Solar Hydrogen Generation

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Toward a Renewable Energy Future

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Dedication

Krishnan Rajeshwar

To the three girls in my life, Rohini, Reena, and Rebecca: I could not have done this
without your love and support

Robert McConnell

To my wife Suzie Star whose love and support made this possible. To my children and
especially my grandson Tharyn. My hope for them is to live in a cleaner
world powered by renewable energy and hydrogen.

Stuart Licht

To my children: Reeva, Gadi, Ariel, Jacob and Dov; I hope to open a
path to a sustainable energy future for them. To my wife Bregt, this is here
because you are here.

Preface

This book examines ways to generate hydrogen from sunlight and water. It largely arose out of a desire to bring all the disparate ways to accomplish this goal within the confines of a single edited volume. Thus we are aware of many books and reports discussing the pros and cons of a hydrogen economy but none, that we are aware of, that focus on the science and technology of generating hydrogen from sunlight and water. While renewable hydrogen currently remains an elusive goal, at least from a cost perspective, the *scientific* principles behind its generation are well understood. Thus over and above reviewing this substantial fundamental database, part of the incentive for creating this book was to hopefully inspire future generations of scientists and engineers to respond to the grand challenge of translating the impressive laboratory advances and prototype demonstrations to a practical renewable energy economy. Much of this daunting hurdle has to do with optimizing the efficiency and hence the cost-effectiveness of hydrogen producing solar energy systems.

History certainly is on our side in meeting this challenge. Many early civilizations used the sun, water, and the wind to meet basic needs. Even geothermal heat was used by North American Indians some 10,000 years ago for cooking. The ancient Greeks used hydro power to grind flour and the Persians used windmills to pump water in the first millennium. The human race is very good at solving technological problems and we can certainly wean ourselves from fossil fuels if we collectively put our minds to it. But cost is certainly going to be a driver and no amount of civic sense is going to render the hydrogen economy practically realizable if a gallon of gasoline continues to be substantially cheaper than a kilogram of hydrogen. Unfortunately however we can only give short shrift to the issue of economics in this book because of the rapidly shifting landscape of assumptions that an evolving technology brings with it. Nonetheless, the concluding chapter of this book examines investments, levelized hydrogen prices, and fuel cycle greenhouse gas emissions of a centralized electrolytic hydrogen production and distribution system powered by photovoltaic electricity.

Another important and related topic, not specifically addressed in this book, concerns the issue of how to store hydrogen, especially in a mobile transportation application. We felt that this topic was specialized and wide ranging enough to warrant a separate volume to be created by scientists and engineers far more qualified and knowledgeable than us. While fuel cells are briefly introduced in Chapter 1, how hydrogen is to be utilized to generate power is again left to many other excellent treatises in the literature; some of these are cited in what follows.

Every effort was made to remove redundancy and add homogeneity to the material in this multi-author volume. Indeed, the more authoritative level of discussion afforded by having specialists write each chapter will have hopefully overridden any “rough edges” that remain from chapter to chapter. Undoubtedly, many flaws remain for which we as editors are wholly responsible; we would welcome feedback on these.

A project of this magnitude could not have been completed without the collective contributions of many people, some of whom we wish to acknowledge at this juncture. First, Ken Howell deserves special thanks for his many useful suggestions. His patience as this book production went through countless delays is also much appreciated. Don Gwinner, Al Hicks and their production team at NREL managed to create quality illustrations from the drawings and graphs (many in primitive form) that were furnished to them. Maria Gamboa is thanked for very capably doing the pre-print lay-out of the various manuscripts. Finally we offer simple thanks to our families for their love and support and for putting up with the many weekends away spent in putting this volume together.

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Stuart Licht is a Program Director in the Chemistry Division of the National Science Foundation (NSF) and Professor of Chemistry at the University of Massachusetts, Boston. His research interests include solar and hydrogen energy, energy storage, unusual analytical methodologies, and fundamental physical chemistry. Prof. Licht received his doctorate in 1986 from the Weizmann Institute of Science, followed by a Postdoctoral Fellowship at MIT. In 1988 he became the first Carlson Professor of Chemistry at Clark University, and in 1995 a Gustella

Professor at the Technion Israel Institute of Science, in 2003 became Chair of the Department of Chemistry at the University of Massachusetts Boston, and in 2007 a Program Director at the NSF. He has contributed 270 peer reviewed papers and patents ranging from novel efficient solar semiconductor/electrochemical processes, to unusual batteries, to elucidation of complex equilibria and quantum electron correlation theory.

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Robert D. McConnell recently joined Amonix, Inc., a concentrator photovolatics (PV) company located in Torrance, CA as Director of Government Affairs and Contracts. He earned his PhD at Rutgers University in Solid State Physics following a Bachelor's degree in Physics at Reed College in Portland, Oregon. After a postdoctoral stint at the University of Montreal and employment at the research institute of the electric utility, Hydro Quebec, he joined NREL in 1978. He has authored numerous papers and edited or co-edited five books and chaired four international conferences on centrator PV. His technology interests include concentrator PV, future generation PV concepts, hydrogen, superconductivity, and wind energy. He has served as Chairman of the Energy Technology Division of the Electrochemical Society and is presently Convener of the international working group developing concentrator PV standards under the aegis of the International Electrotechnical Commission located in Geneva, Switzerland.

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Krishnan Rajeshwar is a Distinguished Professor in the Department of Chemistry and Biochemistry and Associate Dean in the College of Science at the University of Texas at Arlington. He is the author of over 450 refereed publications, several invited reviews, book chapters, a monograph, and has edited books, special issues of journals, and conference proceedings in the areas of materials chemistry, solar energy conversion, and environmental electrochemistry. Dr. Rajeshwar is the Editor of the Electrochemical Society Interface magazine and is on the Editorial Advisory Board of the Journal of Applied Electrochemistry. Dr. Rajeshwar has won many Society and University awards and is a Fellow of the Electrochemical Society.

