storage is very good volumetrically, but these materials are usually costly and, because they are heavy, store only about 1 to 2 wt % hydrogen. Hydrogen is condensed to

two times the density of compressed hydrogen gas with an alloy such as FeTi [2]. Alloys of FeTi are relatively inexpensive but easily poisoned and difficult to activate. Magnesium-based alloys require high temperature for both charge and discharge.

Researchers have extensively investigated a wide variety of multicomponent AB<sub>5</sub>-type alloys, where A represents one or more rare-earth or early transition metals and B represents any of the late transition or p-shell metals. LaNi<sub>5</sub> and variations of this alloy have been extensively studied. LaNi<sub>5</sub> alloys are much more active than FeTi at room temperature and low pressures but are not very stable and are corrosion sensitive. LaNi<sub>5</sub> loses capacity with cycling because of pulverization of the alloy, but the addition of other alloying elements improves stability. Combinations of rare-earth elements (e.g., La, Ce, Nd, and Pr) are known as mischmetal (Mm), which is often used as an alloying additive to scavenge substances such as sulfur and oxygen and to improve high-temperature strength. Many combinations and varying ratios of mischmetals have been studied since properties vary with composition. Partial substitution for Ni increases both stability and corrosion resistance [12]. For example, substituting small amounts of Sn for Ni was shown to provide increases in capacity, capacity retention, and kinetics [13]. Substituting Ge reportedly provides even better chargeability, cycle life, kinetics, and operating pressure [14]. Substituting for both La and Ni to form La<sub>1-x</sub>Zr<sub>x</sub>Ni<sub>5-y</sub>Al<sub>y</sub> also increases cycle life and charge retention, with improvements supposedly resulting from Zr and Al forming a denser oxide surface film, which protects the metal hydride from attack by water and oxygen [15].

Low-temperature hydrides have low hydrogen loading but release H<sub>2</sub> at 50 to 80 °C and at low pressure. High-temperature hydrides have higher loading (6 wt %) but require temperatures >100 °C to release H<sub>2</sub>.

Unfortunately, hydrogen-storage alloys used in nickel metal hydride batteries have shown degradation after long-term cycling. After many cycles, the (originally) large smooth alloy particles become oxidized, pulverized, and porous and lose the capability to absorb/desorb hydrogen [16]. Coatings and microencapsulation techniques have been used to preserve the integrity of the alloys. Particles have been encapsulated with cobalt, nickel, palladium, and copper. Cobalt was found to increase capacity because it also adsorbs hydrogen and eliminates capacity fade during repeated cycling [17]. Copper coatings act as an oxygen barrier to protect LaNi<sub>4.7</sub>Al<sub>0.3</sub> alloy from oxidation to allow a fourfold increase in cycle life [18].

Research has also focused on magnesium-nickel alloys. The cost and theoretical hydrogen capacity (about 1000 mAh g<sup>-1</sup>) of Mg<sub>2</sub>Ni are superior to rare-earth alloys (AB<sub>5</sub>, e.g., LaNi<sub>5</sub> is 372 mAh g<sup>-1</sup>) or Laves-phase alloys (AB<sub>2</sub>) [19]. However, hydrogen absorption and desorption occur slowly and only at high temperature (200 to 300 °C) and pressure (up to 10 atm) [19–21]. Mechanical grinding improves reversible hydrogen storage, enabling a first-cycle room temperature discharge capacity of

750 mAh g<sup>-1</sup> (compared to almost none for material that was not mechanically ground) [19]. However, capacity appears to fade quickly with successive cycling. Preparing a composite with graphite reportedly improves capacity and cycle life and permits an increase in the rate of hydrogen absorption [20]. Others have tried mechanical milling and graphite additives with AB<sub>5</sub>-type alloys and have also found capacity increases up to 40 percent [22]. Three cumulative effects have been suggested: (1) graphite acts as a reducing agent to prevent oxide coatings on the AB<sub>5</sub> alloy, permitting better H<sub>2</sub> diffusion, adsorption, and desorption; (2) double-layer capacitance increases with milling time and adds to the faradaic component; and (3) improved electronic conductivity between the alloy and graphite allows better utilization of the alloy [22].

