OVERVIEW OF HYDROGEN STORAGE OPTIONS

David H. Swan

Center for Electrochemical Systems and Hydrogen Research
Texas Engineering Experiment Station
Texas A&M University System
238 Wisenbaker Engineering Research Center
College Station, TX 77843-3402
USA

Abstract

Hydrogen can be stored on-board a vehicle as a high pressure gas, a liquid, or in a semi solid form (hydride, adsorbed in activated carbon, micro spheres and others). The choice of a standardized on-board storage system will be critical to the success of hydrogen fuel cell powered vehicles. The ideal on-board storage system would be intrinsically safe, have a high energy density, would refuel quickly, and have no evaporative or gaseous losses. This paper is a cursory review of vehicle hydrogen storage options.

Introduction

The 1990's are a decade that will lead to major changes in transportation fuels for the next century. There are now mandates for the sale of Zero Emission Vehicles (ZEV) in the states of California, Massachusetts, and New York. The ZEV is fundamentally different in that there can be no on-board combustion. The ZEV propulsion system uses an electric drive. The electric drive will be powered by either batteries, or a fuel cell supplied from an on-board hydrogen storage system. The advantage of on-board hydrogen and a fuel cell over batteries is range and refueling time.

Comparison of ZEV Energy Storage Systems

The following table compares the energy density and relative refueling rates of batteries, hydrogen and gasoline. The energy density is expressed in terms of mass (Watt hours/kg) and volume (Watt hours/liter). The refueling rate is the approximate rate at which energy can be loaded onto a passenger vehicle.

High and low cases are presented for both batteries and hydrogen. The energy density of the two battery cases represent what is available today and the long term goal of the United States Advanced Battery Consortium (USABC). The energy density of the hydrogen cases is presented as a function of weight fraction. Weight fraction is defined as the percentage of stored hydrogen weight to the total storage system weigh. The 2% case can be easily accomplished using compressed natural gas storage tank technology. The 10% case can be easily accomplished using liquid hydrogen tank technology.

Technology	On-Board Energy Density Wh/kg	On-Board Energy Density Wh/l	Vehicle Refueling Rate (kW)
Batteries			
Present EV Batteries	25 to 50	50 to 75	5 to 15
Advanced EV Battery Technology	200	300	100
Hydrogen Storage			
2% System Weight Fraction	660	400 to 1000	90 to 8,000
10% System Weight Fraction	3,300	1000 to 1500	90 to 8,000
Gasoline and Tank	8700	7900	10,000 to 20,000

Table 1. Comparison of ZEV On-Board Energy Storage Systems

Notes; Gasoline refueling rate is based on vehicle loading rate of 4.4 to 8.8 gallons/minute. Battery energy density is based on US Advanced Battery Consortium long term goal. Hydrogen refueling rate is based on author estimates from Mercedes Benz and BMW prototype systems. Weight Fraction is the percentage of hydrogen weight to total on-board storage system weight.

The comparison table indicates that the energy density of hydrogen is much greater than batteries and the refuel rate approaches that of gasoline. The wide range for hydrogen refuel rate is dependent on the on-board storage technology and refueling system used. The comparison table must be used with caution, as the battery - hydrogen - gasoline comparison does not consider the weight of the fuel cell and internal combustion engine.

The energy density of the 10% weight fraction hydrogen case is much less than gasoline (approximately 1/3 by weight and 1/6 by volume). In a vehicle this problem is overcome by the fact that the fuel cell will probably operate at an efficiency of 2 to 2.5 times higher than an internal combustion engine (driving cycle dependent). Thus for a given range, the weight of a the hydrogen storage system and a gasoline tank would be approximately equal while the volume would be slightly larger.

The following figure uses the table data to present a specific electric vehicle case. While the vehicle chosen is a Chrysler mini Van, the results are applicable to most midsize vehicles. For simplicity, this graphic assumes that the vehicle has a maximum gross vehicle weight that is made up of the chassis, propulsion system and the payload. The chassis weight is taken as a constant 2110 kg, any increase or decrease in the propulsion system weight results in more or less payload.