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Ken Zweibel is President of PrimeStar Solar, a CdTe PV company located in Colorado, USA. He graduated in Physics from the University of Chicago in 1970. He was employed for 27 years at SERI and then NREL in Golden, CO, where he worked on the development of CdTe, copper indium diselenide, and amorphous and thin film silicon. When he left in December 2006, he was manager of the Thin Film PV Partnership Program. He has published numerous papers and articles, and two books on PV, the most recent being, “Harnessing Solar Power: The PV Challenge.” Besides the success of PrimeStar Solar, he is interested in solar policy and solutions to climate change and rising energy prices.

1

Renewable Energy and the Hydrogen Economy

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1 Renewable Energy and the Terawatt Challenge

Technological advancement and a growing world economy during the past few decades have led to major improvements in the living conditions of people in the developed world. However, these improvements have come at a steep environmental price. Air quality concerns and global climate impact constitute two major problems with our reliance on fossil energy sources. Global warming as a result of the accumulation of greenhouse gases such as CO_2 is not a new concept. More than a century ago, Arrhenius put forth the idea that CO_2 from fossil fuel combustion could cause the earth to warm as the infrared opacity of its atmosphere continued to rise.[1] The links between fossil fuel burning, climate change, and environmental impacts are becoming better understood.[2] Atmospheric CO_2 has increased from ~275 ppm to ~370 ppm (Figure 1); unchecked, it will pass 550 ppm this century. Climate models indicate that 550 ppm CO_2 accumulation, if sustained, could eventually produce global warming comparable in magnitude but opposite in sign to the global cooling of the last Ice Age.[3] The consequences of this lurking *time bomb* could be unpredictably catastrophic and disastrous as recent hurricanes and tsunamis indicate.

Every year, a larger percentage of the 6.5 billion global population seeks to improve their standard of living by burning ever-increasing quantities of carbon-rich fossil fuels. Based on United Nations forecasts, another 2.5 billion people are expected by 2050 with the preponderance of them residing in poor countries.[4] Coupled with this growing population's desire to improve their quality of life are the developed countries already high and rising per capita energy use which promises to add to the environmental pressure.

Oil, coal, and natural gas have powered cars, trucks, power plants, and factories, causing a relatively recent and dramatic buildup of greenhouse gases in the atmos-

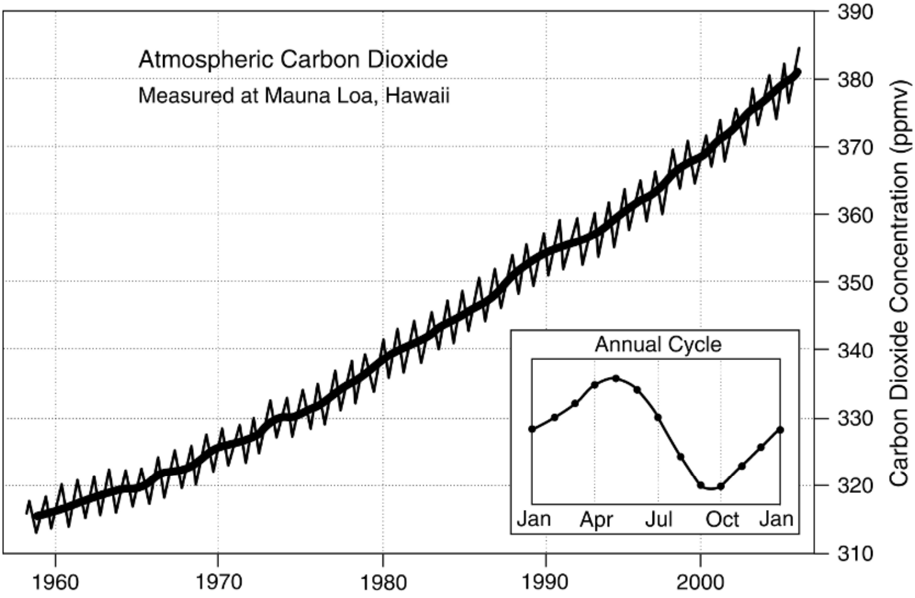

Fig. 1. Atmospheric carbon dioxide record from Mauna Loa. Data courtesy of C. D. Keeling and T. P. Whorf.

phere, most notably CO_2. The anthropogenic buildup of heat-trapping gases is intensifying the earth's natural greenhouse effect, causing average global temperatures to rise at an increasing rate. We appear to be entering into a period of abrupt swings in climate partially due to buildup of human-released CO_2 in the atmosphere. Most alarming is not the fact that the climate is changing but rather the rate at which the buildup of CO_2 is occurring.