## 10. Nonreversible Metal Hydride

Although reversible metal hydrides are inefficient storage materials based on weight, nonreversible metal hydrides store hydrogen very efficiently based on both weight and volume. Hydrogen stored in nonreversible metal hydrides is released chemically when reacted with water. The exothermic reaction of hydrides, such as LiH, NaBH<sub>4</sub>, and LiAlH<sub>4</sub>, produces twice the amount of H<sub>2</sub> stored in the alloy, since half of the hydrogen comes from the water used in the reaction. Although toxicity is an issue, LiH is attractive since stoichiometric quantities of hydrogen are produced when reacted with water, matching hydrogen requirements with the water produced in the fuel cell. However, carrying water is also necessary to start the reaction. At ambient temperatures, the reaction between LiH and H<sub>2</sub>O is not LiOH, but LiOH·H<sub>2</sub>O. For only LiOH to be formed, the temperature must exceed 125 °C. Because the reaction with water is highly exothermic, the reaction tends to seal off the surface of the pellet with a dry solid product that blocks further reaction if limited amounts of water are used [23]. High pH will also inhibit reaction kinetics. Water in excess of stoichiometric quantities is required to dissolve and wash away hydroxide reaction products (e.g., LiOH, NaOH), which then introduce new problems of corrosion and disposal. If a nonreversible metal hydride is used only intermittently, there is a start-up time delay before producing H<sub>2</sub>, and upon shutdown, the exothermic reaction continues for some time even after demand has ceased. Proper storage of these materials is critical, since they are unstable when stored in a humid environment. Otherwise, the wt % of stored hydrogen is attractive; e.g., LiH is 25 percent.

Thermal stability of pure alkali and alkaline earth-metal hydrides is generally greater than mixed metal hydrides, as shown in table 1 [23]. Calculated capacities [23] of some hydrides are shown in table 2.

A load-responsive hydrogen generator has been demonstrated with CaH<sub>2</sub> and LiH by A. F. Sammer Corp. that feeds water under pressure to a water-wicking manifold contained in a disposable hydride cartridge. In

**Table 1.**  
Decomposition  
temperature of metal  
hydrides.

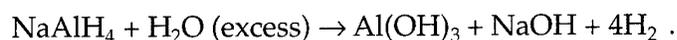
Metal hydride	Decomposition °C
CaH <sub>2</sub>	600
NaH	800
LiH	800+
MgH <sub>2</sub>	280
LiBH <sub>4</sub>	275
LiAlH <sub>4</sub>	105

**Table 2. Calculated  
capacities of metal  
hydrides.**

Hydride	Ah g <sup>-1</sup>	Ah ml <sup>-1</sup>
LiH	6.74	5.26
CaH <sub>2</sub>	2.55	4.85
LiAlH <sub>4</sub>	5.65	5.20
LiBH <sub>4</sub>	9.83	6.49
NaBH <sub>4</sub>	5.56	5.17
KBH <sub>4</sub>	3.97	3.36

another system from Physical Sciences, Inc., waste heat caused vaporization of water that would not react efficiently with LiH, requiring a method for cooling the reaction vessel [24]. Also, after shutdown and subsequent restart, delay time for hydrogen production increased with the fraction of spent load of fuel.

A Kipp generator uses sodium aluminum hydride (NaAlH<sub>4</sub>) and water in an exothermic chemical decomposition to produce hydrogen and metal hydroxides:



The hydride is stored as a solid pellet that delivers 2000 Wh/kg [25]. Hydrogen is produced on demand. When there is no hydrogen demand, pressure builds up and forces water away from the fuel pellet, causing the reaction to stop.

