

Hydrogen production by water electrolysis

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DOI: 10.1533/9780857097736.2.159

Abstract: An electrolyzer combines an oxidation and a reduction reaction, driven by electricity, to produce separate streams of hydrogen gas and oxygen gas by a process called electrolysis. The hydrogen contains a portion of the electrical energy, and it can be used to generate electricity in a fuel cell by a process that is the reverse of electrolysis. If water electrolysis is driven by renewable electricity, it can be used in fuel-cell electric vehicles to displace petroleum, increase vehicle efficiency, and reduce the environmental impact of vehicles. The fundamental aspects of electrolytic hydrogen and its use as energy carrier are discussed.

Key words: water electrolysis, hydrogen, electrolyzer, fuel cell, energy, renewable energy.

6.1 Introduction

The electrolysis of water to produce hydrogen and oxygen will someday be used to capture vast amounts of renewable energy in the generated hydrogen. The overall reaction is simple: direct current (DC) electricity splits water into its gaseous elements, hydrogen and oxygen. In reality, this is a complex reaction that requires much more than the minimum energy that is the difference between that of water and its elements. This excess electrical energy that is needed is a major reason why water electrolysis is currently only a minor source of the overall amount of hydrogen that is produced in the world. In some specialized cases, for example on submarines, the oxygen is the product of interest in water electrolysis, but we will focus on the hydrogen in most of our discussion.

Ten years ago it appeared that water electrolysis, and the overall production of hydrogen, could undergo a major expansion because introducing hydrogen-powered fuel-cell electric vehicles (FCEV) is a goal of major automobile manufacturers worldwide. Hydrogen-powered electric drive systems replacing conventional internal combustion engines (ICE) were referred to as part of a 'new DNA' for future automobiles (Burns, 2009; Mitchell *et al.*, 2010). This exciting scenario lined up with a reinvention of the automobile leading to clean and sustainable automobiles in the twenty-first century.

FCEV powered by hydrogen have no tailpipe emissions other than water vapor, and are roughly twice as energy efficient as ICE-powered vehicles. Water electrolysis powered by renewable energy could provide the hydrogen for such a vehicle fleet, thus achieving an environmentally friendly and sustainable transportation system. In such a system, hydrogen is the energy carrier for the renewable energy (Kelly *et al.*, 2011; Muradov and Veziroglu, 2008).

This goal seems further away today than it did 10 years ago, mainly due to economic downturns and cutbacks in government and private sector funding for a move to a hydrogen economy. In particular, in the United States, hybrid and battery electric vehicles have taken center stage as the new automotive DNA. Perhaps the biggest obstacle on the pathway to FCEV is the lack of a fueling infrastructure. To build fueling stations for FCEV, energy companies need to be sure there will be vehicles to use the fuel, and to build the vehicles, automotive companies need to know there will be fueling stations for the vehicles. Thus, there has not been an increase in hydrogen fueling stations, and auto manufacturers keep pushing back the production date for the introduction of FCEV.

An even more dramatic illustration of the scaling back of ambitious plans for a hydrogen economy is the turn of events in Iceland. Iceland has over 70% renewable energy, due to its unique geothermal and hydroelectric resources. Over 10 years ago the government of Iceland had a plan to completely displace carbon-based fuels and use their geothermal resources to produce hydrogen to power the transportation sector. However, an economic crisis has caused Iceland to scale back their transition to a hydrogen economy to at least 2050, and to focus on battery electric vehicles in the short term, similarly to the United States.

In this chapter on water electrolysis, we focus on FCEV because of the synergy between fuel cells and electrolyzers, both scientifically and economically. For example, research on fuel cells that leads to more efficient and robust systems can also be used to improve electrolyzers. Implementation of fuel-cell vehicles in the marketplace would help to create a demand for electrolytic hydrogen generation systems.

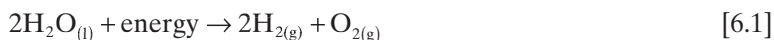
The electrochemistry of water electrolysis and the performance characteristics of available electrolyzers will be reviewed. The experience of the author and his coworkers in designing, building, and testing a solar-powered water electrolysis system for high-pressure fueling of FCEV will be used as an example of the use of electrolysis in a distributed energy system. Photocatalytic and biological water splitting are covered in other chapters, although we will mention photoelectrochemical hydrogen production in which the electrolysis is directly coupled to a photo process in a monolithic device. Finally, we will discuss the improvements in electrolyzers needed to make water electrolysis a major contributor to a future hydrogen economy.