Ice core samples from Vostok, Antarctic, look back over 400,000 years before present at atmospheric CO_2 levels by examining the composition of air bubbles trapped in the polar ice buried over 3623 m (11,886 ft) deep.[5] These data show that the range of CO_2 concentrations over this time period have been relatively stable, cycling between about 180 and 300 parts per million by volume (ppmv). According to the World Meteorological Organization the CO_2 concentration in 2005 reached an unprecedented 379.1 ppmv.[6]

This environmental imperative requires us to quickly come to terms with the actual costs, including environmental externalities, of all of our energy use. Only then will the economic reality of energy consumption be realized and renewable sources expand through true market forces. That is not to say that fossil fuels like oil, natural gas, and coal do not have a future in helping to meet this growing demand. However, it should go without saying that all new sources of CO_2 should be captured and stored (i.e., sequestered). Although integrating the systems required to safely and economically storing CO_2 deep underground have not been realized. More than ever, CO_2 released into the atmosphere by coal-fired power plants must be addressed to effectively deal with global climate change. In addition to greenhouse gas emissions, destructive extraction and processing of the fuel, fine particulates of 2.5 micrometers (µm) released from coal-fired power plants are responsible for the deaths of roughly 30,000 Americans every year.[7]

Even notwithstanding this climate change and global warming concern are issues with the supply side of a fossil-derived energy economy. Gasoline and natural gas supplies will be under increasing stress as the economies of heavily-populated developing countries (such as India and China) heat up and become more energy intensive. It is pertinent to note that this supply problem is exacerbated because the United States alone consumes a disproportionately higher fraction (more than the next five highest energy-consuming nations, Ref. 8) of the available fossil fuel supply. There are no signs that the insatiable energy appetite of the U. S. and other advanced parts of the world are beginning to wane. While there is considerable debate about when global oil and natural gas production is likely to peak,[9] there is no debate that fossil fuels constitute a non-renewable, finite resource. We are already seeing a trend in some parts of the world (e.g., Alberta, Canada) of a switch to "dirtier" fossil fuels, namely, coal, heavy oil or tar sand as petroleum substitutes. This switch would mean an increase in CO_2 emissions (note that the carbon content of these sources is higher than gasoline or natural gas), a greater temperature rise than is now being forecast, and even more devastating effects on the earth's biosphere than have already been envisioned.[10]

Currently, renewable energy only constitutes a very small fraction of the total energy mix in the U. S. and in other parts of the world (Figure 2). For example, in 2000, only about 6.6 quads (one quad is about 10^{18} J) of the primary energy in the U. S. came from renewables out of a total of 98.5 quads.[11] Of this small fraction supplied by renewable energy, about 3.3 quads were from biomass, 2.8 from hydroelectric generation, 0.32 from geothermal sources, 0.07 from solar thermal energy and 0.05 quads from wind turbines.[8] This profile would have to switch to an energy mix that resembles the right-side panel in Figure 2 if the CO_2 emissions are to be capped at environmentally safe levels. This is what the late Professor Rick Smalley, winner of the Nobel Prize in Chemistry, referred to as the *Terawatt Challenge*. Recent analyses[12] have posited that researching, developing, and commercializing carbon-free primary power to the required level of 10-30 TW (one terawatt = 10^{12} W) by 2050 will require efforts of the urgency and scale of the Manhattan Project and the Apollo Space Program.

This book examines the salient aspects of a hydrogen economy, particularly within the context of a renewable, sustainable energy system.

2 Hydrogen as a Fuel of the Future

Jules Verne appears to be one of the earliest people to recognize, or at least articulate, the idea of splitting water to produce hydrogen (H_2) and oxygen (O_2) in order to satisfy the energy requirements of society. As early as 1874 in *The Mysterious Island*, Jules Verne alluded to clean hydrogen fuels, writing:

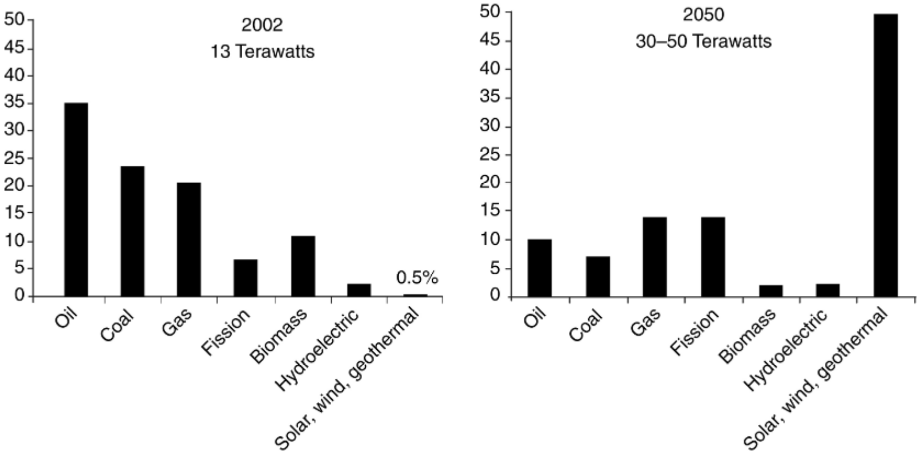

Fig. 2. The terawatt renewable energy challenge; the energy mix has to switch from the panel on the left to the panel on the right to cap CO_2 levels at safe limits. Data from the International Energy Agency.

> "Yes, my friends, I believe that water will someday be employed as fuel, that hydrogen and oxygen, which constitute it, used singly or together, will furnish an inexhaustible source of heat and light….I believe, then, that when the deposits of coal are exhausted, we shall heat and warm ourselves with water. Water will be the coal of the future."

Remarkable words indeed from a prophetic visionary who foresaw also the technological development of spacecraft and submarines. Hydrogen gas was first isolated by Henry Cavendish in 1766 and later recognized as a constituent of water by Lavoisier in 1783.[13] The production of hydrogen and oxygen by the electrolytic decomposition of water has been practiced since the year 1800, when the process was first discovered by Nicholson and Carlisle.[14] Since then, the idea of society using hydrogen as a primary energy carrier has been explored and refined.

In the late 1920s and the early 1930s a German inventor, Rudolf A. Erren, recognized and worked towards producing hydrogen from off-peak electricity and modifying the internal combustion engine to run on hydrogen.[15] Erren's primary objective was to eliminate pollution from the automobile and reduce oil imports. In the 1970s Derek Gregory appears to have been one of the leading advocates in creating the case for a hydrogen-based economy.[13,15,16]

The literature suggests that the term *hydrogen economy* may have been coined by H. R. Linden, one of Gregory's colleagues at the Institute of Gas Technology, in 1971.[13] Gregory points to hydrogen's environmental benefits and recognizes that, while fossil fuels are inexpensive, requiring the atmosphere to assimilate the byproducts of their combustion is not without consequence.

