

Hydrogen as an Energy Carrier

A survey of the production, storage and end use technologies

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Since the late 1990's there has been interest in the idea of hydrogen emerging as a green or low carbon energy system. The idea of a hydrogen-based energy economy has gained traction through increasing coverage on the internet, media stories and several popular science books. The key element of the story of the hydrogen economy is that hydrogen can be manufactured by electrolysis as a storage solution for intermittent renewable electricity. The main popular interest for end use has been for vehicles. This paper was prepared under a consulting contract for an international energy company to explain the technical facts and describe the issues with hydrogen as an energy carrier. The original work was carried out in 2003. The energy company never invested in developing hydrogen technology, or in supplying hydrogen to customers.

1. H₂ Production Technologies

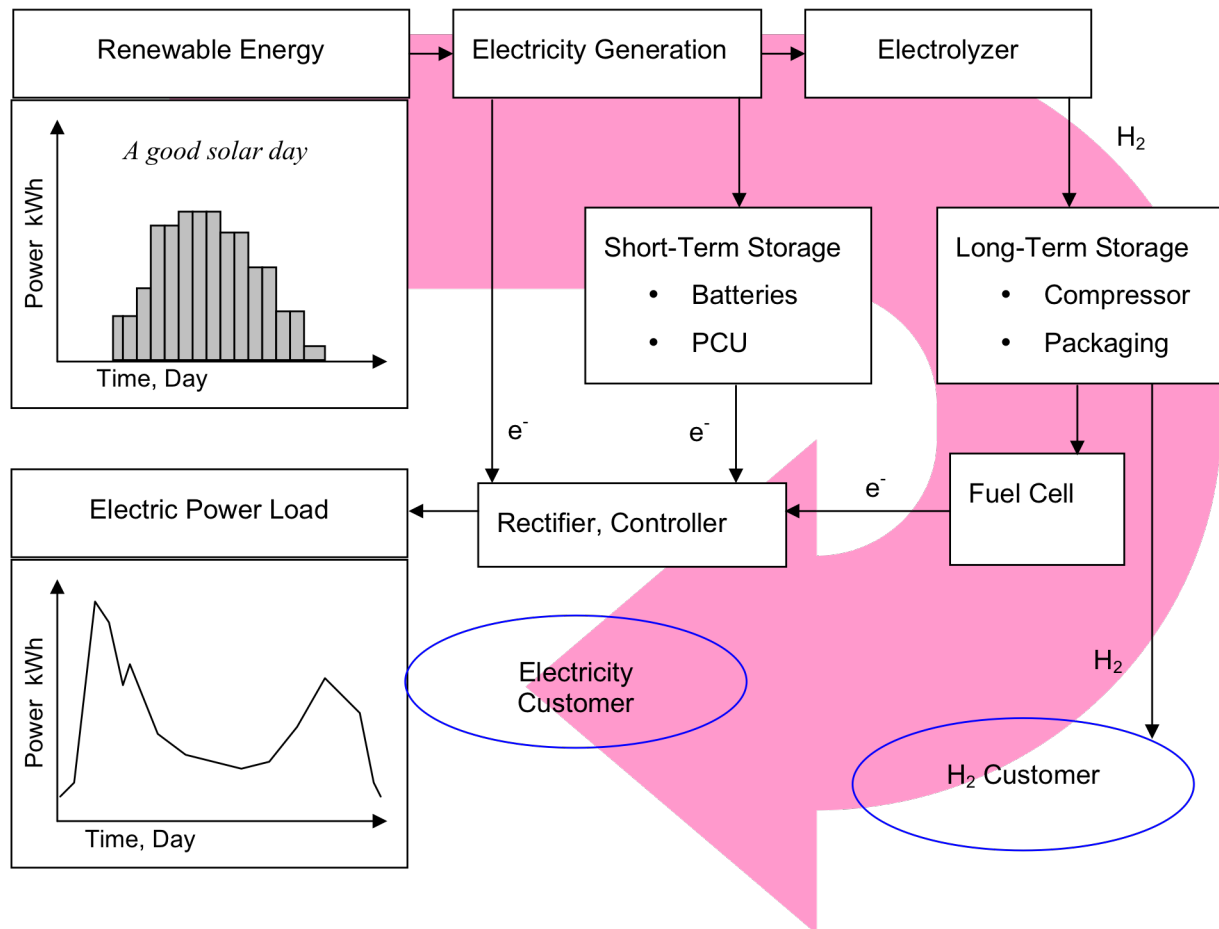
H₂ production from Electrolysis

Electrolysis is well understood, but is not a commercially viable process for large-scale hydrogen production by gas suppliers. Electrolyzers are currently used on-site at research and manufacturing facilities to produce high purity H₂ chemical feedstocks. For example, one of the most lucrative uses for electrolysis hydrogen is in synthesis and manufacture of drugs and pharmaceuticals. The market value of the end product of a medical treatment is vastly different than the market value of a fuel for transport or peak electricity. Electrolysis produced hydrogen was estimated in a [2009 review by NREL](#) to cost \$5.20/kg from a large-scale system using electricity at \$0.053/kWh).

A popular idea is to use hydrogen as an energy storage mechanism for renewable energy in the electric grid. Wind and solar energy are not available on-demand like biofuels, or in high density like or hydropower. Biofuels originate from diffuse sources, but the product fuel (gas, liquid or solid) can be stored and used when the service is needed. Hydropower can be generated on demand if the water resource is available. However, wind energy is available when the wind is blowing within the design range of the turbine, and solar energy is obviously tied to seasonal and daily variation. Maximum solar incidence occurs when cooling loads are highest, so the highest utilization designs for solar PV installations directly supply a portion of the electric load on the generation site. Both wind and solar are converted to electricity, so H₂ production via electrolysis is the focus of renewable energy hybrid fuel cell systems.

The idea of using intermittent renewable energy to produce hydrogen for on-demand end-use would require a whole system approach. The schematic below illustrates the different parts of the hydrogen energy system. Each transformation of energy in the system from conversion of the renewable energy to electricity through to conversion back to electricity for end use results in an over-all net energy return of less than one. In other words, the energy return on energy invested in the solar PV system is in the range of 3 to 10 depending on efficiency, life of the