6.2 Electrolytic hydrogen production

Presently, electrolysis is a minor contributor to the production of hydrogen, only accounting for about four percent of the worldwide inventory (Harrison and Levine, 2008). Fossil fuels, primarily natural gas (methane), are the main feedstocks for hydrogen production via a process called steam reforming. The carbon in the methane is emitted as carbon dioxide. This has adverse environmental effects and is not sustainable in a world with a growing population. Nonetheless, electrolytic hydrogen can be a very large component of a future move to store large amounts of solar or other renewable energy (Baykara, 2004; Barbir, 2005; Dunn, 2002; Kelly *et al.*, 2010; Turner, 2004, 2008). In this regard, hydrogen is the energy carrier and sunlight is the fuel.

6.2.1 The water electrolysis reaction

The chemical reaction for water electrolysis, also called water splitting, can be written:

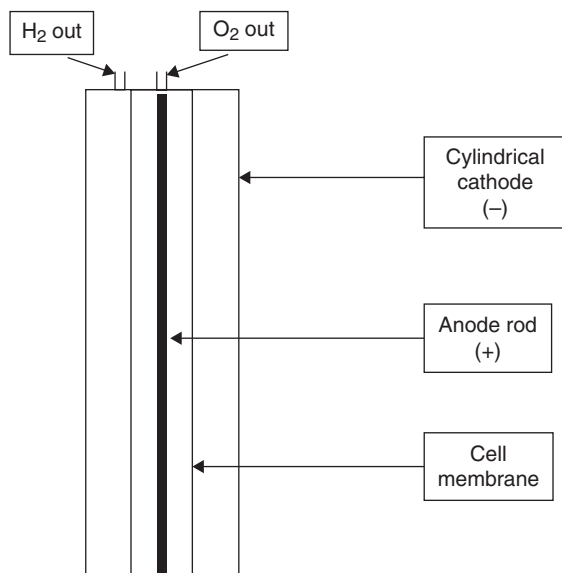


In an electrolyzer the energy is electrical energy from a DC power source. Pure liquid water is a poor conductor of electricity, because at room temperature it dissociates to a very small extent to produce aqueous hydrogen ions, H^+ , and hydroxide ions, OH^- .



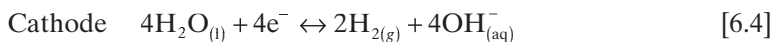
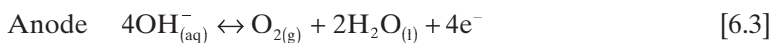
At room temperature, the concentration of hydrogen and hydroxide ions is approximately 10^{-7} moles per liter. In an aqueous solution, the ions are the charged particles that conduct electricity, while in metallic conductors, i.e., wires, electrons are responsible for conducting electricity. Both of these events (ion conduction in an aqueous solution and electron conduction in metal wires and electrodes) occur during water electrolysis in an electrolyzer.

In order to improve the conductivity in water, compounds are added that readily dissociate to form ions in water. The compounds added are typically acids or bases. For example, in an alkaline electrolyzer, a basic solution is used that can be obtained by adding potassium hydroxide (KOH) to water. In water, the KOH splits into K^+ ions and OH^- ions, and these ions readily conduct electricity in a water solution by flowing from one electrode to the



6.1 One electrolysis cell in an alkaline electrolyzer. The cell is filled almost to the top with 5 molar KOH. The hydrogen and oxygen rise to the top of the cell in their respective compartments where they exit the cell. (Source: © International Association for Hydrogen Energy, Figure 2 in Kelly *et al.*, 2011, used with permission.)

other. In a basic solution, we can write the basic chemical equations occurring as two electrochemical half reactions. They are written as follows:



The anode is connected to the positive terminal of a power supply and the cathode is connected to the negative terminal of a power supply. An example of an electrolysis cell used in a commercial alkaline electrolyzer is shown in Fig. 6.1.

As shown in the figure, the hydrogen and oxygen are produced in separate compartments. Very high purity is attained in electrolyzers, typically exceeding 99% for each product. The cell membrane allows ions to be transported between the electrodes but, ideally, does not allow any exchange of the gases. Hydrogen and oxygen form gas bubbles that grow on the electrodes and then, due to buoyancy, rise to the top of the cell. At the top of the cell, each gas exits and can be stored for later use. In many cases only the hydrogen is stored, and the oxygen is vented.

