Chapter 1
Introduction

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1.1 The Energy Challenge

One of the main challenges facing mankind in the twenty-first century is to supply the world's population of sufficient energy to meet the desired living standards. The power consumption of the current (2011) global population of nearly 7 billion people is 15 TW, and these numbers are estimated to increase to ~9 billion and 30 TW by 2050. Fossil fuels, which currently provide about 85% of our energy supply, will be unable to keep up with this increase in demand. In the long run, this is simply a matter of the available reserves. Based on the current consumption rate, estimated reserves range from 150 to 400 years for coal, 40–80 years for oil, and 60–160 years for natural gas. The effect of dwindling reserves, however, will be felt on a much shorter time scale. This is because the available reserves become increasingly hard to recover, and the peak in the production will occur long before the supplies run out. According to the International Energy Agency, the production of conventional (easily recoverable) oil has already peaked in 2006. The oil price has in fact sharply risen since 2001, and it is unlikely that it will ever return to its pre-2001 (inflation-corrected) level.

A perhaps far more serious concern associated with the use of fossil fuels is the impact on the environment. The main concern in this regard is the emission of greenhouse gases, in particular CO_2, and their contribution to global warming. Since the beginning of the industrial revolution, the CO_2 level in the atmosphere

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has risen from 280 to 394 ppm,[1] and it is currently rising by about 2 ppm/year. According to the International Panel on Climate Change (IPCC), a CO_2 level above 450 ppm carries a high risk[2] of causing global warming by more than 2°C. Such a rise is likely to have a severe adverse impact on ecosystems and human society, with effects that will be felt throughout the century. If the temperature change can be limited to less than 2°C, there is a good chance that society can adapt. Several studies agree that the current decade, between 2010 and 2020, is a critical one. Unless we are able to sharply reduce CO_2 emissions within the next 10 years, exceeding the 450 ppm level seems unavoidable [1, 2].

To reduce our dependence on fossil fuels and curb the exhaust of CO_2, we need to make a large-scale transition toward new, sustainable sources of energy. While most scientists and politicians nowadays agree that such a transition is unavoidable, there is much uncertainty about the route to follow, and the speed at which this can and should be done. More often than not, the viability of a certain route is determined by economical considerations, rather than technological impediments. As we see later in this chapter and in Chaps. 7 and 8, cost is indeed a crucially important factor for the photoelectrochemical water splitting route that is the topic of this book.

1.2 Sustainable Energy Sources

While an in-depth review of the various sustainable energy sources and options is far beyond the scope of this chapter, it is instructive to briefly consider their estimated global power generation capacities (Table 1.1). Any future energy infrastructure will

Table 1.1 Overview of global power generating capacities of sustainable energy sources [5, 6]

Energy source	Power (TW)	Remarks
Wind	4	Represents 10–15% of global technical potential for on- and off-shore installations
Hydroelectric	1–2	Remaining untapped potential is 0.5 TW
Tidal and ocean currents	<2	
Geothermal	12	Only a small fraction of this can be exploited
Biomass	10	Requires 10% of earth's land surface to be covered with switchgrass
Nuclear	10	Requires construction of a 1-GW_{peak} power plant every 35 h for the next 40 years. Finite uranium supplies imply need for fast breeder or thorium reactors
Solar	>20	Requires 0.16% of the earth's surface to be covered with 10% efficient solar cells. Total solar power reaching the earth's surface is 120,000 TW

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[1] CO_2 level in May 2011.

[2] Estimates vary between 30 and 80%.

Fig. 1.1 Area of land that needs to be covered with 10% efficient solar cells in order to generate 20 TW of electrical power

almost certainly be composed of a mixture of these – and other – technologies, with local circumstances (geography, climate, population density) determining the optimal mix for a particular region. Due to the massive efforts involved in implementing any of these options on a Terawatt scale [3, 4], it is more than likely that fossil fuels will continue to play an important role for the next few decades. In principle, the estimated total fossil fuel reserves can sustain a 25–30-TW energy consumption for at least a few more centuries [5]. This, however, requires efficient capture and storage of CO_2 on an enormous scale, using yet unproven technology.

Of the sources shown in Table 1.1, solar energy is the only source that has the potential to meet all our energy needs. To generate 20 TW of power from the sun, the area to be covered with 10% efficient solar cells is about 816.000 km^2, which corresponds to an area of about 900×900 km^2. While this appears relatively small when projected onto Africa (Fig. 1.1), it should be realized that this is equal to the total surface area of France and Germany combined. Covering such a large area with solar cells presents a daunting task, even when this is undertaken on a (de-centralized) global scale. To illustrate this one would need to produce on average 650 m^2 of solar cell panels per second, 24/7 for 365 days per year, for the next 40 years in order to reach 20 TW of peak power.