system and utilization factor. But production of hydrogen, storage and fuel cell conversion back to electricity all have such high losses, that the net energy to the end user is less than the energy expended on building and running the system.



Functional Schematic: Distributed hydrogen production utilized as long-term storage for a renewable energy based electricity supply network. Alternatively, hydrogen delivered directly to local customers. Short-term electricity storage (i.e. hourly) is more efficiently and cost-effectively done by batteries.

H₂ production from fossil fuels and biofuels

The fundamental chemistry and processes involved in reforming hydrogen from any hydrocarbon fuel feedstock are well known. Table A1 gives a summary of the key issues which affect hydrogen fuel production technology when using any of the hydrocarbon feed stocks. Petroleum and natural gas are currently used for producing hydrogen gas commercially. Hydrogen is produced by thermal cracking in the petroleum refining process, where most of it is used near the point of generation in the manufacturing of petrochemicals and other products like ammonia. A comparatively small amount of hydrogen is purified and sold as a chemical product. Reforming of biofuels uses essentially the same chemistry. Separation and purification technology will require enhancement for fuel cell applications. Pure hydrogen is required as sulphur and carbon monoxide poison the fuel cell materials.

<p>Higher Heating Value H₂ 142 MJ/kg 0.012 MJ/lit @SPT 10 MJ/lit liquid HHV Petrol = 33.5 MJ/lit</p>
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H₂ production from Manufactured Chemical Carriers

Given the known costs and energy inputs for transporting hydrogen, an alternative or complimentary hydrogen energy supply vector has been proposed which would distribute a refined, hydrogen-grade product, such as desulphurized methanol, purified methane, or chemical carriers such as ammonia or alkali metal hydrides. The hydrogen for the customer's fuel cell would be generated from the carrier fuel either at the point of sale or at the point of use. Ethanol and methanol are produced through fermentation and reforming. Hydrogen produced by reforming is used to process hydrogen-carrying chemical compounds.

Table 1 provides a list of the hydrogen carrier fuels, which have been investigated. Automobile manufacturers are focusing on integrated reformers to produce hydrogen from purified hydrocarbon fuels. Chemical carriers present serious handling issues, including caustic waste disposal. The cost, energy input, and handling of chemical hydride carrier systems have been investigated and are not expected to be viable for transportation applications.