It is specifically noted in Equations [6.3] and [6.4] that water is in the liquid state and both hydrogen and oxygen are diatomic gases. Adding together Equations [6.3] and [6.4], we get the net overall reaction shown in Equation [6.1]. This is an endothermic reaction because water is much more stable than its elements, so energy must be added to split water. In an electrolyzer, the energy to drive the reaction is provided by electrical energy from an external DC power source. Considering the chemistry shown in Equation [6.1], we can understand why the electrolyzer produces twice as much hydrogen as oxygen on a volume basis. Two molecules of hydrogen are produced for each molecule of oxygen that is produced, because that is the ratio of the hydrogen and oxygen atoms in water.

Equation [6.3] is referred to as an oxidation reaction because the OH^- ion is oxidized to water and, as shown, this produces four electrons. This reaction occurs at the solid–electrolyte interface at the positively charged anode. The reaction at the anode is commonly called the oxygen evolution reaction (OER) because the oxygen is produced as bubbles of gas at a metal electrode, such as of platinum or nickel. At the negatively charged cathode, reduction occurs because the water is reduced to hydrogen and OH^- ions. The reaction shown in Equation [6.4] is called the hydrogen evolution reaction (HER), because hydrogen is produced as bubbles of gas at a metal electrode called the cathode.

The potassium ions undergo no net reaction in this system and merely serve as conducting ions in water solution. Other cations that could also be used, because they have a lower electrode potential than hydrogen ions, include alkali metal ions, such as sodium, and alkaline earth metals, such as magnesium.

To drive the reaction, DC electricity must be supplied via wires connected to the anode and the cathode. Electrical energy must be supplied to split water to generate hydrogen and oxygen in an electrolyzer, while energy is produced by the reverse reaction of hydrogen and oxygen to form water in a fuel cell. This round trip in the chemical reactions in Equation [6.1] illustrates the role of hydrogen as an energy carrier.

Although there are many more details that must be considered in producing a commercial water electrolyzer and a hydrogen–oxygen fuel cell, the basic chemical concepts can be understood from the reactions shown in Equations [6.1]–[6.4]. In simplest terms, an electrolyzer decomposes water into hydrogen and oxygen using DC electricity, and the electrical energy is converted into the chemical energy in the hydrogen and oxygen. In a battery, oxidation–reduction reactions also occur during charging, which store the electrical energy as chemical energy in a similar manner to those in an electrolyzer. One major difference between batteries and electrolyzers is that batteries eventually reach a point of 100% state of charge, where further addition of charge could ruin the battery, whereas an electrolyzer can keep receiving DC electricity and producing hydrogen and oxygen as long

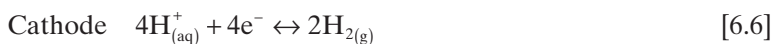
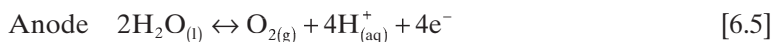
as more water is added. The fact that water electrolysis converts water into gaseous products that rise, escape from the aqueous solution, and can be stored or transported away from the electrolyzer, is an important aspect of the continuous nature of the process.

Typically it is the hydrogen product of water electrolysis that is stored, although both hydrogen and oxygen must be produced in water electrolysis. There are specialized uses for the oxygen product, such as aboard a submarine, but hereafter we will concentrate on the energy stored in the hydrogen. The importance of water electrolysis as a source of hydrogen in the future is intimately tied to the use of fuel cells that use the hydrogen to generate DC electricity aboard vehicles or in stationary power supplies. There is a strong synergy between electrolyzers, fuel cells and renewable energy in a transition to a hydrogen economy.

6.3 Types of electrolyzers

There are two fundamental types of electrolyzers identified by the pH of the aqueous solution: acidic and basic. The chemical half reactions in a basic or alkaline electrolyzer were described in Equations [6.3] and [6.4]. One key advantage of an alkaline electrolyzer is that it does not need to have noble metal electrodes, and nickel or even iron can be used as electrodes. A third type of electrolyzer, referred to as a solid-oxide electrolyzer, operates at high temperature, and splits steam into hydrogen and oxygen, using both thermal and electrical energy to break the bonds in water.

