Future Energy: Opportunities and Challenges

Part II. Energy Sources

Chapter 12. Hydrogen

Future Energy:
Opportunities and Challenges

Thomas W. Kerlin

12
Hydrogen

The Main Points

- **Hydrogen is not an energy resource, but an energy carrier.**
- **Like electricity, the other main energy carrier, hydrogen must be manufactured.**
- **Like electricity, much more energy must be used to make hydrogen than can be produced by using the hydrogen.**
- **Hydrogen can be made from a number of hydrogen-bearing compounds, but any large-scale future hydrogen production will be based on the electrolysis of water.**
- **Hydrogen is difficult to store and transport.**
- **Batteries use energy much more efficiently than hydrogen fuel cells.**

12.1 Introduction

Hydrogen can serve as a fuel, but it, like electricity, is an energy carrier rather than an energy resource. That is, hydrogen must be produced from another material, and this production requires more energy than is contained in the hydrogen produced. Hydrogen can be stored in bulk for use when needed, albeit at significant difficulty and expense. Electricity, on the other hand, cannot be stored except for limited quantities in capacitors. (Some say that batteries store electricity, but, in fact, they store chemical energy that can readily be converted into electricity.)

Hydrogen reacts strongly with other chemicals to form compounds. As a result, hydrogen desired for use as a fuel is locked in hydrogen-bearing compounds. Source materials for producing free hydrogen are water, hydrocarbons, and biomass. Obtaining free hydrogen for use as a fuel requires extracting it from these materials and this extraction requires an expenditure of energy that exceeds the energy subsequently available from the use of hydrogen as a fuel.

The rationale for expending energy to create a new fuel material is to produce a new fuel with greater usefulness. This rationale is analogous to using heat from fossil fuel combustion or nuclear fission to produce electricity, which wastes about two-thirds of the energy released. However, the electricity produced is so uniquely useful that this waste is freely tolerated. Likewise, if using hydrogen as a fuel is to become commonplace, it will require that its usefulness is found to outweigh the problems and costs associated with producing, storing, transporting, and using it.

There has been great enthusiasm for a “hydrogen economy” among many advocates of a sustainable energy future[1]. However, it has been shown that hydrogen use presents problems that are likely to prevent its widespread use for vehicle propulsion[2]. First, the energy efficiency of hydrogen production and use is much lower than that of alternatives for propulsion, such as battery power. Second, the cost and effort required for the changes to our infrastructure that would be needed to accommodate high levels of hydrogen use in transportation are large. Third, the pressurized or liquefied storage of hydrogen raises concerns about the weight and volume penalty and the safety of its use in vehicles.

A more likely use of hydrogen is in electric power plants. Because of daily and seasonal variations in power demand, there is often excess production capacity. Rather than sitting idle, these plants could produce hydrogen during periods of low demand for subsequent electricity production when demand increases. This approach would increase plant utilization, but this approach faces concerns about the cost of added equipment and the low ratio of energy produced from stored hydrogen to the energy required to make the hydrogen.

12.2 Hydrogen Properties

Hydrogen is the simplest atom, and hydrogen gas is the lightest gas. Common hydrogen atoms contain a single proton in the nucleus and a single electron orbiting around the nucleus. Two hydrogen atoms combine and share electrons to yield a hydrogen molecule, H_2.

In the following discussion, the properties of hydrogen are presented and are compared with the properties of methane, the main constituent of natural gas and the current dominant gaseous fuel.

12.2.1 Physical State

Hydrogen's boiling point is -423°F (-253°C). Consequently, hydrogen is a gas at standard temperature and pressure, with a density of around 0.00523 lb/ft^3. (For comparison, the density of methane gas at standard temperature and pressure is 0.0417 lb/ft^3, almost eight times greater than that of hydrogen). The low density of hydrogen complicates the storage of enough material to provide significant energy upon oxidation. The storage issue is especially important in the possible use of hydrogen as a transportation fuel. Pressurization, liquefaction, storage by absorption in the molecular structures of other materials or by storage in compounds that release hydrogen upon decomposition are potential options for reducing the volume of stored hydrogen. All of these approaches involve the use of heavy vessels or chemical storage media that compromise their attractiveness for vehicular applications.