Ammonia has been investigated, but the toxicity is a major problem. Alkali metal hydride solutions react with water, releasing hydrogen and producing alkali solutions. This chemistry is well known, but the system engineering of controlling the process, collecting and processing waste material and the highly costly energy input to make the chemical carriers represent high risks for developing this route.

Table A2. Relevant technical information for the best candidate embedded hydrogen system fuels.

Hydro-grade Fuel	H ₂ Density kgH ₂ /kg fuel	Fuel Properties	Waste	Notes
<i>Gasses</i>				
Methane	0.25	desulphurized, flammable	CO ₂	well known requires steam
Ammonia	0.177	Gas, Liquid at 8 bar	N ₂	Toxic
<i>Liquids</i>				
Methanol	0.125	Liquid, flammable	CO ₂	health hazard man-made
Ethanol	0.13	Liquid, flammable	CO ₂	Man-made, biofuel difficult to reform
<i>Hydrides in water</i>				
30% Sodium borohydride	0.063	Stable liquid buffered with NaOH	Sodium borate	Expensive, non-regenerable
Sodium hydride	0.043	Solid	NaOH solution	Caustic
Calcium hydride	0.05	Solid, powerballs	Ca(OH) ₂ solution	
Lithium hydride	0.127	Solid, oil slurry	LiOH solution	Caustic, 1500°C regeneration temp

1.1 Hydrogen Production Technology

The chemistry and methods for producing hydrogen from hydrocarbon fuels are well known and widely used in industry. Coal can be gasified then reformed, while petroleum and natural gas are reformed directly. Reforming requires high temperatures, water and energy input. The reformed gas must be "cleaned up" to separate out the hydrogen and avoid contamination by CO and H₂S which poison low temperature fuel cells. The CO₂ must be separated from the reformed gas as it dilutes the fuel product and poisons alkaline fuel cells.

Hydrogen Energy System Processing Technology Needs

- 1 Discovery, extraction and transportation of primary energy to a processing facility
- 2 The primary resource is refined or processed and is then used to produce hydrogen gas
- 3 The H₂ gas is processed and packaged for storage, distribution, and delivery to the customer
- 4 At the point of sale, the customer transfers the fuel, either in a container, or by transfer to another container, then uses the energy product in some appliance or machine to provide a desired service.

Feasibility Factors:

- Hydrogen production is a well known industrial process, gas clean-up technologies for fuel cells are in the research phase
- Reforming requires less energy input than electrolysis
- Hydrocarbon reforming requires high temperatures and catalyst
- Hydrocarbon reforming requires post-reformer gas clean-up and separation involving rare noble metals
- Electrolysis requires high activity catalyst, but can be done at low temperature

Electrolysis

The energy input required to separate elements which are chemically bound is a function of the stability of the precursor chemical. In general, oxides are quite stable compounds. Water is hydrogen oxide, and, while it can ionize readily, water is naturally a stable chemical compound. It takes more energy to separate the hydrogen-oxygen bond than it does to separate the hydrogen-carbon bond. Thus, extracting hydrogen from water will always require more energy input than reforming hydrogen from hydrocarbon compounds. The most efficient electrolyzers, with conversion efficiency of 70%, use significant amounts of catalyst, and are thus high in cost.

Issues Affecting Technical Feasibility:

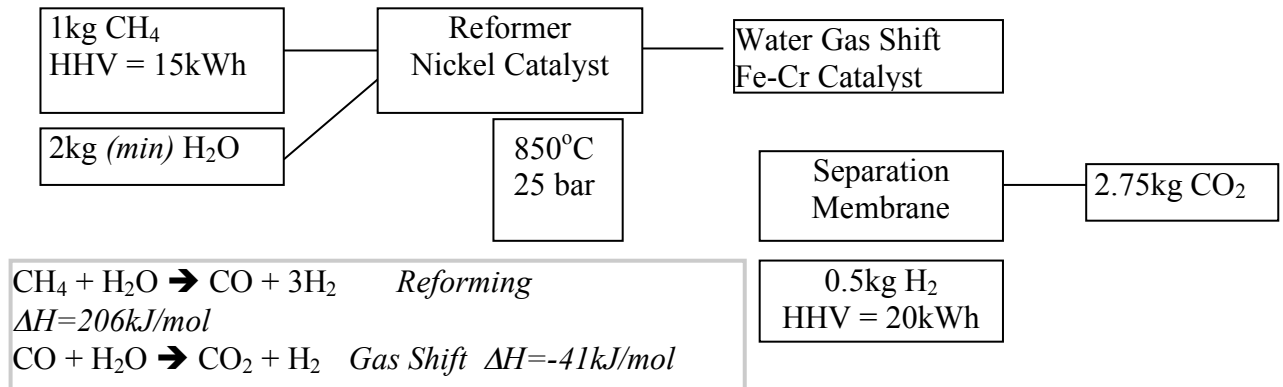
- *Handling: liquid electrolytic solution, KOH, has special temperature, materials, and sealing requirements. Pure oxygen produced in electrolysis is highly corrosive and a combustion hazard.*
- *100 kWh of electricity would produce 20 m³ H₂ @STP*
- *The process must be carefully controlled and monitored*
- *oxygen vented safely as it attacks materials*
- *1.4 - 2.5 units energy in = 1 unit energy out*