Electrolyzers using acidic solutions need noble metal electrodes, especially at the anode where the process is especially corrosive. The overall chemical reactions in an acidic electrolyzer can be obtained by adding hydrogen ions to the reactions in Equations [6.3] and [6.4]:



A common electrolyte in acid-based electrolyzers is sulfuric acid, because it is a strong acid that dissociates to produce hydrogen ions in water solution. The bisulfate and sulfate anions are very difficult to oxidize, so they remain in solution and are not oxidized at the anode.

A special case of an acid-type of electrolyzer is a proton exchange membrane (PEM) electrolyzer, in which a highly-acidic polymer membrane serves as the electrolyte that conducts protons to the cathode, and also as the

separator between the anode and cathode compartments (Marangio *et al.* 2009). No ionic compounds are added to a PEM electrolyzer to increase the water ion conductivity. Only pure water is added to such an electrolyzer where it is converted into pure streams of hydrogen and oxygen. The automotive industry has utilized PEM fuel cells for their test vehicles that use hydrogen as the energy source. The PEM system is especially safe because no caustic or acidic solution is present. Also, the PEM system is compact. However, due to the acidic nature of the polymer membrane, Pt electrodes are needed.

It is important to note that saltwater would not be an appropriate source of a conducting water solution for electrolysis because chloride would be oxidized at the anode to chlorine gas. Hydrogen would still be produced at the cathode. Saltwater electrolysis is used commercially in the manufacture of sodium hydroxide and chlorine where those products are desired. However, it is not useful for making hydrogen unless the sodium hydroxide and chlorine can also be used.

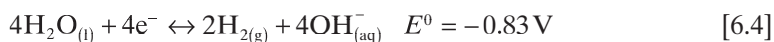
There are also specialized electrolyzers that are under study in research laboratories. One type uses light absorption that is directly coupled with water splitting in a photoelectrochemical reactor (Khaselev and Turner, 1998). Another type uses a combined heat/electrical approach to water splitting (Degiorgis *et al.*, 2007; Licht, 2005; Wang *et al.*, 2012).

6.4 Water electrolysis thermodynamics

The thermodynamics of the water electrolysis reactions relate the voltages for the reactions at the anode and cathode of an electrolytic cell to the energy and entropy changes involved in breaking the chemical bonds in water and forming the chemical bonds in the diatomic hydrogen and oxygen gas products. These quantities are discussed for standard and non-standard conditions.

6.4.1 Standard potential for water electrolysis

The standard potential for water electrolysis can be obtained from the standard potentials, E^0 , for the two half reactions. For a basic solution shown in Equations [6.3] and [6.4] above:



Combining these two half reactions yields:



The voltages shown in Equations [6.3] and [6.4] are the equilibrium potentials, E^0 , of the half reactions, while that in Equation [6.1] is the equilibrium potential of the overall reaction in an electrolyzer under the standard condition of temperature, 298 K, and 1 bar of pressure. Because the reaction is endothermic, and energy must be added to drive the reaction, the voltage shown is negative. We could have written the reactions in the acid solution, Equations [6.5] and [6.6], and the E^0 for the overall reaction would be the same, 1.23 V. That is, the water electrolysis voltage is the same regardless of the solution pH.

If a voltage of at least 1.23 V is applied to electrodes in liquid water at 298 K and 1 bar of pressure, the water will begin to decompose into hydrogen and oxygen as the system equilibrium shifts from pure water and electricity to a system with some hydrogen and oxygen gas present. However, the rate of the HER and OER reactions will be near zero as explained later.

6.4.2 Standard Gibbs free energy, enthalpy and entropy of water electrolysis

The next step in understanding the energetics of the water electrolysis is to introduce the Gibbs free energy (ΔG), the enthalpy (ΔH) and the entropy (ΔS) for the process. The standard enthalpy change, ΔH^0 , is 285.8 kJ/mole and the heat that must be added is equal to the change in the standard entropy, ΔS^0 , multiplied by the standard temperature ($T = 298 \text{ K}$), yielding a value of 48.7 kJ/mole. The standard change in Gibbs free energy, ΔG^0 , for water electrolysis is:

$$\Delta G^0 = \Delta H^0 - T \times \Delta S^0 \quad [6.7]$$

The values for the three thermodynamic quantities, ΔG^0 , ΔH^0 and $T \times \Delta S^0$ (the heat term) are listed in Table 6.1 for splitting liquid water at 298 K and 1 bar of pressure. At this temperature and pressure the reactants and products are in their standard states, so the superscript zero is added to the thermodynamic quantities. The standard voltages corresponding to the change in the standard Gibbs free energy can be computed from the formula relating the standard Gibbs free energy to the standard potential:

$$\Delta G^0 = -n \times F \times E^0 \quad [6.8]$$

Table 6.1 Values of the thermodynamic quantities for liquid water electrolysis at 298 K and 1 bar

	kJ/mole	Volts
Standard Gibbs free energy, ΔG^0	237	1.23
Standard enthalpy, ΔH^0	286	1.48
Standard entropy term, $T \times \Delta S^0$	48.7	0.25

where n is the number of electrons in the half reactions per mole of water split ($n = 2$), F is Faraday's constant ($F = 96\,500$ coulombs mole^{-1}) and E^0 is the standard potential in volts. Notice that under standard conditions, the voltage for water electrolysis is negative and the Gibbs free energy is positive so the reaction is not spontaneous.

As discussed earlier, to split liquid water into its gaseous elements at 298 K and 1 bar of pressure takes a minimum of 1.23 V, the voltage corresponding to standard Gibbs free energy of the process. However, in a closed system, the water would cool, due to the change in entropy. In a real system, this heat would be supplied by the environment and the solution would then not cool. This is an important point: in an electrolyzer, heat will flow into the system to help the process. Conversely, in a fuel cell the exact reverse happens and the reaction of hydrogen and oxygen will naturally produce heat that will flow into the surrounding environment.

The standard enthalpy of 285.8 kJ, corresponding to a voltage of 1.48 V, is referred to as the thermo-neutral voltage, because at that voltage no heat needs to be added from the environment to split water. At that voltage, all of the energy for the process, both the Gibbs free energy and the heat to keep the system temperature constant, is supplied by the added electrical energy.

To define the efficiency of the water electrolysis process we need to determine the energy value of the hydrogen product. Several different values have been assigned to the useful chemical energy in gaseous hydrogen. Some scientists have used the lower heating value (LHV) of 33.3 kWh kg^{-1} corresponding to an electrolyzer voltage of 1.254 V. This value is for a system that combines hydrogen and oxygen to produce gaseous water rather than liquid water. Others use the higher heating value (HHV) of 39.4 kWh kg^{-1} corresponding to the thermo-neutral value of 1.48 V in Table 6.1. The difference between the HHV and the LHV is the heat of vaporization of water. Still others use the standard Gibbs free energy of 1.23 V in Table 6.1. All of these can be justified, and the most important thing to note is that the standard used must be given so that electrolyzer efficiency values from different evaluations of electrolyzer efficiency can be compared. The US Department of Energy (2010) has been using the LHV as a standard in comparing electrolyzers, and that is what we will use.

$$\text{Electrolyzer efficiency} = 100\% \times \text{operating voltage} \div 1.254 \quad [6.9]$$

Thus, if an electrolyzer is operated at 1.254 V, it is 100% efficient in converting electricity to chemical products.

Although the standard Gibbs free energy, 1.23 V, is very close to the LHV of hydrogen, 1.254 V, the two should not be confused. In a fuel cell 1.23 V is the output ideal output voltage in a 100% efficient fuel cell. Thus, in using 1.254 as the standard for computing the electrolyzer efficiency and 1.23 V for computing the fuel-cell efficiency, slightly different standards are used for the two systems.

6.4.3 Pressure and temperature effects on the electrolysis voltage

The effect of pressures greater than one bar on the water electrolysis voltage can be computed using the Nernst equation (Kelly and Girdwood, 2012):

$$\text{Electrolysis voltage} = E^0 - \left((R \times T) \div (2 \times F) \times \ln [\text{H}_2] \times [\text{O}_2]^{0.5} \div [\text{H}_2\text{O}] \right) \quad [6.10]$$

In Equation [6.10] T is the temperature in degrees K , R is the gas constant (8.314 volt coulombs/ K mole), F is the Faraday constant defined earlier, and the H_2 and O_2 concentrations are equal to their pressures. If $[\text{H}_2] = [\text{O}_2] = 1$ bar (0.1 MPa) and the temperature is 298 K, then the electrolysis voltage is -1.23 V. The quantity $((R \times T)/(2 \times F))$ is equal to 0.0128 V at 298 K. The concentration of water is relatively independent of gas pressure and is taken as one since it is in its standard liquid state. Notice that the sign on E^0 is negative, since 1.23 V is needed to split water. If the system was consuming H_2 and O_2 to produce electricity in a fuel cell, the sign of the standard voltage would be positive and the reaction would be spontaneous, that is, the Gibbs free energy would be negative, Equation [6.8].