Hydrolysis of NaBH<sub>4</sub> is slow and incomplete unless performed in acidic solution or in the presence of transition metals (Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>) [26]. A device to react chemically stable alkaline solutions of NaBH<sub>4</sub> with a cobalt boride catalyst to produce hydrogen is currently being developed [27]. Hydrogen is produced only when solution is in contact with the catalyst, providing an effective control mechanism.

Decomposition (as opposed to hydrolysis) of chemical hydrides, such as LiBH<sub>4</sub> and LiAlH<sub>4</sub>, has also been used. The hydrides are stabilized by being mixed with a halide salt (NH<sub>4</sub>Cl) and a polymer binder, and they are reacted by high-temperature ignition. The reaction is highly exothermic and cannot be stopped, so it is obviously an unattractive alternative.

Ligand-stabilized hydrides containing LiBH<sub>4</sub> or Mg(BH<sub>4</sub>)<sub>2</sub> have also been used to store hydrogen [28]. The advantage of these compounds is that although the amount of hydrogen produced is less than that of unbound LiBH<sub>4</sub> and NaBH<sub>4</sub>, the hydrolysis reactions are less violent and release less heat. However, water in excess of the stoichiometric quantities is

needed to efficiently react these materials, which adds to the overall weight and volume of a complete fuel cell system. A comparison of gravimetric and volumetric energy densities of hydrides and some other systems is shown in figure 1.

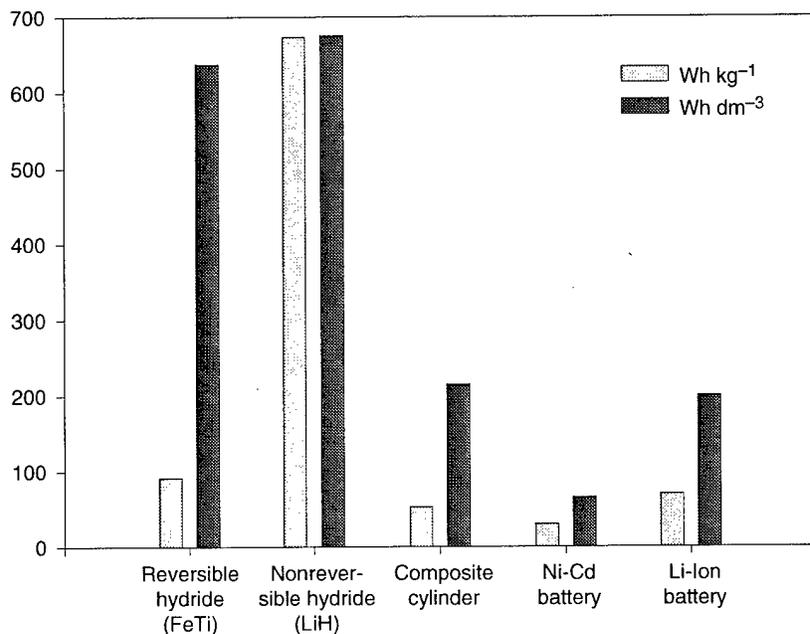
## 11. Organosilane

Ethenyl, ethynyl, and phenyl silanes are being developed for hydrogen storage (6 to 10 wt %), with release of hydrogen by catalytic reaction with water in a homogeneous liquid phase [5]. These and many other organosilanes are currently being studied in efforts to determine the efficacy of generating hydrogen and the feasibility as a practical hydrogen storage system. Current results are proprietary.

## 12. Liquid Hydrogenated Organics

Unsaturated hydrocarbons can be reversibly hydrogenated to store hydrogen that can be released when needed. One such liquid organic hydride scheme combines hydrogen with toluene that is converted and stored as methylcyclohexane [1,5,29,30]. Dehydrogenation is by endothermic reaction (400 to 500 °C) with a noble metal catalyst. This system has been proposed for storing energy for electric power plants. The heat of reaction, chemicals involved, and the high cost make this an unattractive option for portable hydrogen storage.