Steam Reforming of Natural Gas (Methane)

Natural gas is heated to 700°C over an active catalyst with 2kg steam required for each kg of methane. The complete process produces 8kg of H₂ and requires 12.2MJ of process heat per kg of methane reformed. A well designed plant would recover some of the heat from the H₂+CO₂ product gas through special heat exchangers, but recovery of energy from the gas is not

as readily accomplished as it is with steam flows. The separation membrane is usually palladium/platinum membrane, which is well understood and mature technology, although highly sensitive to sulphur and carbon contamination, and very expensive.

Flow Diagram for Methane Reforming



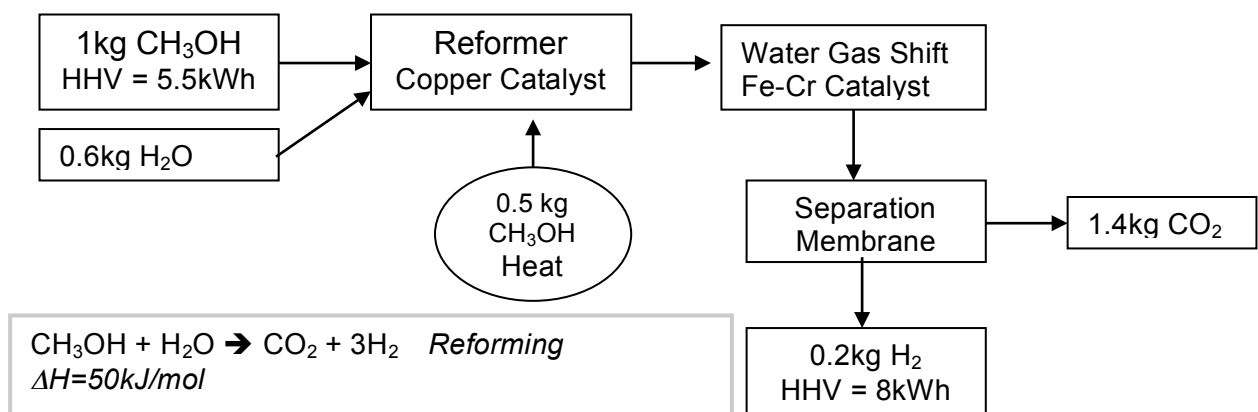
Issues Affecting Technical Feasibility:

- Handling: 1 m³ of CH₄ @STP has a energy content of 36.5 MJ/m³ and would produce 6 m³ H₂ @STP with an energy content of 11.7 MJ/m³
- The process must be carefully controlled and monitored
- Sulfur must be removed from fuel as it attacks catalysts and membranes
- 1.2 units of energy in = 1 unit energy out

Steam Reforming of Methanol

The moderate temperature (250°C) catalytic chemistry of methanol, carbon, carbon oxides, and steam is well known. Mild activity catalysts are sufficient, and thus less costly and less prone to carbon contamination during plant operating fluctuations. While the process favors the production of H₂ and CO₂, small quantities of CO are produced and must be removed with the higher temperature (500°C) water gas shift reaction and active catalyst as described above if the hydrogen fuel is to be marketed to PEM fuel cell users. Methanol reforming inside high temperature fuel cells using the steam in the exhaust stream is the goal of most developers for stationary applications. Mobile transport developers are focusing on methanol on-board reforming as a means to solve the issues of low energy density of hydrogen gas.