The increase in the water electrolysis voltage with increasing pressure is very slight, due to the logarithmic pressure dependence in Equation [6.10]. For example, if both $[\text{H}_2]$ and $[\text{O}_2]$ are increased to 10 atmospheres, then the voltage needed to split water is -1.273 V, an increase of only 3.6%. This provides an incentive for using electrolyzers, rather than mechanical compressors, to produce high-pressure hydrogen (or oxygen).

For higher pressures, one cannot simply use pressure in the Nernst equation, and the activity, called the fugacity for gases, needs to be used to account for the gas non-ideality. The fugacity is equal to the pressure at low pressures, but for gases above their critical temperatures it is higher than the pressure. Fugacity values have been measured for hydrogen and oxygen to very high pressures and are available in the literature. Using the fugacity for hydrogen and oxygen at 700 bar in Equation [6.10], 1.36 V is needed to

split water. This increase of 0.13 V from the value at a pressure of 1 bar is an increase of only 10.6% (Kelly and Girdwood, 2012).

The effect of increasing temperature on the voltage needed for water electrolysis energy can be obtained using standard thermodynamic correlations (Harrison and Levine, 2008). The result is the water-splitting voltage is decreased as temperature increases. Thus, electrolyzer efficiency increases at higher temperatures, i.e., the electrolyzer operating voltages are lower. Due to materials constraints, this opportunity for increasing efficiency has not been used to a significant extent in commercial electrolyzers. However, from a research standpoint, the energy of combined thermal and voltage sources, especially with regard to solar energy, is highly desirable (Joshi *et al.*, 2010; Padin *et al.*, 2000). We will discuss an empirically determined temperature effect for a commercially-available alkaline electrolyzer in a later section.

6.5 Kinetics of water splitting

In a real electrolyzer, voltages higher than 1.23 V must be used to decompose water into hydrogen and oxygen because of the need to drive the reaction away from equilibrium at standard conditions, i.e., to shift the equilibrium to the right in Equation [6.1] and produce the products at a desirable rate. Most importantly, the thermodynamics discussed in the previous section tell us nothing about how fast the reactions will proceed to equilibrium, i.e., the kinetics of the electrolysis process. A good example of this phenomenon is a 2:1 (by volume) mixture of hydrogen and oxygen at room temperature. A thermodynamic analysis of the system shows that the reaction is highly exothermic and the system will eventually consist mostly of water. However, in the absence of a catalyst or a spark, the reaction rate is negligible.

Even though we show the half reactions as single-step processes in Equations [6.3]–[6.6], in reality there are many individual fundamental reactions and rearrangements in the reaction pathway, especially in the OER. The mechanism for the electrode reactions responsible for the OER is still incomplete, despite over 100 years of study.

The first step in understanding the kinetics of an electrochemical reaction is an analysis of the energy or overvoltage needed to drive the reactions toward the product side of the system. The potential difference (voltage) across two electrodes in an electrochemical cell is equal to the standard potential, E^0 , plus the overvoltage, η :

$$\Delta V = E^0 + \eta \quad [6.11]$$

The overvoltage, η , has three components:

$$\eta = \eta_a + \eta_c + \eta_{ir} \quad [6.12]$$

where η_a is the activation overvoltage caused by rate-limiting steps (energy activation barrier), η_c is the concentration overvoltage caused by the decrease in concentration at the electrode surface relative to the bulk phase because of mass transport limitations and η_{ir} is the ohmic overvoltage caused mainly by resistance in the electrolyte and also at the electrode surface. The η_{ir} term is minimized by using an electrolyte with the maximum conductivity (approximately 28% KOH by mass in the alkaline electrolyzers). The η_a term is minimized by using electrodes that catalyze the reactions of interest, and this is by far the main overvoltage in water electrolysis, and in particular in the OER. The η_c term can be minimized by stirring or vibrating the electrode and solution to promote mixing and detachment of bubbles from the electrode solution. It is very important that bubbles of gas form at the electrode and rise out of the liquid solution.