12.2.2 Reaction with Oxygen

When hydrogen reacts with oxygen, as in combustion or in a fuel cell, the reaction products are water and energy. That is:

$$2H_2+O_2 \rightarrow 2H_2O+\text{energy} \qquad (12\text{-}1)$$

Methane, the lightest naturally occurring hydrocarbon gas, also releases energy when it reacts with oxygen. The reaction proceeds as follows:

$$CH_4+2O_2 \rightarrow 2H_2O+CO_2+\text{energy} \qquad (12\text{-}2)$$

Note that the reactions for both materials produce water, but the methane reaction also produces carbon dioxide. Like hydrogen, methane can be used in a fuel cell to produce electricity.

12.2.3 Gravimetric Heating Values (Energy per unit of weight)

The high and low gravimetric heating values of hydrogen are 61,000 BTU per pound (HHV) and 51,500 BTU per pound (LHV)[3]. These are very high. For comparison, the values for methane are 24,000 BTU per pound for the HHV and 21,500 BTU per pound for the LHV.

12.2.4 Energy Density (Energy per unit of volume)

Since storage volume is a major concern, a more important energy measure than the gravimetric heating value is the energy available per unit volume (energy density) of hydrogen. At standard temperature and pressure, the high heating value (HHV) energy density for hydrogen is 325 BTU/cubic foot and the low heating value (LHV) energy density is 275 BTU per cubic foot. This compares with methane's HHV energy density of 1,030 BTU per cubic foot and LHV energy density of 930 BTU per cubic foot. Clearly, hydrogen can provide more energy per pound of gas oxidized than methane, but less energy per cubic foot.

Storing hydrogen at high pressure increases its energy density. For example, at 3,000 psig (about 204 times atmospheric pressure) and 68°F, the LHV energy density of hydrogen increases to 48,900 BTU per cubic foot (a 180-fold increase). However, at 3,000 psig and 68°F, methane still has a much higher energy density (184,100 BTU per cubic foot).

Liquefaction also increases the energy density of hydrogen and methane. Cooling hydrogen to its boiling point (-423°F) at atmospheric pressure creates liquid hydrogen with an LHV energy density of 227,850 BTU per cubic foot. Cooling methane to its boiling point (-259°F) at atmospheric pressure creates a liquid with an LHV energy density of 561,500 BTU per cubic foot.

Table 12-1 summarizes the important properties of hydrogen and methane.

Table 12-1. Properties of Hydrogen and Methane

Property	Hydrogen	Methane
Density (pounds/cubic foot) at standard temperature and pressure	0.00523	0.0417
Boiling Point (°F) at atmospheric pressure	-423	-259
Gravimetric High Heating Value (BTU/pound)	61,000	24,000
Gravimetric Low Heating Value (BTU/pound)	51,500	21,500
Volumetric High Heating Value at standard temperature and pressure (BTU/cubic foot)	325	1,030
Volumetric Low Heating Value at standard temperature and pressure (BTU/cubic foot)	275	930
Volumetric Low Heating Value at 3,000 psi and 68°F (BTU/cubic foot)	48,900	184,100
Volumetric Low Heating Value at Atmospheric Pressure and Boiling Temperature (BTU/cubic foot)	227,850 (-423°F)	561,400 (-259°F)

It should be noted that pressurization and liquefaction both require energy expenditure, thereby reducing the net energy available in pressurized or liquefied fuels.

12.2.5 Diffusion

Because the hydrogen molecule is so small, it can pass through materials that are impenetrable to other gases. Hydrogen leakage by diffusion through containment structures is an issue in storage and transport.

12.2.6 Reactions with Metals

When exposed to hydrogen, certain metals, especially high-strength steel, become brittle. Possible embrittlement is a consideration in selecting materials for storing and transporting hydrogen.

12.3 Hydrogen Production

Any hydrogen-bearing compound is a potential source for producing hydrogen. Currently, most of the hydrogen produced is made from natural gas (mostly methane) for use in the chemical and oil refining industries. Hydrogen production by electrolysis of water is also a mature technology. These technologies, along with several technologies under development and with potential future importance, are discussed in this section.

12.3.1 Hydrogen from Fossil Fuels

Methane Steam Reforming

Steam reforming of methane, discussed in Section 4.8, is a two-step process. First, methane reacts endothermically (absorbs heat) with steam to produce syngas:

$$CH_4+H_2O+\text{heat}\rightarrow 3H_2+CO \tag{12-3}$$

In the second step, the carbon monoxide reacts exothermically with water in the "water shift reaction":

$$CO+H_2O\rightarrow H_2+CO_2+\text{heat} \tag{12-4}$$

The overall reaction is as follows:

$$CH_4+2H_2O\rightarrow 4H_2+CO_2 \tag{12-5}$$

That is, one molecule of methane and two molecules of water yield four molecules of hydrogen and one molecule of carbon dioxide. Note that half of the hydrogen comes from the methane and half comes from the water.