The water electrolyzer industry grew substantially during the 1920s and 1930s, as elaborated later in Chapter 3. This included products from companies such as Oerlikon, Norsk Hydro, and Cominco in multi-megawatt sizes.[14,17,18] Most of these installations were near hydroelectric plants that supplied an inexpensive source of electricity. As more hydrogen was needed for industries, steam reforming of methane gradually took over as the hydrogen production process of choice because it was less expensive.

Hydrogen is often blamed for the 1937 Hindenburg disaster. The shell of the German airship was a mixture of two major components of rocket fuel, aluminum and iron oxide, and a doping solution which was stretched to waterproof the outer hull. Researchers concluded that the coating of the Hindenburg airship was ignited by an electrical discharge and the ensuing explosion to be inconsistent with a hydrogen fire.[19] It turns out that 35 of the 37 people who died in the disaster, perished from jumping or falling from the airship to the ground. Only two of the victims died of burns, and these were from the burning airship coating and on-board diesel fuel.[20] Modern laboratory tests confirmed that the 1930s fabric samples to still be combustible.

> "Although the benefits of the hydrogen economy are still years away, our biggest challenges from a sustainability standpoint are here today,"

said Mike Nicklas, Past Chair of the American Solar Energy Society, during his opening comments at the first Renewable Hydrogen Forum in Washington, D.C., in April 2003.[21]

Hydrogen (H) is the simplest of atoms, consisting of one proton and one electron also called a protium. As atoms, hydrogen is very reactive and prefers to join into molecular pairs (H_2) and when mixed in sufficient quantities with an oxidant (i.e., air, O_2, Cl, F, N_2O_4, etc.) becomes a combustible mixture. Like all other fuels, H_2 requires proper understanding and handling to avoid unwanted flammable or explosive environments. Hydrogen is not a primary source of energy; rather it is an energy carrier much like electricity. Therefore, energy is required to extract hydrogen from substances like natural gas, water, coal, or any other hydrocarbon.

At 25 °C and atmospheric pressure the density of air is 1.225 kg m^{-3} while hydrogen is 0.0838 kg m^{-3}, making it 14.6 times lighter than air. This is an important safety consideration in that a hydrogen leak will dissipate quickly. Hydrogen's positive buoyancy significantly limits the horizontal spreading of hydrogen that could lead to combustible mixtures. Hydrogen is the lightest (molecular weight 2.016) and smallest of all gases requiring special considerations for containing and sensing a leak.

Figure 3 shows the two types of molecular hydrogen distinguished by the spin, ortho- and para-hydrogen. They differ in the magnetic interactions as ortho-hydrogen atoms are both spinning in the same direction and in para-hydrogen the protons are spinning anti-parallel. At 300 K, the majority (75%) is ortho-hydrogen, while at 20 K 99.8% of the hydrogen molecules are para-hydrogen. As the gas transitions from gas to liquid at 20 K heat is released and ortho-hydrogen becomes unstable.[22] Hydrogen becomes a liquid below its boiling point of −253 °C (20 K) at atmospheric pres-

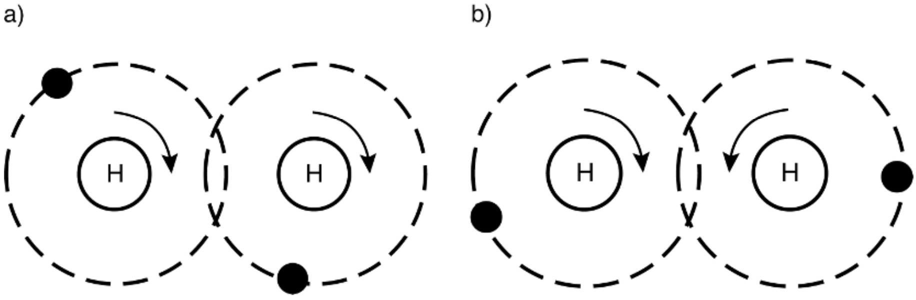

Fig. 3. Ortho- (left) and para-hydrogen (right).

sure. Pressurization of the hydrogen to 195 pisg (13 barg) increases the boiling point to –240 °C (–400 °F), pressures above that don't return a significant improvement.[22]

At ambient temperature and pressure hydrogen is colorless, odorless, tasteless and nontoxic. However, leaks of hydrogen (or any gas for that matter) can displace oxygen and act as an asphyxiant. Any atmosphere with less than 19.5% oxygen by volume in considered oxygen deficient and asphyxiation can lead to physiological hazards.

The primary hazard associated with gaseous hydrogen is the unintentional mixing of the fuel with an oxidant (typically air) in the presence of an ignition source. Hydrogen fires and deflagrations have resulted when concentrations within the flammability limit were ignited by seemingly harmless ignition sources. Ignition sources include electrical, mechanical, thermal and chemical. For example; sparks from valves, electrostatic discharges, sparks from electrical equipment, mechanical impact, welding and cutting, open flame, personnel smoking, catalyst particles and lightning strikes in the proximity of hydrogen vent stacks.[23]

With the exception of helium, hydrogen has the lowest boiling point at atmospheric pressure of where it becomes a transparent and odorless liquid. Liquid hydrogen has a specific gravity of 0.071, which is roughly 1/14th the density of water and is neither corrosive nor reactive. The low specific gravity of liquid hydrogen further reveals hydrogen's low volumetric energy density in that a cubic meter of water contains more hydrogen (111 kg) than a cubic meter of pure hydrogen in liquid state (71 kg). The values of the main physical properties of gaseous hydrogen are shown in Table 1.