Conceptually, the overvoltage is a form of friction that we must pay for with extra voltage (energy) to force the reactions to occur at a greater rate. Typically 1.4–2.0 V per cell must be used to split water in commercial electrolyzers. Overvoltages are also responsible for voltages lower than 1.23 V as the open circuit voltage from a hydrogen–oxygen fuel cell. Open circuit voltages in fuel cells are typically about 1 V.

Kinetic effects lead to relatively large inefficiencies in electrolyzers. To illustrate this, consider that in a practical water electrolysis system, i.e., one that evolves hydrogen and oxygen at a useful rate, the voltage necessary is approximately 2 V, an overvoltage of about 0.8 V. Using Equation 6.9, this gives an efficiency of 63%, so 37% of the energy is wasted by conversion to heat rather than chemical products. Notice that the kinetic overvoltage for water splitting at standard pressure conditions far outweighs the thermodynamic overvoltage at 700 bar computed earlier (0.13 V). This comparison shows the major importance of kinetic effects versus the minor influence of pressure-related thermodynamic effects on the water-splitting voltage (Janssen *et al.*, 2004; Kelly and Girdwood, 2012; Onda *et al.*, 2004). Reducing the kinetic overvoltages can lead to significant energy savings in the water-splitting process.

It is important to conceptually understand what fundamental processes are responsible for the overvoltages in order to know where research and engineering is needed to improve electrolyzer performance (Ulleberg, 2003). The main contributor to the overvoltage in water electrolysis is due to the activation polarization, and an improved catalyst is vitally needed to reduce that overvoltage in the OER for electrolyzers and reduce the voltage loss for the oxygen reduction reaction (ORR) in fuel cells. In contrast, only small overvoltages or voltage losses, respectively, occur for the HER in electrolyzers or the hydrogen oxidation reaction (HOR) in fuel cells. Smaller improvements

in electrolyzer performance can be achieved by reducing the concentration polarization overvoltage by promoting bubble formation and removal from the electrodes by mixing or vibrating the electrode.

An example of the importance of kinetic overvoltages is in the charging of a Pb-acid battery. Such batteries are charged to about 2.1 V per cell. Water electrolysis should begin at about 1.23 V, yet there is little gas evolution until near the end of the charging process. The Pb electrodes have a very large overvoltage for water splitting, so although the thermodynamics favors water splitting, the kinetics favors battery charging.

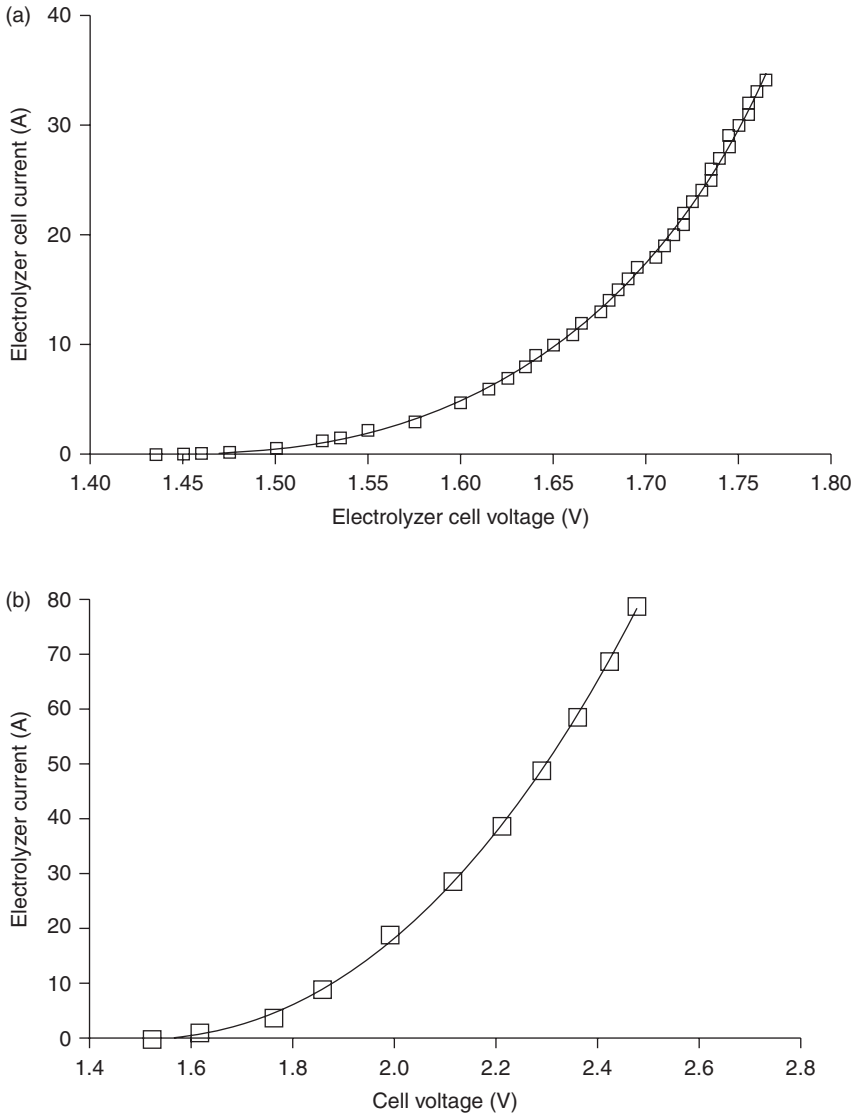
6.6 Electrolyzer current-voltage (I–V) curves