Steam reforming followed by the water shift reaction is also possible with other hydrocarbons besides methane, but methane is now most widely used.

Methane Partial Oxidation

Syngas can also be produced exothermically by reacting methane with limited oxygen:

$$2CH_4+O_2 \rightarrow 2CO+4H_2+heat \tag{12-6}$$

These products are subsequently converted into hydrogen and carbon dioxide by the water shift reaction. The overall reaction is:

$$2CH_4+O_2+2H_2O \rightarrow 2CO_2+6H_2 \tag{12-7}$$

Note that two-thirds of the hydrogen comes from the methane and one-third comes from the water.

Converting natural gas into hydrogen fails to provide a new fuel with greater usefulness for energy production than the material from which it was produced. If hydrogen is to become a widely used fuel, other production methods will be required. Also note that producing hydrogen from methane releases carbon dioxide into the atmosphere.

Coal

Hydrogen can also be obtained by reacting water with coal. Coal is a complex mixture of hydrocarbons and carbon. The steam reforming of the hydrocarbon component proceeds as follows:

$$C_nH_m+nH_2O \rightarrow nCO+(n+m/2)H_2 \tag{12-8}$$

The reaction with the carbon component proceeds as follows:

$$C+H_2O \rightarrow CO+H_2 \tag{12-9}$$

Reaction products from both reactions can then be used to produce carbon dioxide and additional hydrogen by the water shift reaction. The overall reaction for the carbon component of coal is:

$$C+2H_2O \rightarrow CO_2+2H_2 \qquad (12\text{-}10)$$

Hydrogen production from coal converts a less useful (solid) fuel into a more useful (gaseous) fuel. Note, however, that using coal to produce hydrogen releases carbon dioxide, the major contributor to climate change.

Heavy Oils

Heavy oils, including oil sands and oil shale, contain hydrocarbons of limited usefulness in the as-found state. An option for increasing their usefulness is conversion to gaseous fuel. Steam reforming to produce hydrogen is a possibility.

In addition, thermal decomposition of the hydrocarbons at very high temperature produces carbon and hydrogen as follows:

$$C_nH_m+heat \rightarrow nC+(m/2)H_2 \qquad (12\text{-}11)$$

12.3.2 Hydrogen from Biomass

Biomass can be used to produce hydrogen. Processes for this include gasification, photosynthesis and fermentation.

As was discussed in Chapter 7, syngas can be produced via the gasification of biomass as well as from fossil fuels. Biomass decomposes at high temperature, yielding syngas and carbon dioxide. This mixture can be further processed by the water shift reaction to yield additional hydrogen by reacting the carbon monoxide with water (see Section 4.7).

In photosynthesis, the energy in sunlight causes water to split, producing hydrogen and oxygen. In most plants, the hydrogen then becomes part of the carbohydrates, proteins, and oils that make up the biomass. However, some algae and bacteria, and even some genetically modified terrestrial plants, produce and release molecular hydrogen under certain conditions. Basically, the hydrogen is released rather than entering the reactions that produce biomass. This process, called *biophotolysis*, is a way to split water molecules with energy from sunlight using plant matter as an enabler.

The A.B.E. process (discussed in Appendix N) for producing acetone, butanol, and ethanol (hence A.B.E.) is a two stage fermentation process in which butyric acid and hydrogen are produced in the first stage. Fermentation processes for hydrogen production from biomass and from various types of wastewater have also been formulated. Waste fermentation has the added benefit that it neutralizes contained pathogens while producing useful hydrogen. Each process has specific requirements for enzymes used and processing conditions.

None of the biological hydrogen production methods are now commercially viable, yet the possibility that a simple and economical way might be developed to produce hydrogen has stimulated a large research effort to understand and optimize the biological processes. Thousands of scientists are exploring plant genetics, plant and enzyme modification by genetic engineering, and conditions (such as light vs. dark fermentation and aerobic vs. anaerobic fermentation) that maximize hydrogen yields.