The solar cell market is currently growing by 35–40% per year, and is one of today's fastest growing markets. In 2010, the global production of solar cells was 16.6 GW peak, resulting in a total installed capacity of ~40 $\mathrm{GW_{peak}}$. While it is difficult to predict how this market will develop over the next few decades, estimates range from 3 to 7 TW of installed PV capacity in 2050. Irrespective of the uncertainties involved, there can be little doubt that solar energy will become an important component of the energy mix in the decades to come.

1.3 From Solar to Fuel

As the contribution of solar energy to the total energy mix increases, it will become difficult for electricity network operators to cope with the intermittent nature of solar power (day/night cycle, clouds). At a certain point, grid-based storage capacities will be exceeded and large-scale energy storage solutions need to be implemented. One of the more attractive possibilities is to store solar energy in the form of a chemical fuel. The energy of a visible-light photon ranges between 1 and 3 eV, or 100–300 kJ/mol, which is more than sufficient for many chemical synthesis routes. Compared to, e.g., batteries and mechanical or gravity-based storage systems such as flywheels and pumped water reservoirs, chemical fuels combine the advantages of high energy storage densities and ease of transportation. Examples of chemical fuels include hydrogen, methane, methanol, gasoline, diesel, etc.

Except for hydrogen, all of these examples require a source of carbon. While CO_2 is an obvious candidate in view of the environmental concerns discussed in Sect. 1.1, capturing CO_2 from the atmosphere comes at a huge entropic cost because of its dilute nature. Fossil fuel-based power plants seem attractive point-sources of highly concentrated CO_2, but the goal of the exercise was to avoid the use of fossil fuels in the first place. A conceptually more attractive route would be to capture the CO_2 emitted by, e.g., cars, and to reuse it by synthesizing fuels with sunlight as the energy source. This would close the CO_2 loop. One of the challenges that would have to be addressed is to minimize the energy penalty involved in capturing the CO_2. Direct photo(electro)chemical conversion of CO_2 to a fuel seems to be even more challenging, as the electrochemical half-reactions for the conversion of CO_2 to, e.g., methanol or methane involve complex six- and eight-electron transfer steps, respectively.

Based on these considerations, the conversion of solar energy into hydrogen appears to be a much more attractive route. Water is a convenient and abundant source of hydrogen, and there is more than enough water available. A back-of-the-envelope calculation shows that ~3.5×10^{13} L of water is needed to store the energy the world uses in 1 year (4.7×10^{20} J) in the form of hydrogen. This corresponds to 0.01% of the annual rain fall, or 0.000002% of the amount of water in the world's oceans. The water splitting reaction can be written as follows:

$$2\mathrm{H_2O} + \text{sunlight} \rightleftarrows 2\mathrm{H_2} + \mathrm{O_2} \quad \Delta G = 237\,\text{kJ/mol}. \tag{3.1}$$

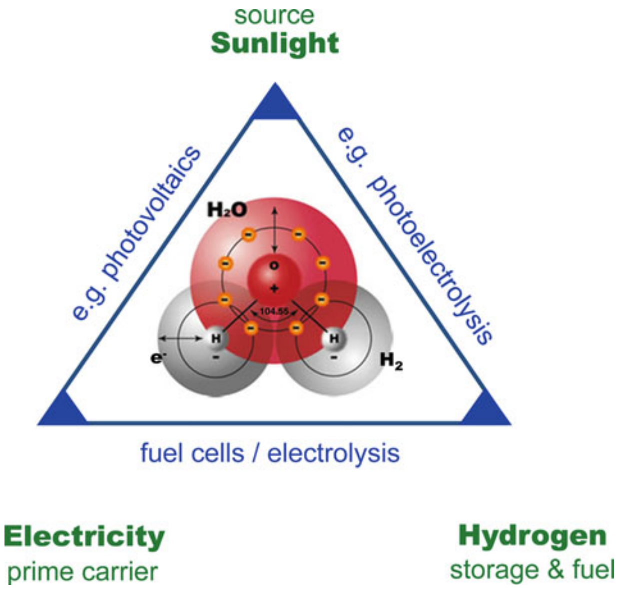

Fig. 1.2 Possible future energy triangle (courtesy of Dr. Andreas Luzzi)