**Figure 1.**  
Comparison of gravimetric and volumetric energy densities of various power systems.



Source: D. Browning, P. Jones, and K. Packer, "An investigation of hydrogen storage methods for fuel cell operation with man-portable equipment," *J. Power Sources* 65 (1997), p 187.

## 13. Indirect Methanol

Direct oxidation of methanol (discussed under sect. 5.1) at low temperatures with the use of Pt-Ru catalysts is possible, but fuel cell voltage is low and the catalyst is expensive and subject to poisoning by carbon monoxide. An indirect use of methanol involves a steam reforming step using metal oxide catalysts (e.g., CuO-ZnO) to process methanol into gaseous hydrogen fuel and CO<sub>2</sub>.

## 14. Biochemical

The metabolic processes of some microorganisms (or merely immobilized enzymes) can generate useful gases (e.g., H<sub>2</sub>, CH<sub>4</sub>, and NH<sub>3</sub>) or liquids (e.g., ethanol) that can be used as fuels. Bacterial cultures can often be grown inexpensively on otherwise useless waste products from other processes, but may require strictly controlled conditions, such as pH, temperature, cell and substrate concentrations, and removal of metabolic waste products. In one study, hydrogen was produced from cells immobilized in agar gels that used the wastewater from the production of tofu. The maximum rate of hydrogen produced was 2.1 L h<sup>-1</sup> m<sup>2</sup> gel [31]. Such a system would have limited application based on its complexity, start-up delay, and low hydrogen output.

Other systems involve isolated enzymes immobilized on electrodes that react to produce electrons that can be used directly in a biofuel cell. Dehydrogenase enzymes can utilize methanol to produce CO<sub>2</sub> and the reduced form of nicotinamide adenine dinucleotide (NADH) for use as the anodic fuel. In one study, a pyrroloquinoline quinone-containing electrode was used to oxidize NADH, while a peroxidase enzyme on the cathode was used to reduce H<sub>2</sub>O<sub>2</sub> [32]. This biofuel cell system had an open-circuit potential of 0.32 V and a short-circuit current density of 30 μA cm<sup>-2</sup>. Other enzymatic systems that have been demonstrated also suffer from very low outputs of 25 μA cm<sup>-2</sup> at 0.5 V [33] and 1.37 mA cm<sup>-2</sup> at 0.49 V (only within the first minute of operation) [34]. These values are for maximum output, whereas under continuous operation, performance will decrease significantly because of concentration polarizations.

## 15. Gasoline and Diesel Fuel

Reforming heavier fuels requires several processes at high temperatures. POX reformers require temperatures over 1300 °C (also see sect. 8). Impurities (e.g., sulfur compounds) that foul catalysts must also be removed. Present systems are heavy, large, and expensive. Technology to miniaturize the components compatible with small systems has to be developed.

A plasma reformer (without the use of catalysts) that would reduce the weight and volume of the reformer has been proposed as an alternative [35]. Fast reaction rates can occur because high temperatures  $>2000\text{ }^{\circ}\text{C}$  can be achieved that result in high conversion efficiencies. Without catalysts, a wide range of fuel options is available.

## 16. Fuel-Flexible Fuel Processors

Many groups are involved in developing 50-kW (automotive-sized) fuel processing systems that will accept a wide variety of fuels, including gaseous hydrocarbons, alcohols, gasoline, and even diesel fuel. Within the next few years, 50-kW system deliverables are expected from several companies, including Plug Power (Latham, NY), International Fuel Cells Corp. (South Windsor, CT), Epyx Corp. (Cambridge, MA), McDermott Technology, Inc. (Alliance, OH), and Hydrogen Burner Technology, Inc. (Long Beach, CA). Argonne National Laboratory is to demonstrate a partial-oxidation reformer integrated with a 10-kW fuel cell in 1999, and Los Alamos National Laboratory is to demonstrate a 50-kW preferential oxidation reactor to generate PEM-quality reformat (also in 1999). Epyx (formed from Arthur D. Little, Inc.) has a hybrid partial oxidation-based multifuel processing technology that it has demonstrated in fuel cells using ethanol, methane, propane, and gasoline. However, some technical areas that require more progress are catalysts, CO cleanup, transient controls, and reformer start-up/shutdown time.