Leaking hydrogen gas and (once ignited) its flame are nearly invisible. The pale blue flame of a hydrogen fire is barely visible and is often detected by placing a standard household wicker broom in the path of the suspected hydrogen flame. The hydrogen flame temperature in air (2045 C, 3713 F) releases most of its energy in the ultraviolet (UV) region requiring UV sensors for detecting the presence of a flare or fire. The UV radiation from a flaring hydrogen fire can also cause burns akin to over-exposure to the sun's damaging UV radiation.

Table 1. Selected properties of gaseous hydrogen at 20 °C and 1 atm.

Physical Property		Units
Molecular weight	2.016	
Density	0.0838	kg/m^3
Specific gravity	0.0696	(Air = 1)
Viscosity	8.813 x 10^{-5}	g/cm sec
Diffusivity	1.697	m^2/hr
Thermal conductivity	0.1825	W/m K
Expansion ratio	1:848	Liquid to gas
Boiling point (1 atm)	−253 (−423)	°C (°F)
Specific heat, constant pressure	14.29	J/g K
Specific heat, constant volume	10.16	J/g K
Specific volume	11.93	m^3/kg
Diffusion coefficient in air	6.10	cm^2/sec
Enthalpy	4098	kJ/kg
Entropy	64.44	J/g K

The amount of thermal radiation (heat) emitted from a hydrogen flame is low and is hard to detect by feeling (low emissivity). Most commercially available combustible gas detectors can be calibrated for hydrogen detection. Typically alarms from these sensors are set by the manufacturer between 10%–50% of the lower flammability limit (LFL) of hydrogen to avoid the presence of an unwanted flammable environment.

Table 2 compares the same fuels as above and reports their volumetric energy density in kg m^{-3}. Hydrogen has the highest energy content per unit mass than any fuel making it especially valuable when traveling into space. As mentioned earlier, hydrogen suffers volumetrically when compared with traditional fuels making storing sufficient on-board terrestrial vehicles an engineering challenge.

The LFL of hydrogen represents the minimum concentration required below which the mixture is too lean to support combustion.[24] Hydrogen has a wide flammability range of (4%–75%) while gasoline is (1.5%–7%) when mixed with air at standard temperature (25 ºC) and pressure (1 atm). Hydrogen in oxygen has a slightly wider flammability range (4%–95%). Table 3 summarizes a selected number of important combustion properties of hydrogen.

Table 2. Comparing hydrogen properties with other fuels. Based on LHV and 1 atm, 25 °C for gases.

	Hydrogen	Methane	Gasoline	Diesel	Methanol
Density, kg m^{-3}	0.0838	0.71	702	855	799
Energy density, MJ m^{-3}	10.8	32.6	31,240	36,340	14,500
Energy density, kWh m^{-3}	3.0	9.1	8680	10,090	4030
Energy, kWh kg^{-1}	33.3	12.8	12.4	11.8	5.0

*Energy density = LHV ∗ density (◘), and the conversion factor is 1 kWh = 3.6 MJ.

Table 3. Selected combustion properties of hydrogen at 20 °C and 1 atm.[a]

Combustion Property		Units
Flammability limits in air	4 – 75	vol%
Flammability limits in oxygen	4 – 95	vol%
Detonability limits in air	18 – 59	vol%
Detonability limits in oxygen	15 – 90	vol%
Minimum ignition energy in air	17	□J
Auto ignition temperature	585 (1085)	°C (°F)
Quenching gap in air	0.064	cm
Diffusion coefficient in air	0.061	cm^2/sec
Flame velocity	2.7 – 3.5	m/s
Flame emissivity	0.1	
Flame temperature	2045 (3713)	°C (°F)

[a] From Ref. 19.

Each fuel is limited to a fixed amount of energy it can release when it reacts with an oxidant. Every fuel has been experimentally tested to determine the amount of energy it can release and is reported as the fuel's higher heating value (HHV) and lower heating value (LHV). The difference between the two values is the latent heat of vaporization of water, and the LHV assumes this energy is not recovered.[22] In other words, LHVs neglect the energy in the water vapor formed by the combustion of hydrogen in the fuel because it may be impractical to recover the energy released when water condenses. This heat of vaporization typically represents about 10% of the energy content.

It is often confusing to know which heating value to use when dealing with similar processes such as electrolysis and fuel cells. The appropriate heating value depends on the phase of the water in the reaction products. When water is in liquid form, the HHV is used; if water vapor (or steam) is formed in the reaction, then the LHV would be appropriate. An important distinction is that water is produced in the form of vapor in a fuel cell as well as in a combustion reaction and, therefore, the LHV represents the amount of energy available to do work. Table 4 shows both the LHV and the HHV for common fuels.

Obviously, the most important virtue of using hydrogen as a fuel is its pollution-free nature. When burned in air, the main combustion product is water with O_2 in a fuel cell to directly produce electricity; the only emission is water vapor. Indeed this

Table 4. HHVs and LHVs at 25 °C and 1 atm of common fuels, kJ g^{-1} [a]

Fuel	HHV	LHV
Hydrogen	141.9	119.9
Methane	55.5	50.0
Gasoline	47.5	44.5
Diesel	44.8	42.5
Methanol	20.0	18.1

[a] From Ref. 22.