Flow Diagram of Methanol Steam Reforming



Issues Affecting Technical Feasibility:

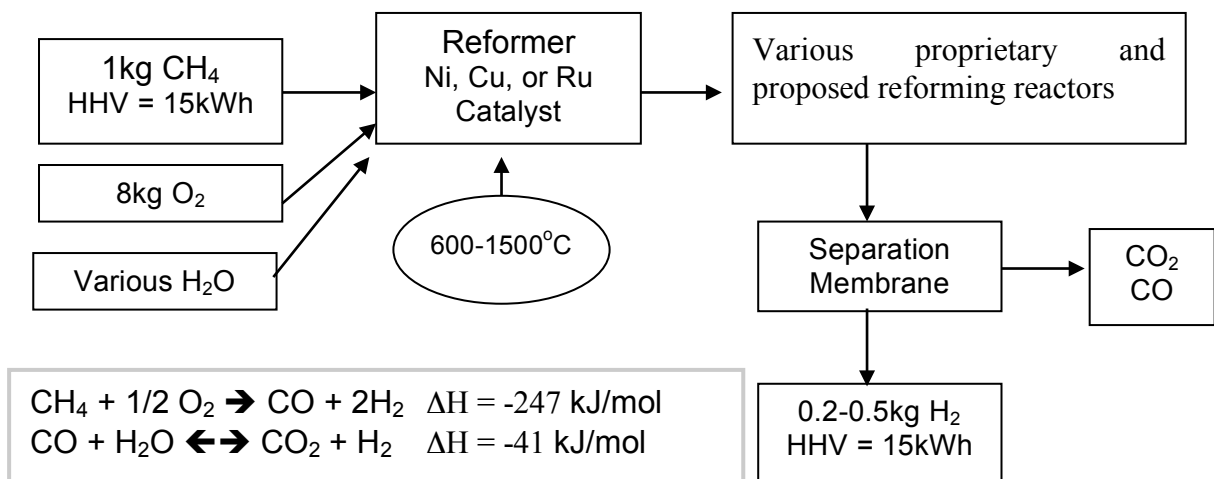
- *Handling: 1kg of liquid CH₃OH @STP has a energy content of 20MJ/kg and would produce 2.4 m³ H₂ @STP with an energy content of 11.7MJ/m³*
- *Methanol is a health hazard, but much easier to transport for mobile applications than gas.*
- *The process must be carefully controlled and monitored*
- *Sulfur must be removed from fuel as it attacks catalysts and membranes*
- *1.3 units energy in = 1 unit energy out*

Catalytic Partial Oxidation (POX), Thermal Cracking, and Autothermal Reforming

If a desulphurized fuel can be delivered to the customer, then mobile reformers would be required to produce the hydrogen for fuel cell vehicles (FCV's). If steam is not available, then the system must be simple and compact. Heat for the reforming provided by oxidizing some of the fuel on the catalyst, referred to as autothermal reforming. At high temperatures (650°C to 850°C) in the presence of a platinum catalyst, the fuel is partially oxidized, resulting in a mixed stream of carbon monoxide and hydrogen. For PEM fuel cells, the CO must then be removed from the H₂. This could be done using another catalytic bed and exhaust containing water vapor from the fuel cell. If water is not added, the process is termed “dry” reforming, and produces 1/3 less hydrogen than steam reforming. The development of high temperature fuel cells is focusing on having the reforming take place in the cell itself, with the resulting CO used as fuel by the cell.

Methane, methanol, and some other fuels can be reformed with CPO. While the chemistry of catalytic partial oxidation and high temperature (1150°C) cracking appear straight forward, the processing details are under study, and building on-board reformers remains a challenge not yet solved.

Flow Diagram of various partial oxidation processes



Issues Affecting Technical Feasibility:

- *At the highest temperatures may not require the catalyst*
- *Must be precisely controlled*
- *Must remove CO below 2.5 ppm for PEM fuel cell*
- *The O₂ would come from Air, which would dilute the fuel stream with N₂*

Desulphurisation: HDS Process, also PURASPEC Process

The chemistry and industrial processes for removing sulphur from liquid or gas fuel streams are well known to the energy industry. The HDS process is suitable for natural gas and light petroleum liquid fuels. The process consumes one mole of H₂ for every mole of sulphur removed from the fuel. Hydrogen reacts with the sulphur in the fuel in the presence of a catalyst to form H₂S, which is then adsorbed in an adsorbent medium (ZnO).