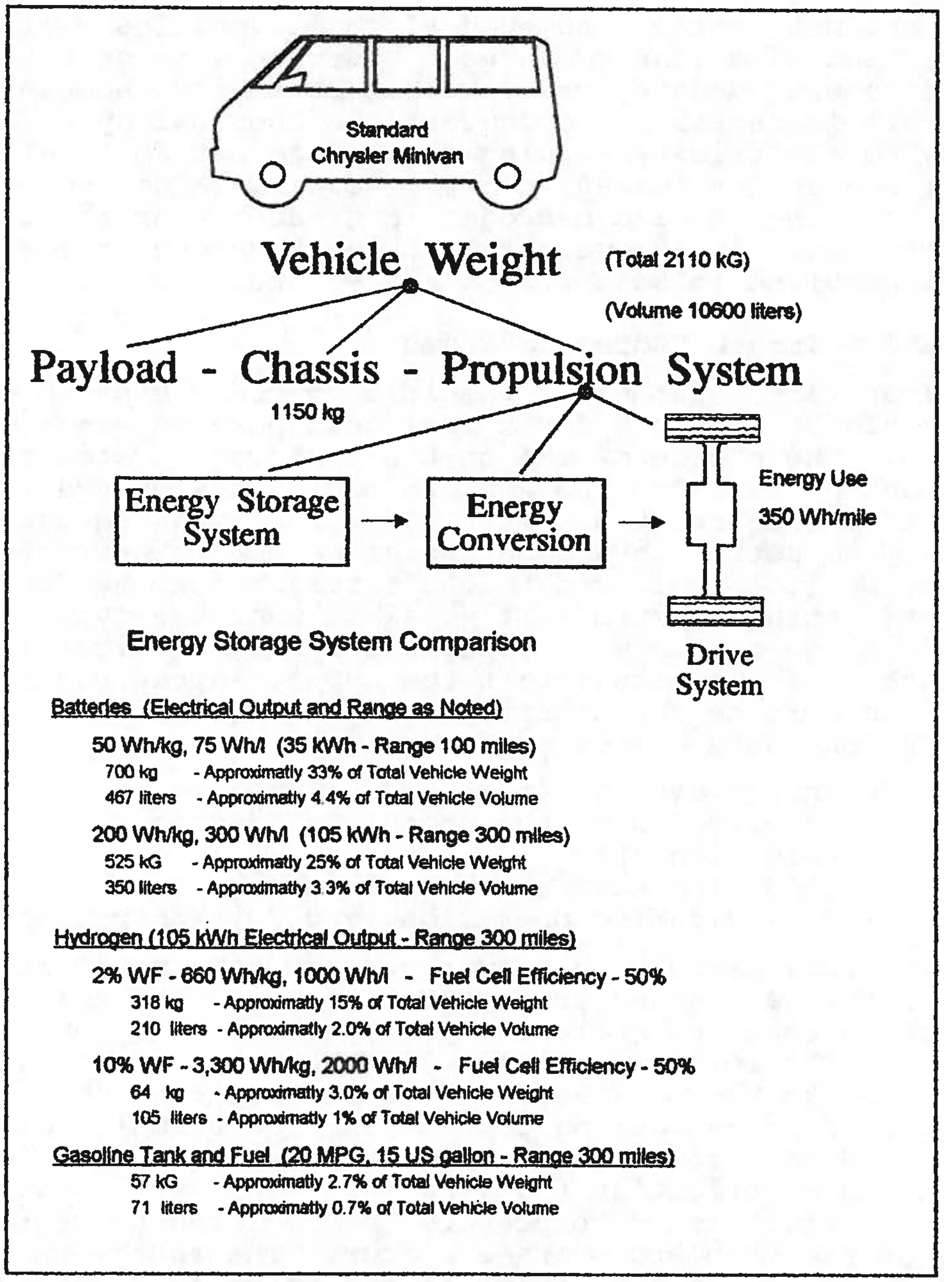

Figure 1. Vehicle drive system/energy storage schematic

Notes: All values are approximate and are author estimates. 100 mile range requires 35 kWh of electricity to the motor controller, 300 mile range requires 105 kWh, fuel cell efficiency is based on lower heating value of hydrogen. One US gallon of gasoline was taken to be 2.65 kg in mass and 3.79 liters in volume.

The data presented in Figure 1 indicates that hydrogen storage coupled with the high efficiency of a fuel cell can approximately match the characteristics of a gasoline tank and internal combustion engine. The first battery case is typical of advanced electric vehicles today, 1/3 of the total gross vehicle weight is battery and a range of 100 miles. The second battery case indicates that if the USABC goals are met, battery powered electric vehicles will become lighter and have longer ranges. Hydrogen storage systems have an energy density greater than batteries, however the fuel cell is necessary to convert the chemical hydrogen energy to electricity. Using an average net fuel cell efficiency of 50% (based on lower heating value) the energy density of the 2% case hydrogen is greater than the advanced battery case. At 10% weight fraction hydrogen approximately equals gasoline in both weight and volume.

On-Board Hydrogen Storage Systems

There are a number of possible on-board storage systems that would be suitable for a fuel cell powered electric vehicle. The choice of the on-board storage system is important not only to the vehicle but to the over all hydrogen infrastructure. Transportation could be the largest end user of hydrogen and as a result the fuel pathway would be tailored to the refueling of the favored on-board storage system. It possible that the type of on-board storage system will change with technological advances and thus it is important that the supply infrastructure be chosen to service the possibly changing technology.

The on-board system must consider:

- energy density (mass and volume)
- interface with the propulsion system
- refueling rate
- refueling station infrastructure
- safety during operation, standby and refueling

The fuel pathway that hydrogen can take makes it more complex than any other transportation fuel. The energy of production could be nuclear, hydro, solar, wind, and other sources. The following Figure 2 depicts the steps in production to the end user. It is important to note that energy is required during production (for example, natural gas to hydrogen reforming is 65% to 75% energy efficient) and during distribution (pumping and transport losses). Energy is also needed to prepare the hydrogen to meet the needs of the on-board storage system. The energy necessary for preparation is a function of the technology used for the on-board storage system. For example a high pressure storage tank will require a higher pressure system to refuel it. This may be accomplished through a cascade system of tanks and a local compressor. Sufficient fuel storage at the local refueling station will be needed to service many vehicles an hour. Considering the hydrogen fuel pathway, the refueling station and its infrastructure are key elements in the choice of the on-board storage system.