## 17. Commercial Hydrogen Production Technologies

Hydrogen-fueled PEM cells have been expected to eventually replace internal combustion engines in vehicles, thereby increasing fuel efficiency and significantly reducing vehicle-generated air pollution in urban areas. However, there is presently no infrastructure to produce, store, and distribute hydrogen in the large quantities needed for such a transition. Without the infrastructure to ensure availability and concomitant reduction in price, hydrogen for PEM fuel cell applications will most likely remain costly even for small-scale applications. Currently, several commercial technologies are available for the production of hydrogen, each with strengths and weaknesses:

- Steam reforming of methane is the predominant method of producing hydrogen today [36].  $\text{H}_2$  and CO are produced by reacting natural gas with steam over an Ni catalyst at  $850\text{ }^{\circ}\text{C}$  under high pressure. When the gas is cooled to  $400\text{ }^{\circ}\text{C}$  and reacted with more steam over a water-gas-shift catalyst, more  $\text{H}_2$  is produced, along with  $\text{CO}_2$ . The  $\text{CO}_2$  and other impurities are removed by pressure swing adsorption.

- Liquid hydrogen is produced by cryogenic cooling and is usually used if hydrogen needs to be shipped over large distances. Because processing requires a lot of energy, this storage method is economical only in large-scale processes where low-cost power is available.
- Electrolysis of water is limited in production capacity by electrode surface area, so it is not suited for large-scale operations.
- Partial oxidation of heavy oil is a large-scale process that uses low-value refinery byproducts [36]. A reaction with  $O_2$  at 1200 to 1350 °C produces  $H_2$  and CO, which can then undergo a water-gas-shift reaction to form more  $H_2$  and  $CO_2$ . A waste hydrogen stream and excess steam are produced that make this process uneconomical unless these byproducts can be used [36].
- Methanol reformation is easily accomplished with water over a catalyst at 250 to 300 °C, producing  $H_2$  and  $CO_2$ . Methanol is easily transported and stored, making it an especially attractive alternative in areas wherever natural gas is not available [36]. The cost of methanol determines if this technology is economically appealing.

## 18. Summary

The requirement for a man-portable hydrogen supply for use with a low-temperature PEM fuel cell severely restricts the number of technologies that are reasonable to consider. Low-temperature systems and high-temperature processes require a large amount of energy and thermal insulation, which make them impractical. Some of the chemical storage systems pose handling and disposal issues in addition to complex processing of the fuels. Gas sorption technologies show promise but are currently very costly and are in the research stage of development. Processing of gasoline or diesel fuel currently requires heavy, expensive, and large equipment. Miniaturization of components and improvements in catalysts are required before this can be considered feasible. Gaseous hydrogen in containers is simple but extremely unattractive based on weight, although some progress is being made using conformable composite carbon materials. Reversible metal hydrides store large amounts of hydrogen, but are heavy, costly, and of questionable stability. Nonreversible metal hydrides can store large amounts of hydrogen and are very efficient and attractive from weight and volume considerations. However, these materials have problems with reaction kinetics associated with their hydrolysis. Direct oxidation of methanol is also very attractive, but CO-tolerant catalysts and methanol-impermeable membranes are needed to prevent degradation of performance. A summary of the hydrogen storage technologies is given in table 3.

