

HYDROGEN ENERGY: THE GOOD, THE BAD, AND THE ENVIRONMENTALLY ACCEPTABLE

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ABSTRACT

Hydrogen is in many respects the ultimate fuel: it is the most abundant element in the universe; as a molecular species it possesses the highest gravimetric energy density of any chemical substance; it can be burned cleanly to produce only water as a reaction product; and its simple and rapid electrode kinetics open the possibility of high efficiency fuel cell-driven power trains. On the other hand, as a gaseous substance under standard conditions, it is inconvenient to use as an on-board fuel without severe compromises with respect to distance between refueling stops; rapid rates of effusion and wide combustibility range limits give rise to safety concerns; and finally, under terrestrial conditions, H₂ is seldom found in Nature—it must be derived from other compounds, often at considerable expense. The various aspects of hydrogen energy combine to paint a picture that is compelling but also technologically challenging.

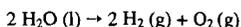
INTRODUCTION

Hydrogen is in many respects the ultimate fuel. First off, it is the most abundant element in the universe. It is estimated that hydrogen makes up 90% of all the atoms or 75% of the mass of the universe. While this fact has little bearing on our current energy economy on Earth, the recent revelation that abundant frozen water deposits may lie below the polar regions of the Moon has galvanized the space technology community over the possibility of producing hydrogen fuel from extraterrestrial sources [1]. While the elemental abundance of hydrogen on earth is also great, almost none of it is found in diatomic molecular form. Free H₂ can be found in the atmosphere at the 0.5 ppm level [2,3], but otherwise it exists principally in combined form with water, biomass, and fossil fuels. H₂ must then be derived from other materials; depending on the source, the energy cost of liberating the hydrogen as H₂ can be quite high, and becomes a major cost component in its manufacture.

For example, H₂ can be had from methane by reaction with steam at 500° C over a Ni catalyst:



The enthalpy of this process per mole of H₂ is only 10.33 kcal, and can be performed with a 65-75% energy efficiency (H₂ heating value out compared to energy input) [4]. In contrast, there is great interest in economically obtaining H₂ directly from liquid water:



Here one is essentially inputting the entire heat of combustion with the hope of getting the free energy back at a later time. The standard enthalpy per mole of H₂ here is 68.3 kcal, a more energetically challenging proposition. Nevertheless, the use of solar based, renewable energy sources to drive the reaction is conceptually very attractive, both from an environmental preservation and a long term sustainability point of view.

While H₂ as a fuel today seems relegated only to certain types of space travel, its energetic nature is in fact greatly in demand as a chemical commodity. US H₂ consumption is already something on the order of 9×10^6 tons/year [5]. Most of this represents internal consumption: the oil refineries account for half of the total, employing it for hydrocracking and hydrodesulfurization; another third is used for ammonia production; much of the remainder is used in methanol production, hydrogenation of polyolefins, and various other chemical and manufacturing processes. The electrolytic production of Cl₂ also yields an equimolar amount of by-product H₂ that is usually used internally for brine concentration or other process heat applications.

Only a few percent of the total is actually sold as a market commodity. Of that, NASA is by far the largest single consumer, requiring some 7000 tons of liquified H₂ per year [5]. Despite its major position in certain industries, annual non-refinery H₂ production (6.7×10^{12} l) represents only 2 day's US gasoline consumption [6].

In Table I, a comparison of relevant fuel properties of H₂ are compared to those of methane, methanol, and gasoline. Many of the superlative characteristics of H₂ are apparent. With the LHV heat of combustion of -57.8 kcal/mol (LHV= lower heating value: product water is left in the vapor state, so that the latent heat of vaporization is not included in the total reaction enthalpy), H₂ is certainly not an exceptional energy producer on a molar basis. However, because it is the lightest element in the Periodic Table, it has a gravimetric energy density of 1.20 x 10⁵ kJ/kg, or 51,590 Btu/lb. This can be compared to jet fuel at about 18,400 Btu/lb, or coal and biomass at 7500 Btu/lb. H₂ has indeed been considered as a substitute for jet fuel: the US Air Force ran Project Bee from 1955-57, where a B-578 twin engine bomber containing a Curtis Wright J-65 turbo-jet engine ran on liquid H₂ [7].