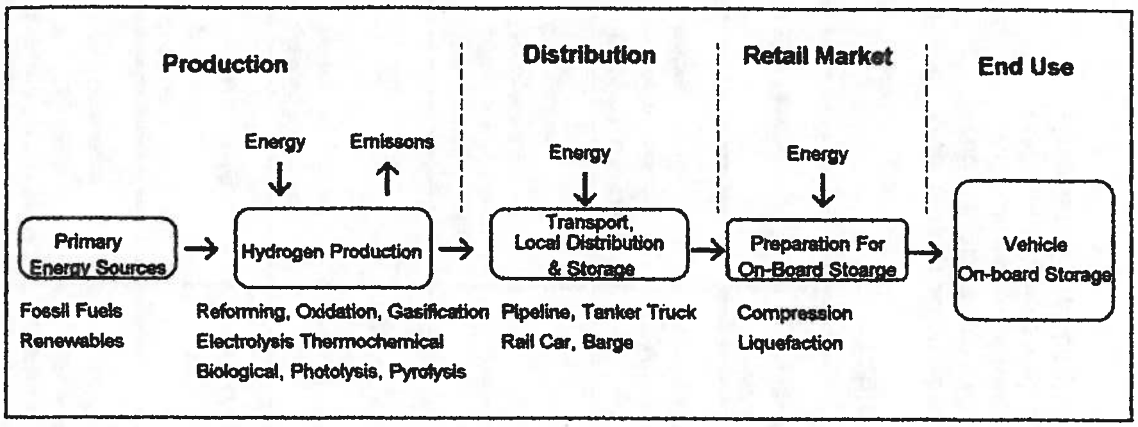

Figure 2. Hydrogen Fuel Pathway

The following Table 2 is an author characterization of different on-board storage technologies. The technologies described include hydrogen storage by high pressure, by hydride, by adsorption, and in liquid form. The table compares the storage system weight and volume fraction, the system energy density, refueling infrastructure, and propulsion system interface.

The system weight and volume fractions describe the weight and size of the fuel to the total storage system. By considering the lower heating value of the fuel the system energy mass density is calculated. By considering the heating value and density of hydrogen the system volumetric energy density is calculated.

The refueling infrastructure is a simple indication of the equipment that would be needed at the refueling station to refuel the given on-board storage system.

The propulsion system interface refers to how the storage system is interconnected to the propulsion system. The storage system must supply hydrogen to the fuel cell and depending on the storage technology used there may need to be a feedback such as thermal energy or a control signal. For example the hydrogen hydride systems that have been demonstrated in the internal combustion engine Mercedes Benz vehicles have utilized an exhaust system heat exchanger to supply the hydride endothermic reaction to release the hydrogen.

On-Board Storage System Technology Conditions	System Weight and Volume Fraction (WF/VF)	System Mass Energy Density (Wh/kg)	System Volumetric Energy Density (Wh/l)	Refueling Infrastructure	Propulsion System Interface	General Notes 1) Advantages 2) Disadvantages
.1) Compressed Hydrogen System 200 to 400 Atm.	WF ≈ 1 to 5% VF ≈ 70 to 90%	300 to 1700	450 to 900	High pressure storage tanks and compressor	Supply, Possible Venting	1) Simple rugged system, 2) High pressure; safety; low capacity
2) Hydrogen in a Hydride System	WF ≈ 1 to 4%	300 to 1300	600 to 1600	Low pressure storage tanks and compressor	Supply, Thermal and Control Feedback	1) Crash safety; high volumetric capacity 2) Hydride Poisoning (loss of capacity); low mass capacity
3) Hydrogen in an Activated Carbon Storage System (Adsorption & Compression)	WF ≈ 4 to 8%	1300 to 2600	600 to 950	Medium pressure storage tanks and compressor; refrigeration equipment	Supply, Possible Thermal and Control Feedback Possible Venting	1) Lightweight; crash safety, possible low cost. 2) Low temperature operation, possible venting loss;
4) Hydrogen in Liquid Form in a Cryogenic Storage System	WF ≈ 10 to 20% VF ≈ 40 to 60%	3300 to 6600	950 to 1400	Low pressure cryogenic storage tanks and ; cryogenic refrigeration equipment	Supply, Possible Thermal and Control Feedback, Evaporative Control	1) High capacity, mass & volumetric 2) Evaporative loss; very low temperature; safety
Gasoline Tank	WF ≈ 70% VF ≈ 85%	8700	7900	Low pressure storage tanks and pumps	Supply, Evaporative Control	1) Simple known system; low cost,

Table 2. Comparison of On-Board Hydrogen Storage Technologies

Notes:
- Fuel Weight fraction = Fuel Weight /(Loaded Storage System Weight)
- Fuel Volume fraction = Fuel Volume /(Loaded Storage System Volume) always < 1.
- Hydrogen Properties used, Lower Heating Value 33.3 kWh/kg, LH2 - 70.8 kg/m^3 (2357 Wh/l) GH_2 - 0.08988 kg/m^3 at 1 Atm. 273^{o}K (2.99 Wh/l)
- Gasoline Properties used, Lower Heating Value 12.4 kWh/kg, 9.3 kWh/l
- Propulsion System Interface refers to the need for the storage system to be interconnected to the propulsion system for thermal or other purposes.