Table 1.2 Gravimetric and volumetric energy densities of several fuels (at 1 bar)

	Energy density	
Fuel	Gravimetric (MJ/kg)	Volumetric (MJ/L)
Coal	24	–
Wood	16	–
Gasoline (petrol)	44	35
Diesel	46	37
Methanol	20	18
Natural gas	54	0.036
Hydrogen	143	0.011

The reduction half-reaction is an easy two-electron transfer reaction, while four electrons are involved in the oxidation of water to form oxygen. While by no means trivial, it is considerably easier to photo-oxidize water than it is to photoreduce CO_2. Moreover, hydrogen can be readily converted into electricity – and back again – with fuel cells and electrolyzers. This offers the prospect of a future energy infrastructure based on sunlight, hydrogen, and electricity, as illustrated in Fig. 1.2.

One of the main concerns associated with hydrogen is the difficulty in storing it. While hydrogen has a very high gravimetric energy density, the volumetric energy density is rather low (Table 1.2). Solutions can be found in the form of high pressure storage containers (up to 700 bar), liquid cryo-storage, or physisorption at high-surface area metal organic frameworks (MOFs) or in clathrate hydrate cages.

Another solution is to store hydrogen by forming chemical bonds. This can be in the form of metal hydrides, such as MgH_2, $LaNi_5H_6$, and $LiBH_4$, or by using hydrogen and CO_2 to make chemical fuels. The latter is a much easier route than the direct photochemical or electrochemical activation of CO_2. For example, CO_2 and hydrogen can be converted into CO via the slightly endothermic reverse water–gas shift reaction:

$$CO_2 + H_2 \rightleftarrows H_2O + CO \quad \Delta H = +\,42\,\text{kJ/mol}. \tag{3.2}$$

The CO and H_2 (*syngas*) can be separated out with a membrane and converted to liquid hydrocarbon fuels, such as methanol and diesel, using well-established Fischer–Tropsch technology.

1.4 Routes to Solar Hydrogen

Many pathways exist for the conversion of water and sunlight into hydrogen:

- Photoelectrochemical water splitting
- Photocatalytic water splitting
- Coupled photovoltaic – electrolysis systems
- Thermochemical conversion
- Photobiological methods
- Molecular artificial photosynthesis
- Plasma-chemical conversion
- Mechano-catalytic, magnetolysis, radiolysis, etc.

Some of these methods are described in more detail in the recent books by Rajeshwar and Grimes [7, 8]. This book focuses exclusively on the first method in the list: photoelectrochemical water splitting with semiconductor photoelectrodes. There are several reasons why this approach is appealing. One of the main advantages is that hydrogen and oxygen are produced at separate electrodes. This avoids serious safety concerns[3] and allows easy separation of these gases without having to pay a heavy energy penalty for postseparation. A second advantage is that it can be carried out at room temperature, i.e., there is no need for large-scale solar concentrators that would limit its application to large central facilities in sunny regions of the world. A third advantage is that a photoelectrochemical water splitting device can be constructed entirely from inorganic materials. This offers a degree of chemical robustness and durability that is difficult to achieve for organic or biological systems.

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[3] The explosion limits of hydrogen are between 18 and 59%, and the flammability limits are between 4 and 74% (in air).

1.5 Benchmark for Photoelectrochemical Water Splitting

It should be noted that the advantages mentioned above for photoelectrochemical (PEC) systems are equally applicable to coupled photovoltaic–electrolysis systems. All the necessary components of such a system (solar cell, electrolyzer, dc–dc converter) are commercially available, and solar-to-hydrogen efficiencies around 8% have already been demonstrated. This approach can therefore be considered as a benchmark for PEC water splitting. The PEC approach offers two potential advantages over PV + electrolysis. The first advantage lies in the fact that commercial electrolyzers require cell voltages of ~1.9 V in order to reach their optimal operating current densities of ~1 A/cm^2. Since the thermodynamically required potential for water splitting is 1.23 V, this places an upper limit of 65% (1.23/1.9) on the overall energy conversion efficiency [9]. In contrast, the current density at a semiconductor photoelectrode immersed in water is much smaller (10–20 mA/cm^2 at most) and the required overpotential is therefore substantially lower.[4] The second advantage is that a PEC system can be constructed as a single, monolithic device. This requires fewer packaging components (frame, glass, connections, etc.) and may lead to significantly lower costs. The cost per kg of hydrogen is in fact the key benchmark figure. Estimated costs for hydrogen produced with PV + electrolysis exceed $8/kg, well above the $2–4/kg target set by the US Department of Energy for future hydrogen production pathways. As discussed in more detail in Chaps. 7 and 8, photoelectrochemical water splitting may offer a route toward hydrogen production costs of $3–5/kg, which is competitive with existing energy sources.