12.3.3 Hydrogen from Water

As is often demonstrated in high school chemistry courses, passing direct electrical current through water produces hydrogen and oxygen. This process is called hydrolysis. An electrolyte, commonly potassium hydroxide, is dissolved in the water to make it conductive. Figure 12-1 shows the basic principle. Hydrogen gas bubbles from the negative electrode and oxygen bubbles from the positive electrode.

It is noteworthy that in electrolysis, one energy carrier (electricity) is used to make another energy carrier (hydrogen). Producing large volumes of hydrogen by electrolysis is logical if electricity is abundant and cheap and if the hydrogen can serve a useful purpose that is not practically achievable with electricity.

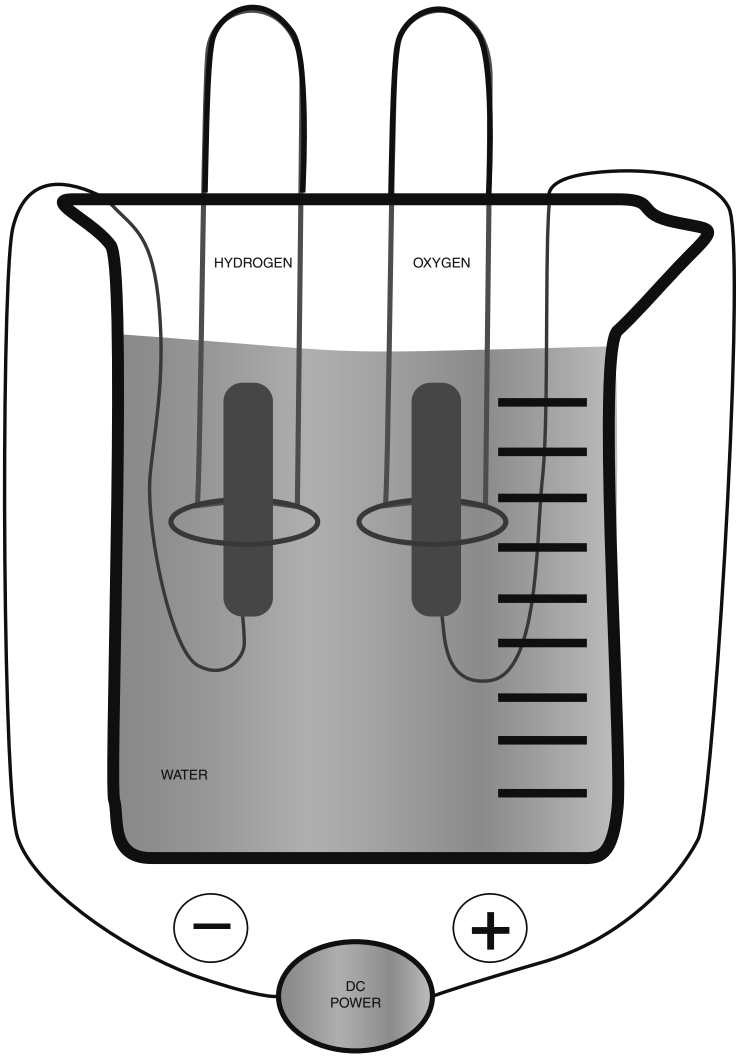

Figure 12-1. Water Electrolysis

The environmental impact of water electrolysis depends on the method used to make the electricity consumed in the process. Fossil-fueled power plants produce carbon dioxide, while solar, wind, geothermal, hydroenergy, and nuclear sources produce electricity without releasing carbon dioxide. Of course, grid electricity used for electrolysis normally comes from all of the sources that feed electricity to the grid.

The electrical energy required to electrolyze water decreases with increasing temperature. Part of the energy needed to split the water molecules can be provided by heat. Possibilities for obtaining inexpensive heat to reduce electricity requirements for electrolysis include the use of waste heat from industrial processes, solar heat or heat from a high temperature nuclear reactor.

Hydrolysis of water using sunlight can be performed in a unit that combines the photovoltaic production of electricity and the use of that electricity to split water.

Biophotolysis was discussed in the previous section.

Water spontaneously decomposes into hydrogen and oxygen at high temperature (4,500°F).