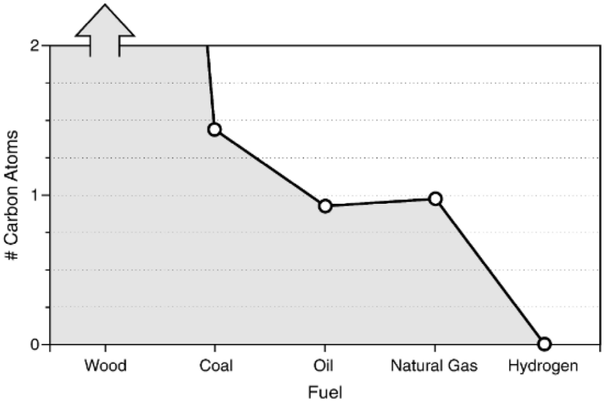

Fig. 4. Decarbonization of the energy source over the centuries.

fuel cell product is clean enough to furnish drinking water to the crews in spacecraft! Crucially, the use of hydrogen completes the *decarbonization* trend that has accompanied the evolution of energy sources for mankind over the centuries (Figure 4). The combustion of H_2, unlike fossil fuels, generates no CO_2. Unlike fossil fuels, however, hydrogen is not an energy *source* but is an energy *carrier* since it almost never occurs by itself in nature, at least terrestrially. (The atmospheres of other planets, e.g., Mars, are rich in hydrogen. Should space travel prove to be economical and accessible in the future, we may have a viable means to "mine" H_2 as we are doing for petroleum and coal these days!)

In the interim timeframe: Where is the H_2 to come from? Historically, H_2 has been used for energy since the 1800s. It is a major constituent (up to ~50% by volume) of *syngas* generated from the gasification of coal, wood, or municipal wastes. Indeed, syngas was used in urban homes in the U. S. for heating and cooking purposes from the mid-1800s until the 1940s and is still used in parts of Europe, Latin America and China where natural gas is unavailable or too expensive. Most of the H_2 manufactured these days comes from the steam reforming of methane (see above). Other processes for making H_2 from fossil fuel sources include the water gas shift reactions. Neither of these approaches is carbon-neutral in that significant amounts of CO_2 are generated in the H2 manufacture process itself.

The ultimate goal would be to produce H_2 with little or no greenhouse gas emissions. One option is to combine H_2 production from fossil fuels with CO_2 sequestration. Carbon sequestration, however, is as yet an unproven technology. Another approach is biomass gasification—heating organic materials such as wood and crop wastes so that they release H_2 and carbon monoxide. This technique is carbon-neutral because any carbon emissions are offset by the CO_2 absorbed by the plants during their growth. A third possibility is the electrolysis of water using power generated by renewable energy sources such as wind turbines and solar cells. This approach is discussed in Chapters 3 and 4.

Although electrolysis and biomass gasification involve no major technical hurdles, they are cost-prohibitive, at least at present: \$6–10 per kilogram of H_2 pro-

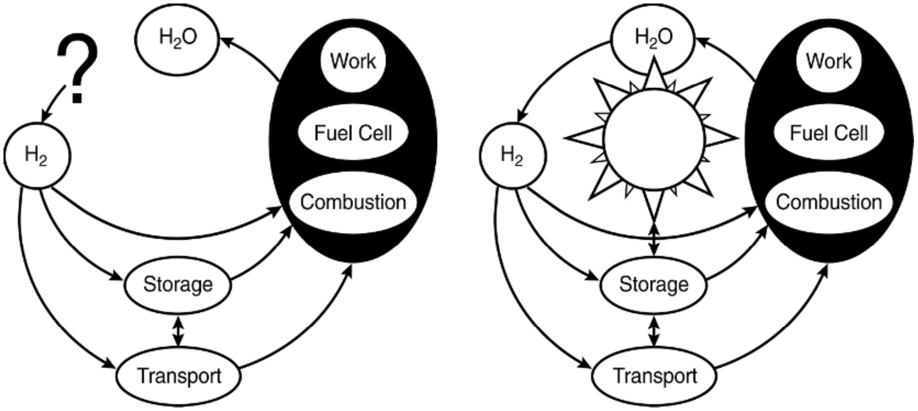

Fig. 5. The water splitting/hydrogen fuel cycle without (left panel) or with (right panel) inclusion of solar energy input.

duced.The goal is to be able to develop and scale-up technologies to afford a pump price for H_2 of \$2–4 per kilogram. In such a scenario, hydrogen in a fuel cell powered car would cost less per kilometer than gasoline in a conventional car today.

Clearly, water would be the ideal and most sustainable source for H_2 and this H_2 generation concept dates back two centuries. Table 5 summarizes various schemes for generating H_2 via splitting of water and Figure 5 depicts the water splitting/hydrogen fuel cycle without (left panel) or with (right panel) inclusion of solar energy input. The approaches considered in Table 5 and Figure 5 form the topics of discussion in Chapters 4 through 7 of this book.

The power needed for water electrolysis could come from nuclear energy although producing H_2 this way would not be significantly cheaper than using renewable power sources. Nuclear plants can generate H_2 in a non-electrolytic, thermal mode because of the intense heat generated in a thermonuclear reaction. This ap-

Table 5. The ability of nuclear and various renewable energy sources to meet the 14-20 TW demand of carbon-free power by 2050.[a]

Source	Power available TW	Comments
Biomass	7–10	Entire arable land mass of the planet must be used excluding the area needed to house 9 billion people
Wind on land	2.1	Would saturate the entire Class 3 (wind speed at 5.1 m/s at 10 m above ground) global land mass with windmills
Nuclear	8	Requires the construction of 8000 new nuclear power plants
Hydroelectric	1.5	Would require damming of all available rivers