- Suitable only for large scale refinery processing
- Well known to industry, commercially available
- Temperature = 350°C - 400°C
- Requires nickel or cobalt catalyst
- Petrol would require energy input of 1MJ/kg for heating
- Methanol would require 2MJ/kg for treatment
- Consumes H₂ equal to sulphur content

2. Hydrogen Energy Product Packaging

Hydrogen is not a useful energy product at standard temperature and pressure (STP = 25°C, 1 bar) as it has a higher heating value of 0.012MJ/liter. (Compared to petroleum at STP HHV = 33.5MJ/liter). If hydrogen is to be a viable energy product it would need to be compressed or otherwise packaged to increase the energy density and improve the handling.

Compressed H₂

At 200 bar hydrogen gas can be stored in standard pressure containers and has an energy density of 2.5MJ/liter. At 800 bar, hydrogen is near its liquid density, with energy content of 10MJ/liter. Special high-strength containers are required, and must be handled with extra caution. The energy required to compress hydrogen is somewhere between the adiabatic and the isothermal work of compression:

$$\text{Adiabatic Compression Work [J/kg]} \quad W = [n/(n-1)]P_o V_o [(P_1/P_o)^{(n-1)/n} - 1]$$

$$\text{Isothermal Compression Work [J/kg]} \quad W = P_o V_o \ln(P_1/P_o)$$

Where P_o = initial pressure [Pa], P₁ = final pressure [Pa], V_o is the initial specific volume [m³/kg], and n is the adiabatic coefficient (ratio of specific heats).

A hydrogen compressor must have an oil-free special design to avoid contamination of the hydrogen gas. Given the extreme low gas density of hydrogen, the compression must be done in multiple stages, with intercooling. The required specialist technology means that economies of scale will apply, and equipment on a larger scale will be both more energy efficient and more cost effective. A feasibility study of a hydrogen compression plant with 5-stage compression of 1000 kg per hour to 200 bar estimates that the compression process would consume 7.2% of the HHV of the hydrogen. The same plant with compression to 800 bar would consume 10% of the HHV, for the compression work alone (neglecting other plant losses).

Packaging Energy Input for H₂

Compression 200bar	2 kWh/kg
Compression 800bar	4 kWh/kg
Liquefaction -253°C	14 kWh/kg
Metal Hydride 30bar	2 kWh/kg

*Analysis based on 1000 kg/hr production
HHV of H₂ = 40 kWh/kg*

Liquid H₂

Cryogenic hydrogen is currently available through specialty gas suppliers. Multiple compression and cooling stages are required to take hydrogen gas to -235°C and around 800bar. Current cryogenic hydrogen production is done on a large scale, because at production rates around 10 kg/hr, the energy input to the process exceeds the energy content of the hydrogen. Thus, liquid hydrogen as an energy product would not be energetically feasible for distributed production. With current production methods, 40% of the HHV of the hydrogen is invested in liquefying. Cryogenic containers are significantly more expensive and heavier than pressurized containers.

Adsorption in Metal Hydrides

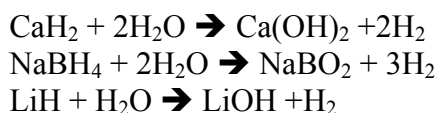
Certain metal alloys are well known to chemically and/or physically adsorb hydrogen. This is a well understood physical process, used in industry for chemical processing. Hydrogen is adsorbed into zirconium-chromium and lanthanum-nickel alloys at a pressure of around 30 bar. The chemical adsorption releases heat. Hydrogen will be evolved from the alloy if heat is added or if the pressure is released. Assuming that heat from a running fuel cell could be used to provide the activation heat of release, then the energy invested in charging a metal hydride storage container would be around 2kWh/kg. The storage density of the product would be around 58 kg/m³, and the volumetric heating value would be around 2.2 kWh/liter.

The main problems with metal hydrides are:

- Cost of the alloy material
- Weight: Metal hydrides were dismissed as options for transport energy products many years ago, as the packaged weight density is uneconomic at around 0.2kWh/kg.