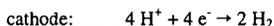
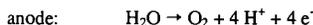
H₂ ELECTROCHEMISTRY

Another asset of H₂ lies in the simplicity of its chemistry. With relatively few bonds being broken and formed, its energy is quickly released. The high intrinsic rate constants enables one to consider the possibility of electrochemically releasing its energy. The exchange current density, or fundamental dynamic charge transfer rate at zero applied voltage, for H₂ discharge on a Pt electrode is 1.0 x 10⁻³ A/cm² [8]. One can operate a continuous flow hydrogen-air electrochemical cell, or fuel cell, by introducing H₂ to the anode or fuel compartment, and air or O₂ to the cathode or oxidant compartment. Product water is exhausted from the cathode compartment. By utilizing gas diffusion electrodes, where the reactant gases penetrate a thin, finely porous, hydrophobic matrix of fluorocarbon polymer, carbon fiber, and supported noble metal catalyst, current densities in the 100's of mA/cm² can be obtained. This translates to a specific power on order of 100 W/kg.

The free energy of reaction is manifested as a voltage that can be used to power an external load. One is then freed from the Carnot efficiency limitations of combustion engines. Fuel cells offer the possibility of obtaining operating fuel efficiencies of 40-50% for vehicular applications. This represents on order of a 50% improvement in fuel efficiency over internal combustion engines. As an example, to match the range of an average-sized vehicle equipped with an IC engine rated at 19 mpg and carrying 111 lb (18 gal) of gasoline, its H₂ fuel cell counterpart would only need to carry 15 lb of H₂ [9].

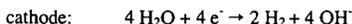
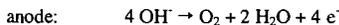
By the same token, one can electrolyze water and produce H₂ by application of a voltage sufficient to exceed its free energy of formation, or 1.23 V:

acidic electrolyte



The mechanism written above assumes an acidic electrolyte. While electrolysis using simple mineral acids is indeed possible, the leading technology at low pH is based on solid polymer electrolytes [10]. Alkaline electrolysis is also possible, and in fact is the most longstanding and least expensive electrolytic technology. The respective half cell reactions then become:

alkaline electrolyte



The energy efficiency of electrolysis is generally taken as 60-80%. These are practical, as opposed to theoretical, values. The basic relationship between current and applied voltage enables one to operate the cell at any desired efficiency. The determining factor is the relationship between current density and capital cost. Smaller voltages make for less energy per volume unit of H₂, but the current density (H₂ evolution rate per unit area) is also less, and so the electrolyzer must be made larger and more costly for a given H₂ production capacity. An can be run at 99% efficiency, but the H₂ output would be so low as to be impractical.

While generally not as economical as steam reforming of natural gas, electrolysis has already carved out various market niches for H₂ production where the cost of electricity is low, the

availability of natural gas is poor, the required H₂ purity is high, or the required production rate is modest (< 10,000 scf/day).

H₂ STORAGE

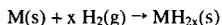
As a gaseous substance under standard conditions, it is inconvenient to use H₂ as an on-board fuel without severe compromises with respect to distance between refueling stops. This is perhaps its greatest limitation, and a large segment of the hydrogen community is committed to increasing the range limits of H₂-fueled travel by reducing the volumetric energy density of the stored material.

The simplest answer is to carry the H₂ as a pressurized gas; unfortunately, the H-content of a standard 2200 psi cast iron vessel is less than one percent [11]. It has been estimated that tank pressure must be increased to >10,000 psi using carbon fiber-reinforced cylinders in order for a H₂-powered vehicle to have the same range as a gasoline-powered one [12].