Thermochemical processes can also produce hydrogen. These processes involve the repeated decomposition and regeneration of chemicals used in the process. For example, a process based on reactions between iodine and sulfuric acid proceeds according to the following series of reactions:

1. Decomposition of sulfuric acid to produce sulfur dioxide, water and oxygen:

$$2H_2SO_4+heat \rightarrow 2SO_2+2H_2O+O_2 \quad (12\text{-}12)$$

2. Reaction of sulfur dioxide with iodine and water to regenerate the sulfuric acid and produce hydrogen iodide, HI:

$$I_2+SO_2+2H_2O \rightarrow H_2SO_4+2HI \quad (12\text{-}13)$$

3. Decomposition of hydrogen iodide to regenerate iodine and produce hydrogen:

$$2HI+heat \rightarrow I_2+H_2 \quad (12\text{-}14)$$

Basically, water and heat are the input quantities and hydrogen and oxygen are the output quantities. The other chemicals are repeatedly used and regenerated within the process.

12.4 Hydrogen Storage

If it is to become a significant energy carrier, facilities will be needed to store hydrogen for stationary and mobile applications. Hydrogen storage poses some significant engineering challenges, especially storage in vehicles. An often-stated design objective for hydrogen-fueled vehicles is a range of 300 miles while achieving adequate safety and acceptable weight and volume. The quantity of hydrogen needed for a range of 300 miles is 7 to 14 pounds, depending on vehicle characteristics. This does not sound like much weight, but the vessels required to hold this amount of hydrogen are heavy.

12.4.1 Pressurized Storage

The pressurization of hydrogen to increase its energy density requires an energy expenditure that increases as the storage pressure increases. The estimated energy required for pressurization ranges from around 7 percent of the energy contained in the hydrogen (at a pressure of 200 atmospheres) to 12 percent (at 800 atmospheres)[4].

Pressurized storage requires strong vessels that can withstand the high pressure, and these vessels must prevent significant hydrogen leakage and must tolerate contact with hydrogen without suffering significant embrittlement. The weight and volume of pressurized storage vessels are limiting factors for fuel storage in vehicles.

12.4.2 Liquefied Storage

The liquefaction of hydrogen at cryogenic temperatures also requires energy expenditures to cool the gas to below its boiling temperature. The amount of energy needed to cool hydrogen for cryogenic storage is even higher than the amount required for pressurization.

Liquefied storage also requires highly insulated vessels to minimize heat transfer from the surroundings.

12.4.3 Storage in Solids

Hydrogen can be stored in solids by absorption in a solid matrix or by reacting it with suitable materials to form hydrogen-bearing compounds that will decompose to yield hydrogen when it is needed. For use as a hydrogen storage medium, desirable properties are:

- Ease of capturing hydrogen in the solid
- Large mass of stored hydrogen per unit of solid mass
- Ease of hydrogen release when needed
- Ease of restoring the material used to capture hydrogen

Metal hydrides and alanates (compounds such as sodium alanate, $NaAlH_4$), show some promise for storing hydrogen, but as yet, no practical method for hydrogen storage in solids is available.

12.5 Options for Hydrogen Production Sites

Hydrogen can be produced in a large centralized production facility or in smaller local electrolysis units that use electrical energy transferred over the electrical transmission and distribution system. Thus, the choices are to deliver hydrogen or to deliver electricity. Larger centralized plants would have lower costs per pound of hydrogen produced, but localized production avoids the need for large-scale hydrogen transport and storage.

12.6 Hydrogen Distribution

Hydrogen distribution usually refers to the transfer of hydrogen from a bulk storage facility into a vehicle's storage system. It is analogous to filling a gasoline tank at a filling station. A high degree of safety and adequate speed of refueling are design requirements for hydrogen filling stations.

12.7 Use of Hydrogen as a Fuel

Hydrogen may be used to provide mechanical energy by combustion and for producing electrical energy with a fuel cell or with a turbine-generator. Using hydrogen in a combustion system is similar to applications using other gaseous fuels such as methane. Fuel cells are basically batteries with continuous replenishment of reactants.

12.7.1 Stationary Applications

Electric utilities must build enough capacity to satisfy peak demands. During periods of lower demand, some capacity will be idle and available for producing electricity for electrolyzing water. There are no fuel costs for an idle plant, but capital costs (and some operation costs) continue. Producing hydrogen during low-load periods (generally at night and in the spring and fall) is envisioned as a way to achieve a higher financial return on the investment in a power plant. The hydrogen produced could be sold, or stored and later used by the utility to produce electricity during high-load periods. This approach is an example of "load leveling."

12.7.2 Mobile Applications

The use of hydrogen to propel vehicles imposes additional considerations and requirements. The weight and volume of on-board hydrogen storage vessels are important in mobile applications.