**Table 3. Summary of hydrogen storage technologies.**

Storage system	Characteristics
Gaseous hydrogen	Simplest storage method, but poor weight efficiency (1%). Can triple wt % if composite carbon fiber wound cylinder with aluminum or plastic inner liner is used.
Liquid hydrogen	Requires low temperature, well-insulated container, and vent for boil-off. Efficient on weight and volume basis.
Cryoadsorbed hydrogen	High-surface-area material (carbon) is used to store hydrogen at modest pressure and low temperature (150 to 77 K). Good system on weight and volume basis. Complex.
Catalytic oxidation of hydrocarbons	Methanol—easy to store and transport, but cell voltage and current less than that from direct hydrogen resulting from methanol crossover to cathode. Produce CO as byproduct that poisons catalyst. Trimethoxymethane—higher boiling point and lower toxicity than methanol. Complete oxidation with methanol as an intermediate. Ammonia—oxidized at high temperature to nitrogen and water. Toxicity and handling issues. Hydrazine (N <sub>2</sub> H <sub>4</sub> )—decomposes easily to hydrogen and nitrogen but is toxic and expensive.
Hydrogenated organic liquid	Hydrogenated unsaturated hydrocarbon, such as toluene to methylcyclohexane. Requires heat, noble catalyst, and lot of equipment. More applicable for large-scale storage.
Carbon sorption	Carbon fullerenes—store up to 6% hydrogen, but high heat required to release hydrogen—expensive. Nanotubes—hydrogen trapped in tubes. Poor kinetics and costly. Graphite nanofibers—up to 50 wt % hydrogen absorbed on graphite bundles at high pressure. Release hydrogen by releasing pressure.
Zeolites	Force hydrogen into interior space under high temperature and pressure. Hydrogen trapped upon cooling. Release hydrogen with heat. Small amount of H <sub>2</sub> stored based on weight (0.08%).
Glass spheres	50- to 100- $\mu$ m-diam microspheres with high heat and high pressure. Upon cooling, hydrogen trapped until heated again. Theoretically can store up to 40 wt % hydrogen. In research stage, technical difficulties.
Short chain hydrocarbon gas, gasoline, and diesel	Methane—steam reforming yields highest conversion of any reformer type. Must desulfur, high heat. Liquid fuels use partial oxidation (POX) reforming to produce H <sub>2</sub> and CO, then CO is water-gas shifted to H <sub>2</sub> and CO <sub>2</sub> . Requires high heat, catalysts. POX reformed gasoline and diesel required very high temperature. Systems are large, heavy, and expensive.
Reversible metal hydrides	Hydrogen reversibly absorbed by metal alloys at low temperature and released by heating. Good volumetrically, but heavy and costly. Wide variety of alloys and preparative techniques have been studied. Mg alloys—require high temperature. FeTi alloys—inexpensive but difficult to activate and susceptible to poisoning. LaNi <sub>5</sub> alloys—easier to activate, resists poisoning, but poor cycling stability. Characteristics improve with substitutions of rare-earth elements (mischmetals).

**Table 3. Summary of hydrogen storage technologies (cont'd).**

Storage system	Characteristics
Hydrolysis of non-reversible metal hydrides	Metal hydrides store high amount of hydrogen based on weight and react with water to release hydrogen (e.g., LiH, NaBH <sub>4</sub> , LiAlH <sub>4</sub> ). Half of released hydrogen comes from the water. Kinetics inhibited by high pH and insoluble reaction products. Start-up and intermittent use issues.
Decomposition of chemical hydrides	Stabilize hydride with halide salt and polymer binder; ignite with high temperature. Reaction is highly exothermic and cannot be stopped.
Organosilane	Ethenyl, ethynyl, and phenyl silanes store 6 to 10 wt % H <sub>2</sub> . React with water and catalyst to produce hydrogen.
Biochemical	Bacteria or immobilized enzymes can convert fuel into useful gases or liquids. Complex controls needed and small amount of hydrogen produced. Enzymes can also directly produce electrons but produce very small currents.

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