One can then consider liquifaction as a means of carrying H₂. As a liquid, it has one-tenth the weight of an equal volume of gasoline, but only one-quarter the energy as well. While this represents a tremendous improvement in volumetric energy density over the gaseous state, one should consider that the liquid must be stored at 20.3 K. As a result, vacuum-insulated, stainless steel storage tanks must be used. For vehicles such as NASA's space shuttle, the low surface-to-volume ratio of its 10⁵ plus gallon tanks minimize boil off losses. For domestic transportation, boil-off would be a greater problem, although it is estimated that boil-off could be held to 2% per day [13]. The resulting H-content of an insulated LH₂ storage system would be on order of 20%.

Since the freezing point of H₂ is only 6.5 degrees less than its liquifaction temperature, engineers have sought to increase the LH₂ density by about 15% by mixing solid and liquid to make a slurry, or "slush H₂". It is typically mixed as 50% solids at the triple point of H₂ (13.8 K, 52.8 torr). A further advantage of this approach is that the refrigeration heat capacity is increased by 82.7 kJ/kg, resulting in a 24% increase in the effective heat of vaporization [14,15].

Another way of storing H₂ in the solid state is to combine it with various electropositive metals to form metal hydrides:



There are a number of low molecular weight metal hydrides whose H-contents lie in the 4-7% range, such as CaH₂ and MgH₂. While the numbers may appear low, as noted above, they are well in excess of what can be obtained with conventional pressurized gas cylinder technology. These hydriding reactions are typically exothermic, so that to recover the stored H₂, the hydride must be heated to overcome the enthalpy of formation and shift the equilibrium back toward the free gas. This becomes a problem when the heat of formation of the hydride becomes comparable to the heat of combustion of H₂.

There are some metal alloys for which the hydride heat of formation is low enough that the equilibrium can be controlled at ambient temperature simply by pumping H₂ into and out of the hydride storage bed. Two families of metal alloys that have received much attention are the AB₂'s and the AB₃'s. The former group consists of some combination of low valency first row transition metals, such as Ti, V, and Fe. The latter group is represented by LaNi₅. With H-contents on order of 3%, they represent only a modest improvement over compressed gas. Nevertheless, because of their stability under negative potential in alkaline electrolyte, these materials have attracted great attention in the battery business, where Ni-metal hydride batteries are rapidly replacing Ni-Cd secondaries in high cost portable devices, such as laptop computers.

THE ENVIRONMENTAL IMPERATIVE

The idea of hydrogen energy has been with us since the days of Jules Verne, but events in recent years have begun to stimulate serious public discussion.

One was the push in California to mandate the used of zero emission vehicles. In 1991, California enacted legislation creating a market for clean vehicles that will require significant changes in the automobile of today. A series of categories defining progressively more stringent emissions standards were defined: Transitional Low Emission Vehicles (TLEV); Low Emission Vehicles (LEV); Ultra-Low emission Vehicles (ULEV); and Zero Emission Vehicles (ZEV) [16]. The TLEV will allow hydrocarbon emissions of 0.18 g/mile, 3.4 g/mile of CO, and 0.4 g/mile of NO_x. The ZEV is exactly what it says: 0.0 g/mile for the above pollutants. A H₂-powered fuel

cell vehicle is one of the few that could meet these standards. While the original legislation mandated that by 1998, 2% of all vehicles sold by major automakers must be ZEV's, the California Air Resources Board has since relaxed that requirement until 2003, at which time 10% of sales must qualify [17].

Another recent event is the signing of the Kyoto Protocol. This treaty requires industrialized countries to reduce greenhouse gas emissions on average by 5.2 percent below 1990 levels during the first "commitment period" between 2008 and 2012. There are differentiated targets ranging from 92 and 110 percent of 1990 levels. The US must reduce emissions by 7%. US greenhouse gas emissions in 1990 were estimated at 1.46×10^9 metric tons in carbon equivalent [18].

With the likelihood of future carbon tax assessments, clean burning H_2 is a clear advantage. In truth, H_2 does make for some NO_x formation, as does any fuel using air as oxidant in a combustion process. However, the extent of NO_x formation per energy unit is estimated to be some 80% less than for petroleum-based fuels [19].