[a] From Ref. 26

proach, while potentially cost-effective, has not been demonstrated yet. It must be noted that any option involving nuclear power has the same hurdles that have dogged the nuclear electric power industry for decades, namely those of waste disposal problems, proliferation concerns and lack of public acceptance. (This contrasts with the success of the nuclear power industry in some countries, e.g., France.) Producing 10 TW of nuclear power would require the construction of a new 1-GW$_e$ nuclear fission plant somewhere in the world every other day for the next 50 years![25]

3 Solar Energy and the Hydrogen Economy

Solar energy is a virtually inexhaustible and freely available energy source. More sunlight (~1.2×10^5 TW) falls on the earth's surface in 1 h than is used by all human activities in 1 year globally. The sun is earth's natural power source, driving the circulation of global wind and ocean currents, the cycle of water evaporation and condensation that creates rivers and lakes, and the biological cycles of photosynthesis and life. It is however a dilute energy source (1 kW/m^2 at noon, Chapter 2); about 600–1000 TW strikes the earth's terrestrial surfaces at practical sites suitable for solar energy harvesting.[27] Covering 0.16% of the land on earth with 10% efficient solar conversion systems would provide 20 TW of power,[28] nearly twice the world's consumption rate of fossil energy and an equivalent 20,000 1-GW$_e$ nuclear fission plants. Clearly, solar energy is the largest renewable carbon-free resource amongst the other renewable energy options.

Consider the total amounts possible for each in the light of the 14–20 TW of carbon-free power needed by 2050. Table 5 provides a summary;[26] clearly the additional energy needed per year over the 12.8 TW fossil fuel energy base is simply not attainable from biomass, wind, nuclear and hydroelectric options. The answer to this supply dilemma must lie with solar energy. Chapter 2 provides an overview of the solar energy resource with particular emphasis on the solar spectrum.

Solar energy can be harnessed in many ways[25] but three routes of particular relevance to the theme of this book rely on *electrical*, *chemical*, and *thermal* conversion. Thus the energy content of the solar radiation can be captured as excited electron-hole pairs in a semiconductor, a dye, or a chromophore, or as heat in a thermal storage medium. Excited electrons and holes can be tapped off for immediate conversion to electrical power, or transferred to biological or chemical molecules for conversion to fuel. Solar energy is "fixed" in plants via the photosynthetic growth process. These plants are then available as biomass for combustion as primary fuels or for conversion to secondary fuels such as ethanol or hydrogen. All of these possibilities are addressed in more detail in the Chapters that follow.

While there is tremendous potential for solar energy to contribute substantially to the future carbon-free power needs, none of the routes listed above are currently competitive with fossil fuels from cost, reliability, and performance perspectives. Photovoltaic solar cells have been around for decades and have been widely deployed in space vehicles. Terrestrially, their utilization thus far has been limited to niche applications or remote locales where less expensive electricity is not available. Costs for turnkey installations were 6–10 times more expensive in 1999 for solar electrical energy than for electricity derived from coal or oil. The present cost of photovoltaic (PV) modules is ~\$3.50/peak watt. Considering the additional balance of system costs (land, maintenance, etc.) this translates to an energy cost of ~\$0.35/kWh. The target at present is ~\$0.40/peak watt corresponding to electricity at \$0.02/kWh or H_2 produced by PV hybrid water electrolyzers at \$0.11/kWh. Major advances in electrolyzer technology could bring this hydrogen cost to \$0.04/kWh,[29] which is about the present cost of H_2 from steam reforming of natural gas. These issues are further elaborated in Chapters 2, 3, and 9. A cost goal of \$0.40/peak watt requires solar photovoltaic conversion at a total cost of \$125/m^2 combined with a cell energy conversion efficiency of ~50%. Such combinations of cost and efficiency require truly disruptive photovoltaic technologies. Many such approaches are being actively pursued in research laboratories around the world. A critical discussion of outstanding issues, including dispelling the *seven myths of solar electricity* may be found in Refs.25, 29, and 30.

The economic outlook for the other two solar approaches is not much rosier, at least at present. Solar fuels in the form of biomass produce electricity and heat at costs that are within the range of fossil fuels, but their production capacity is limited. The low efficiency with which plants convert sunlight to stored energy means large land areas are required. To produce the full 13 TW of power used by the planet, nearly all the arable land on earth would need to be planted with switchgrass, the fastest growing energy crop. Artificial photosynthetic systems, however, are more promising (see next Section) and these are discussed in Chapter 6. Solar thermal systems provide the lowest-cost electricity at the present time, but require large areas in the Sun Belt in the U. S. and continuing advances in materials science/engineering.

4 Water Splitting and Photosynthesis

The decomposition of liquid water to form gaseous hydrogen and oxygen:

$$H_2O(\ell) \rightarrow H_{2(g)} + \frac{1}{2}O_{2(g)} \qquad (1)$$

is a highly endothermic and endergonic process with $\Delta H° = 285.9$ kJ/mol and $\Delta G° = 237.2$ kJ/mol. This reaction may be driven either electrochemically or thermally via the use of solar energy.