Chemical Storage in Alkali Metal Hydrides

Recent interest has sprung up around the use of liquid solutions of water and alkali metal hydrides, such as sodium borohydride (NaBH₄), calcium hydride (CaH₂), sodium hydride (NaH), or lithium hydride (LiH). These compounds have been used for many years as sources of hydrogen for reducing reactions in chemical and pharmaceutical processing. At room temperature, in the presence of a catalyst, the hydride spontaneously reacts with the water, producing hydrogen and heat. From the technological and consumer point of view, these solutions are ideal. A liquid fuel can be easily stored, dispensed, pumped and metered out for use in the fuel cell. The energy density for liquid NaBH₄ solution would be about 0.42kWh/liter, and as can be seen from the chemical formulas, some of the hydrogen released comes from the water in the solution.



The cost of manufacturing these chemicals as energy products can be assessed on one hand, by the amount of energy that is required. The hydride compounds are synthesized from common and naturally occurring substances, such as calcium carbonate and salt. These are very chemically stable compounds, and a great deal of energy is required to "undo" nature's chemistry. The boron chemistry is the most energy intensive and production requires more than twice the amount of energy in the product. Between 64kWh/kg and 70kWh/kg are used to make limestone and salt into "energy" carriers, compared to the 40kWh/kg energy value of the hydrogen which they contain.

Storage in Carbon Nanotubes

There are many scientific papers reporting progress in forming carbon nanotubes and fullerenes. These are molecular scale structures, produced through processes such as chemical vapor deposition. The most common route is to seed a substrate with catalytic molecules, then, at high temperature, a vapor containing benzene flows over the substrate, and the molecular carbon rings are deposited. The resulting structures have high molecular strength and electrical conductivity along the tube length, and thus are usually sought as connectors in next generation electronics. However, it has been demonstrated that relatively large amounts of hydrogen gas can be physically absorbed into these structures.

Carbon nanotubes are currently produced in research laboratories, with very low yield. While most introduction sections in reported research mention the potential use in hydrogen storage, the technical feasibility is limited. The production quantities will main very small, and the costs high. However, the weight is low compared to metal hydrides. Exploratory studies have demonstrated that the absorption process into the nanotubes is quite slow, on the order of several hours to a day. Carbon nanotubes are touted for applications in hand-held devices, if a controlled way to release the hydrogen is devised.

2.1 Hydrogen Energy Product Distribution

The cost of transport of fuel products to the point of sale is well known to the energy industry. Fully loaded with 26 tons of gasoline, a tanker truck consumes about 1kg of diesel fuel for every ton of gasoline that is moved 100km. This is an economic investment of one unit of energy to distribute 700 units of energy product to consumers. This same truck, refitted with a hydrogen storage tank could deliver 300kg of hydrogen at 200bar. The delivery truck would still consume about 40kg of diesel to travel 100km (500kWh), and it would deliver 11833 kWh of product. This system would represent a cost of one unit of energy for every 24 units delivered.

3. Energy Conversion Efficiency

The engineering definition of energy conversion efficiency does not directly apply to hydrogen as an energy product. The general definition of energy efficiency is the useful energy product produced, divided by the energy input. Energy conversion means taking one useful form of energy - diesel fuel - and converting it to another useful form of energy - electricity. This is worth doing because you could not run a computer on diesel fuel. The issue of using hydrogen for transport or for producing electricity is that the fuels it is made from are equally useful for these purposes.

The energy used to make any of the machinery, transport the energy to or away from the process, or clean up any of the environmental damage of the process are not usually included in the determination of energy conversion efficiency. On this standard basis, hydrogen has a negative energy conversion efficiency, that is, it takes more energy to produce hydrogen than is contained in the hydrogen fuel. If the energy for compression and transport are also included, then hydrogen is an energy deficit product.

Production

- Solar photovoltaics: 1000W solar incidence → 100W electricity 10% conversion
- Hydropower: 100m³/sec flow over 10m head → 8000kW electricity 82% conversion
- Diesel: 100kg/hr (42 MJ/kg) → 133kW electricity 20% conversion

- Electrolyzer: 1kWh electricity → 0.7kWh H₂ → 0.28kWh electricity 72% loss
- CH₄ Reformer: 1kg CH₄ (50MJ) + 12MJ heat/steam + → 0.5 kg H₂ (16.6kWh) 3% loss

Packaging

- H₂ Compression to 200 bar 7% loss
- H₂ Compression to 800 bar 10% loss
- H₂ Liquefaction (100 kg/h plant) 50% loss
- H₂ Metal Hydride Adsorption - Desorption (30 bar) 6% loss
- Chemical Packaging - Alkali Metal Hydrides 160% loss