SAFE H_2 ?

The H_2 flammability limits vary from 4 to 75% in air, the widest of any fuel. From a safety point of view this is thought to be a negative attribute: leaks that contain H_2 may ignite while other fuels would be too concentrated or too dilute. H_2 detectors should alarm when $[H_2] > 1\%$, at 20-25% lower flammability limit. On the other hand, a plume of H_2 gas leaking into the air quickly rises and dissipates because of its lower density. Engine tolerances must be made more precise to prevent significant blow-by during compression; pronounced "flashback" effects (engine backfire through intake system) require direct cylinder injection.

Just as with natural gas, safety codes will undoubtedly require that an odorant be added to H_2 to alert consumers to leakage. This is a matter of concern to fuel cell manufacturers, who need ultrapure H_2 to prevent poisoning of their noble metal electrocatalysts.

Regardless of the advances made in H_2 energy technology, to achieve widespread acceptance the public image of H_2 must change. Few public conversations on H_2 can go for very long without mention of the either the Challenger space shuttle or Hindenburg disasters. Recently, research by A. Bain has shown that the shell material of the Hindenburg was sufficiently flammable that it would have burned even if the dirigible had been filled with helium [20]. Indeed, there have been less publicized instances where He-filled balloons have caught fire. Burning H_2 produces a largely transparent flame, so that hydrogen's role in the enormous conflagration caught on film in 1937 could only have been indirect.

The economics of H_2 transport basically follow that of natural gas: for many users at close distance, pipeline is the preferred way of transporting H_2 ; for few users at longer distance, liquifaction is cheaper. Much effort has gone into determining whether the existing natural gas pipeline network could some day be used for transporting H_2 . The ability of H_2 to penetrate and embrittle metallic parts is a matter of concern. Carbon steel is embrittled by H_2 , making it more susceptible to stress fractures. The general view is that at modest pressures (< 700 psi) H_2 would be compatible; at higher pressure, seamless stainless steel piping would be necessary [4]. Actually, some 500 miles of pipelines dedicated to H_2 transport currently exist worldwide, with major concentrations in Germany's Ruhr Valley and near LaPorte, Texas [21].

CONCLUSION

While most consider H_2 to be a fuel of the future, it is actually all around us today as a basic chemical commodity. It will always be there when we need it, first from fossil fuels, then biomass, and finally from water. The obvious gravimetric advantage is tempered by its gaseous state. A number of storage technologies offer trade-offs between weight and volume. The simplicity of its chemistry invites the more efficient electrochemical option. Its widespread implementation may ultimately hinge on what levels of air quality our society is willing to accept.

ACKNOWLEDGEMENT

The author would like to thank the many co-workers at the Florida Solar Energy Center who assisted in the preparation of this report, as well as the U.S. Department of Energy, Office of Solar Thermal, Biomass Power, and Hydrogen Technologies, for their financial support.