Table 2. indicates that all hydrogen on-board storage technologies have a lower system mass and volume energy density than gasoline. In comparing hydrogen storage technologies; the system mass energy density varies from a low of 300 to a high of 6600 Wh/kg (a factor of 22). The volumetric energy density varies from 450 to 1400 Wh/l (a factor of 3.1) This indicates that moving to a high mass storage system does not proportionately reduce volume.

The choice of which on-board storage system is best to serve the needs of the vehicle and the refueling infrastructure is very complex. Compressed gas storage tanks are available and they are intuitively simple, however, they have a relatively low capacity and a high capital cost. The refueling station would require large banks of cascaded pressure tanks to refuel many vehicles an hour.

Hydrogen in hydride form has a comparable mass energy density to compressed gas (low) and a volume energy density comparable to liquid hydrogen storage (high). The relatively high weight is the result of the hydride material (a metal alloy). The high volumetric density is the result of the hydrogen being stored in atomic form. The resultant bond energy to go from atomic (H) to diatomic (H_2) hydrogen is manifested in an exothermic reaction during refueling and endothermic during discharge. Due to the necessary heat transfer, which controls the rate of refueling/discharge, an internal heat exchanger is required. In an accident that causes tank rupture the limiting hydrogen release rate due to heat transfer may be a safety advantage. A concern may be the likelihood of poisoning the hydride due to impurities in the supply hydrogen.

Hydrogen is stored in an activated carbon storage system by a combination of absorption on the carbon surface and low compression. The normal storage temperature is in the range of liquid nitrogen (77°K). As a result, the mass energy density is relatively high but the volume energy density is less than hydride storage.

Hydrogen in liquid form is attractive due to its high energy density and relatively low cost storage tanks. This is also attractive for the fueling station storage. However the capital cost for liquefaction equipment and its energy use is high. Evaporative losses from standing tanks must be considered, the refueling operation is complex due to the low temperatures.

It is likely that the first hydrogen refueling stations will be natural gas stations that reform hydrogen. At this time natural gas service stations dispense by high pressure to on-board high pressure tanks. However some fleets such as the Houston Transit system have elected to use liquid natural gas. Large quantities of liquid natural gas can be stored and dispensed quickly. Perhaps the hydrogen refueling station will also store hydrogen in the liquid form. If the on-board vehicle storage system is a cryogenic system, the hydrogen would be loaded directly. If it is a high pressure system, some of the liquid hydrogen will be flashed off in a tank under pressure and loaded as cool hydrogen. This would also be possible for the carbon storage system and perhaps the hydride tank.

7. Summary

Concerns over air pollution has resulted in the extraordinary mandate for Zero Emission Vehicles (ZEV)in California, New York and Massachusetts. The initial mandates will be met with battery power electric vehicles. As the ZEV mandates increase the rapid refueling and long range of a hydrogen fuel cell vehicle will become attractive. Hydrogen fuel cell vehicles may even become necessary to fill the needs of both the ZEV mandates and the market requirement for a versatile vehicle.

The technological choice for the on-board storage technology will affect the vehicle and refueling infrastructure. If multiple technologies compete in the marketplace, each requiring its own refueling system, the introduction of hydrogen as a transport fuel will be difficult and expensive. As a result the choice of an on-board storage system must be carefully considered and possibly standardized if hydrogen is to be practical and cost effective.

There is no ideal on-board hydrogen storage system and it is far from obvious which system is the best. The hydrogen refueling station of the future may want to employ local liquid storage so as to serve all types of on-board vehicle systems.