12.8 Energy Efficiency

Hydrogen may be used to store and carry energy in the future. Consequently, it is important to examine the energy efficiency of these activities. Energy is needed to produce, store, transport, distribute, and use hydrogen. These energy expenditures reduce the net energy available when the hydrogen is used as a fuel.

The main competitor to hydrogen fuel cells for electric vehicle energy is the battery. Fuel cells and rechargeable batteries both use electrical energy to create chemical energy that is subsequently transformed back into electrical energy. Consequently, the relative energy efficiency of fuel cells and batteries is an important issue. Section 18.5 provides a breakdown of the energy efficiencies of the steps in the use of fuel cells and batteries. Accounting for all of the energy-consuming steps in getting from grid electricity to electricity produced with a battery or a fuel cell shows that batteries are currently about 2.5 times as efficient.

12.8.1 Energy Efficiency in Production

The main current and potential future hydrogen production methods have been described in previous sections. For the consideration of energy efficiency in hydrogen production, the focus here will be on production by electrolysis. Production from natural gas is currently the dominant way to make hydrogen, but future resource availability, cost, and environmental acceptability will prohibit its widespread use. One or more of the other methods described above may prove superior, but they are currently too underdeveloped to warrant reliance on them. Electrolysis is a proven technology that is ready for immediate deployment.

As with all energy conversions, the production of hydrogen by electrolysis results in unavoidable energy losses. The energy efficiency of electrolysis (energy in hydrogen produced/energy in electricity consumed) is around 70 percent with current technology. High temperature electrolysis could replace some of the electrical energy with heat energy.

12.8.2 Hydrogen Energy Conversion

Consider electrical energy production using hydrogen. The process involves using electrical energy to make hydrogen, then later using that hydrogen to make electricity. Since energy losses occur with both conversions, the only rationale for pursuing this route is that energy can be stored in hydrogen.

The conversion from chemical to electrical energy can be accomplished in a fuel cell or a heat engine (typically a dual-cycle turbine-generator). The maximum energy efficiency for either approach is 50 to 60 percent. Therefore, the combined energy efficiency of the production step and the conversion step is 35 to 40 percent. Additional energy is required for ancillary processes such as pressurization and liquefaction. Overall, the energy efficiency of producing electricity with hydrogen is less than 25 percent[5]. That is, at least four kilowatt-hours of grid electricity are consumed in producing one kilowatt-hour of electricity with hydrogen.

12.9 Hydrogen's Future

Clearly, proponents of a hydrogen economy have overstated the potential for hydrogen to be a major energy supplier in the future. In 2002, for example, in the National Hydrogen Energy Roadmap[1], Spencer Abraham, the U.S. Secretary of Energy, stated, "A hydrogen economy will mean a world where our pollution problems are solved and where our need of abundant and affordable energy is secure … and concerns about dwindling resources are a thing of the past." This type of excessive enthusiasm has infected politicians, bureaucrats, and journalists. Policy has been misdirected and the public has been misled.

A more likely outcome than that envisioned in the "hydrogen economy" is one in which hydrogen will play a role in our energy future, but a much smaller role that is touted by its proponents. Continued work on hydrogen technology is needed, but funding for this work should not result in weak funding for more promising alternatives.

Note: On 8 May 2009, the *New York Times*[6] reported that the U.S. Department of Energy was ending all funding for research on fuel cells for vehicle applications.

References

1. U.S. Department of Energy "National Hydrogen Energy Roadmap" Based on the results of the National Hydrogen Energy Roadmap Workshop, Washington, D.C., November, 2002 at http://www.hydrogen.energy.gov/pdfs/national_h2_roadmap.pdf.

2. Romm, J. J. *The Hype about Hydrogen* Washington, DC: Island Press, 2004.

3. "Module 1: Hydrogen Properties" College of the Desert at http://www1.eere.energy.gov/hydrogenandfuelcells/tech_validation/pdfs/fcm01r0.pdf.

4. Bossel, U., Eliason, B., and Taylor, G. "The Future of the Hydrogen Economy: Bright or Bleak" at http://www.efcf.com/reports/E08.pdf.

5. Bossel, U. "Efficiency of Hydrogen Fuel Cell, Diesel-SOFC-Hybrid and Battery Electric Vehicles" European Fuel Cell Forum, 20 October 2003 at http://www.efcf.com/reports/E04.pdf.

6. Wald, M. L., "U.S. Drops Research into Fuel Cells for Cars," *New York Times*, 8 May 2009).