REFERENCES

- 1- R.A. Kerr, Science, 1998, Vol. 279, 1628.
- 2- W. Zittel and M. Altmann, "Molecular Hydrogen and Water Vapour Emissions in a Global Hydrogen Energy Economy," Hydrogen Energy Progress XI, proceedings of the 11th World Hydrogen Energy Conference, T.N. Veziroglu, C.-J. Winter, J.P. Baselt, and G. Kreysa, eds, Schön and Weitzel GmbH, Frankfurt am Main, 1996, p. 71-81.
- 3- D.R. Lide, ed., CRC Handbook of Chemistry and Physics, 74th edn, CRC Press, Boca Raton, 1974, p. 4-14.
- 4- R.L. Mauro, "The Hydrogen Technology Assessment, Phase I," National Hydrogen Association, Washington, DC, 1994.
- 5- J.R. Birk, B. Mehta, A. Fickett, R. Mauro, and F. Serfass, Hydrogen Energy Progress IX, additive, proceedings of the 9th World Hydrogen Energy Conference, International Association of Hydrogen Energy, p. 101.
- 6- R.L. Bechtold, Alternative Fuels Guidebook. Properties, Storage, Dispensing, and Vehicle Facility Modifications, Society of Automotive Engineers, Warrendale, PA, 1997.
- 7- J.L. Sloop, "Liquid H₂ as a Propulsion Fuel," NASA report SP4404, 1978.
- 8- J.O'M. Bockris and S. Srinivasan, "Electroodic Reactions of Oxygen," ch. 8 in Fuel Cells, McGraw-Hill, New York, 1968.
- 9- "Feasibility Study of Onboard Hydrogen Storage for Fuel Cell Vehicles," US Department of Energy, Office of Transportation Technologies, January, 1993.
- 10- A.B. LaConti, A.R. Fragala, and D.L Smith, in "Proceedings of the Symposium on Electrode Materials and Processes for Energy Conversion and Storage," J.D.E. McIntyre, S. Srinivasan, and F.G. Will, eds., The Electrochemical Society, Inc., Pennington, NJ, 1977.
- 11- A.J. Appleby, "Fuel Cells and Hydrogen Fuel," Hydrogen Energy Progress IX, proceedings of the 9th World Hydrogen Energy Conference, Paris, France, June 22-25, 1992, T.N. Veziroglu, C. Derive, and J. Pottier, eds, MCI, Paris, 1992, p. 1375-1383.
- 12- D.L. Block, S. Dutta, and A. T-Raissi, "Storage of Hydrogen in Solid, Liquid, and Gaseous Forms," Florida Solar Energy Center, FSEC-CR-204-88, June, 1988.
- 13- W. Strobl and W. Peschka, "Liquid Hydrogen as a Fuel of the Future for Individual Transport," BMW AG Presse, Munich, Germany.
- 14- Fujiwara, M. Yatabe, H. Tamura, M. Takahashi, J. Miyazaki, and Y. Tsuruta, Int. J. Hydrogen Energy, Vol 23, (1998) 333-338.
- 15- R.L. Mauro, "The Hydrogen Technology Assessment, Phase III," National Hydrogen Association, Washington, DC, 1994.
- 16- D.L. Smith, "Strategy for Fuel Cells in Vehicles," National Hydrogen Association, Washington D.C., March 4, 1994, p. 1.
- 17- "Guide to Alternative Fuel Vehicle Incentives and Laws," 2nd edition, November, 1996, U.S. Department of Energy, Clean Cities Program.
- 18- B. Hileman, Chemical and Engineering News, Vol. 74, Jan. 15, 1996.
- 19- "Liquid Hydrogen Powers Third EQHPPP Demonstration Bus," Hydrogen and Fuel Cell Letter, P. Hoffmann, ed., Vol. 11, No. 5, May 1996, p. 4.
- 20- M. DiChristina, Popular Science, November 1997, p 71-76.
- 21- "Direct-Hydrogen-Fueled Proton-Exchange-Membrane Fuel Cell System for Transportation Applications," C.E. Thomas, Directed Technologies, Inc., Department of Energy, DOE/CE/50389-502.

Table I. Selected Fuel Properties of Hydrogen, Methanol, and Gasoline

property	hydrogen	methane	methanol	gasoline
molecular weight (g/mol)	2.018	16.043	32.042	100-105
carbon content (wt %)	0	75	37.5	85-88
specific gravity	0.0838 g/l (g) 0.070 g/cm ³ (l)	0.6512 g/l (g) 0.466 g/cm ³ (l)	0.796	0.69-0.79
boiling point (°C)	-252.87	-162	65	27-225
heat of combustion (HHV, kcal/mol)	68.3	212.9	173.5	1307
lower flammability limit (vol %)	4.1	5	7.3	1.4
upper flammability limit (vol %)	75	15	36	7.6
diffusion coefficient (cm ² /s) STP in air	0.61	0.16	-	0.05