1.6 Materials for PEC Devices

The key component for PEC systems is the semiconductor photoelectrode. The ideal photoelectrode fulfills several tasks at once: light absorption, charge separation, charge transport, and H_2 or O_2 evolution at its surface. Moreover, it needs to be stable in an aqueous solution, and have the potential to be made at low cost. No semiconducting material has yet been found that comes even close to meeting these contradictory demands. This means that trade-offs have to be made, leading to the development of composite photoelectrodes in which different materials fulfill different functionalities.

Figure 1.3 illustrates some of the approaches currently being studied in the field. The left-hand figure shows a monolithic PEC device developed by John Turner's group at NREL [9]. It is based on a p-type $GaInP_2$ photocathode that is biased by an

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[4] This depends on the catalytic activity of the semiconductor surface, which can be quite low. By attaching suitable co-catalysts, overpotentials as low as 0.3–0.4 V can be achieved.

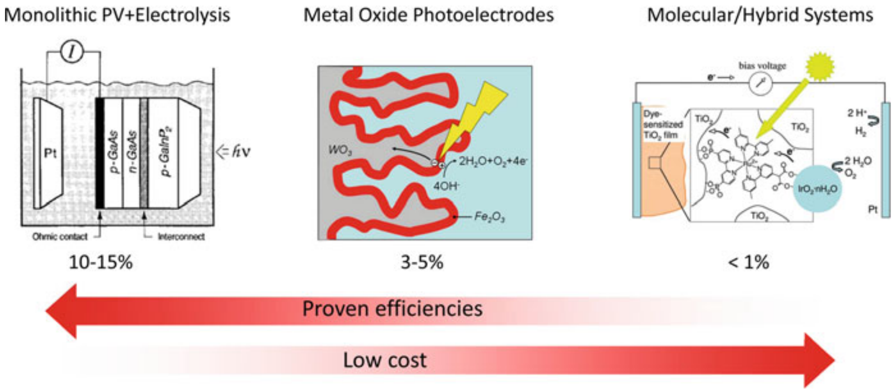

Fig. 1.3 Different approaches toward photoelectrochemical water splitting [9–11]. *Left-hand figure* from ref. [9], reprinted with permission from AAAS. *Right-hand figure* reprinted with permission from ref. [11], copyright 2009 American Chemical Society

integrated GaAs pn junction. With an impressive solar-to-hydrogen efficiency of 12.4%, this example is often quoted as the efficiency benchmark for PEC devices. Challenges to be addressed for this approach are the inherently poor stability of the employed semiconductor materials in water (lifetime only a few hours) and the prohibitively high cost of the GaAs and $GaInP_2$ compounds. The approach shown in the right-hand side of Fig. 1.3 represents a much cheaper solution. It was reported by the group of Thomas Mallouk at Penn State University, and consists of a dye-sensitized nanoporous TiO_2 system in which water oxidation was catalyzed by attaching an IrO_2 nanoparticle to the ruthenium-based dye molecule. The dye molecule and the TiO_2 function as optical absorption centers and charge separators, respectively. The challenges for this system are to improve the performance (currently less than 1% quantum yield) and the degradation of the Ru-based dye by optimizing the kinetic pathways for the reactions of the photogenerated charge carriers.

The middle part of Fig. 1.3 shows an approach in which metal oxide semiconductors, such as Fe_2O_3 and WO_3 are used as light absorbers and charge separators. Inorganic catalysts such as IrO_2 or cobalt-based compounds are generally necessary to catalyze the oxygen evolution reaction. These systems are studied by the authors' groups at EPFL [10, 12] and TU Delft [13, 14], and many other groups around the world. The main advantage of using metal oxides is their low cost and excellent stability against (photo)corrosion in aqueous solutions – although this does depend on the pH of the solution and the choice of metal oxide. One of the main challenges for metal oxide-based absorbers is the combination of modest light absorption and poor charge transport properties. Solutions for these and other challenges have been proposed in the form of mesoporous materials, guest–host nanostructures, tandem junctions, plasmonics, and combinatorial search methods for new metal oxide semiconductors. Chapters 4, 5, 6, 7, and 9 discuss the exciting developments that have been reported in this field over the past few years.

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