Transport

- Electric line transmission 10-15% loss
- Petroleum tanker truck (100km) 0.12% loss
- Methanol tanker truck 0.42% loss
- Compressed 200bar H₂ tanker truck (100km) 6.27% loss
- Natural Gas pipeline 1000km 2.5% loss
- Hydrogen pipeline 1000km (assuming no leaks) 10% loss

4. Hydrogen Energy Cost

In 2003 the George W. Bush administration in the USA announced that the research and development effort for fuel cell cars would be funded at \$720 million. The [2009 DOE report](#) on the state of hydrogen energy technology found that hydrogen technology had improved substantially. It also stated that costs were expected to fall further. However, in 2009 the Energy Secretary Steven Chu conducted a review of the hydrogen and fuel cell technology development programs and goals and recommended that the federal funding for hydrogen-powered automobiles should be discontinued. Funding was reduced to \$100 million in 2011, down from \$177 million in 2010. The Obama administration has put more focus on battery electric vehicles and biofuels as alternatives, and has made major policy gains by increasing the fleet fuel efficiency standards significantly. Automobile manufacturer Toyota said that they would continue with plans to have a fuel cell car ready for the market by 2015. Honda reported that it had leased 17 fuel cell vehicles in 2011, but none in the next year. Daimler reported 4 leased vehicles in 2011. The reader should search costs and availability that are up to date.

Current cost of hydrogen is a function of the cost of production and storage equipment, plus the cost of energy input for production, compressing, packaging, and delivering the hydrogen. A survey of research literature shows that there are no new technological break-throughs that provide the resolution to the issues for hydrogen production, storage or delivery. The cost of manufacturing pure hydrogen plus a high pressure container with a life of 5+ years, and compression and safety costs, would make the consumer price of hydrogen energy products in the range of \$50-\$100/kWh. This price range will not be competitive with grid electricity, natural gas, coal or petroleum for most applications. Over the past 20 years, the US Department of Energy (DOE) has done many studies on hydrogen technology development, has funded research in a wide range of technologies and basic sciences, and set targets for development that would make hydrogen cost-acceptable.

The niche market of interest is the market now served by batteries. Although battery electricity storage is twice as electrically efficient as fuel cell electricity production, batteries are very

expensive to use just once \$200-\$250/kWh, and they are heavy, with a low energy density (even compared to hydrogen). We are familiar with the other systems challenges of batteries, they have limited range, a long recharge time, and contain toxic chemicals. Table A2 gives relative alternative cost ranges for hydrogen-fuelled services.

Table A2. Comparison of hydrogen energy costs to current energy costs

Service	Applications	H ₂ Cost	Current
Transportation		[per person-km]	[per person-km]
General	Full Size Automobile	\$***.**	\$0.**
	Electric Mini-Car	\$**.**	\$0.**
	Subways, Buses	\$**.**	\$0.0* - 0.**
	Scooter, Motorcycle	\$*.**	\$0.0*
	Bike or Walking		\$0.00
Transportation	Military	\$***.**	\$0.**
Special Classes	Forklifts - Hazardous	\$**.**	\$0.**
	Mines, Factories	\$**.**	\$*.**
Electricity		[per kWh]	[per kWh]
Grid Power		\$*.**	\$0.0*-0.**
Uninterrupted Power Supply	50-250 kW	\$**.**.*	\$0.0*-**.**
Stationary	10-50 kW	\$**.**.*	\$0.0*-0.**
Hand Held Devices	1-10 kW	\$***.**-***.**	\$0.0*-0.**
	10-500 W	\$***.**	\$***.**

The "interest" in fuel cell vehicles is not driven by the engineering feasibility of a more attractive product, nor through market research indicating a consumer interest. The major automobile manufacturers are developing fuel cell vehicles because they are required to or they will face restrictions on traditional vehicle sales in California.

Cost of Hydrogen Energy	\$USD/kWh
Natural Gas Reforming	\$20
Coal Gasification / Reforming	\$38
Electrolysis	\$72
Sodium Borohydride	\$235
Metal Hydrides	\$30
<i>Cost of Advanced Batteries (one use)</i>	<i>\$200-250 /kWh</i>
<i>Cost of Grid Power</i>	<i>\$0.04-0.20 /kWh</i>