The standard potential $\Delta E°$ for Reaction 1 corresponding to the transfer of two electrons is given by:

$$\Delta E° = -\Delta G°/2\mathrm{F} = -1.23\ \mathrm{V} \qquad (2)$$

In Eq. 2, F is the Faraday constant (96485 C mol^{-1}) and the negative sign denotes the thermodynamically non-spontaneous nature of the water splitting process. The actual *voltage* required for electrolysis will depend on the fugacities of the gaseous products in Reaction 1 as well as on the electrode reaction kinetics (overpotentials)

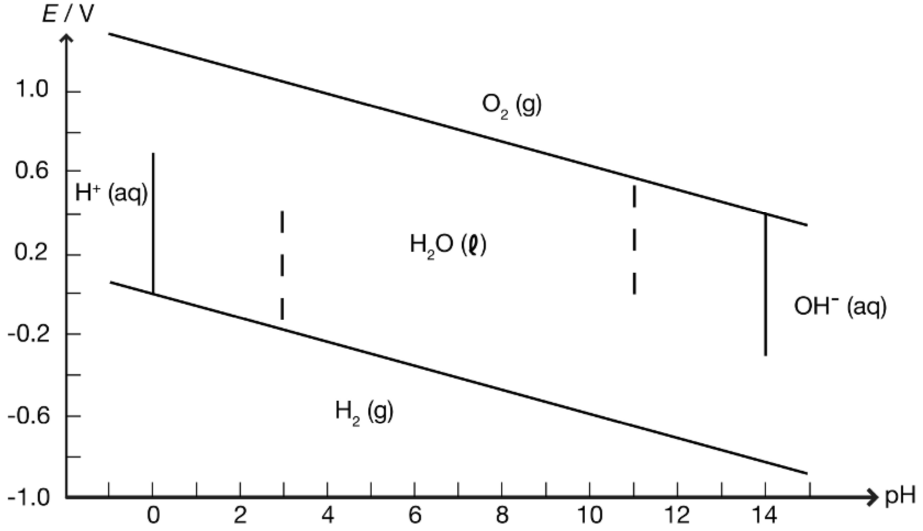

Fig. 6. Pourbaix diagram of water.[31]

along with the Ohmic resistance losses in the cell. In practice, steady-state electrolysis of water at 298 K requires the application of ~1.50 V.

Figure 6 contains a Pourbaix diagram for water;[31] the zones in this diagram are labeled by the formulas for the predominant species at the electrode potential and pH indicated on the axes. Thus the threshold (thermodynamic) potentials for the decomposition of water via:

$$H_2O_{(\ell)} \rightarrow 4\,e^- + 0_{2(g)} + 4\,H^+_{(aq)} \tag{2a}$$

or

$$4\,OH^-_{(aq)} \rightarrow 4\,e^- + O_{2(g)} + 2\,H_2O_{(\ell)} \tag{2b}$$

and

$$2\,H^+_{(aq)} + 2\,e^- \rightarrow H_{2(g)} \tag{3a}$$

or

$$2\,H_2O_{(\ell)} + 2\,e^- \rightarrow H_{2(g)} + 2\,OH^-_{(aq)} \tag{3b}$$

clearly depend on solution pH and they vary at a Nernstian rate of –0.059 V/pH at 298 K.

Optimizing the rates of the electrochemical processes (Reactions 2 and 3) constitute much of the R&D focus in electrochemical or photoelectrochemical splitting of water. Two-compartment cells are also employed to spatially separate the evolved gases with special attention being paid to the proton transport membranes (e.g., Nafion^R). Chapter 3 provides a summary of the progress made in water electrolyzer technologies.

Water is transparent to the wavelengths constituting the solar spectrum. Therefore, photocatalytic or photoelectrochemical splitting of water requires an agent (semiconductor, dye, or chromophore) capable of first absorbing sunlight and generating electron-hole pairs. Molecular approaches are discussed in Chapter 6 and semiconductor-based approaches are described in Chapter 7.

Thermochemical splitting of water involves heating water to a high temperature and separating the hydrogen from the equilibrium mixture. Unfortunately the decomposition of water does not proceed until temperatures around 2500 K are reached. This and other thermal routes are discussed in Chapter 5. Solar thermal processes are handicapped by the Carnot efficiency limits. On the other hand, solar *photonic* processes are limited by fundamental considerations associated with bandgap excitation; these have been reviewed in Refs.32 and 33.

The water splitting reaction, Eq. 1, have been stated here as the Holy Grail[21] of hydrogen generation using solar energy. However other chemical reactions have been investigated and include, for example:[34,35]

$$2\,HBr \xrightarrow{h\upsilon} H_2 + Br_2 \tag{4}$$

$$2\,H_2O + 2\,Cl^- \xrightarrow{h\upsilon} 2\,OH^- + Cl_2 + H_2 \tag{5}$$

However, these alternative schemes are fraught with problems associated with the generation and handling of toxic or hazardous by-products such as Br_2 and Cl_2.

Turning to photobiological schemes for producing H_2 (Chapter 8), a complex reaction scheme uses solar energy to convert H_2O into O_2 and reducing equivalents which appear as NADPH. In photosystem 1, the reducing equivalents in NADPH are used to reduce CO_2 to carbohydrates:

$$6\,H_2O + 6\,CO_2 + 48\,h\upsilon \rightarrow C_8H_{12}O_6 + 6\,O_2 \tag{6}$$

or in bacteria, used directly as a reductive energy source.[36,37] In artificial photosynthesis, the goal is to harness solar energy to drive high-energy, small-molecule reactions such as water splitting (Reaction 1) or CO_2 reduction, Reaction 7:[38]

$$2\,H_2O + 2\,CO_2 + 4\ h\upsilon \rightarrow 2\,HCOOH + O_2 \tag{7}$$

Photobiological processes for H_2 production are considered in Chapter 8.

5 Completing the Loop: Fuel Cells

The high-energy chemicals such as H_2 that form in the reactions considered in the preceding reaction, can be recombined in fuel cells to extract the stored chemical energy as electricity. A fuel cell is an electrochemical device that converts the chemical energy in a fuel (such as hydrogen) and an oxidant (oxygen, pure or in air) directly to electricity, water, and heat. Fuel cells are classified according to the electrolyte that they use (Table 6). For automobile applications, the polymer-electrolyte-membrane (PEM) type of fuel cell is the leading candidate for developing zero-emission vehicles. Other types of fuel cells (e.g., solid oxide fuel cells or SOFCs)