The operation of an electrolyzer is often characterized at a given temperature by determining its operating current as a function of the applied voltage, referred to as an I–V curve. Other performance characteristics, such as the operating power (current \times voltage) and efficiency (Equation [6.9]) can be easily derived from an I–V curve. An example of an I–V curve is given in Fig 6.2a. This data was obtained on a Proton Energy, Hogen model 40 electrolyzer stack (Gibson and Kelly, 2008, 2010). Notice that the electrolyzer starts conducting current at an applied voltage of about 1.4 V per cell. The current increases monotonically with the applied voltage and can be fit with a quadratic function over the voltage range shown.

The efficiency, as defined by Equation [6.9], is highest at the lowest operating voltage. The starting efficiency for this electrolyzer is nearly 87%, and it decreases to 71% at the highest voltage tested. However, the amount of hydrogen produced by the electrolyzer occurs at the highest current because it is the current flow that is driving the electrochemical reactions to produce products. Therefore, both the efficiency and the mass of hydrogen produced in a given time must be taken together to assess the electrolyzer performance.

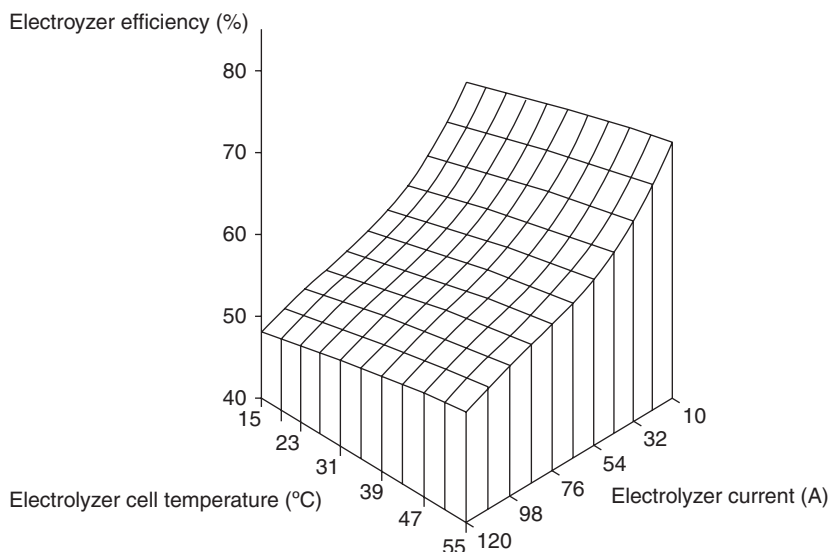
Another I–V curve shown in Fig. 6.2b was obtained on an Avalence alkaline electrolyzer (Kelly *et al.*, 2008, 2011). At very high current, the efficiency dropped to about 50%. From a field study using the Avalence electrolyzer run on solar photovoltaic (PV) electricity, a mathematical model of the electrolyzer efficiency as a function of the operating current and temperature was developed. The electrolyzer efficiency, derived using Equation [6.9], was fit to a polynomial function of the current and temperature. The regression equation was:

$$\begin{aligned} \text{Electrolyzer efficiency, \%} = & 68.6 - (0.486 \times I) + (4.52 \times 10^{-3} \times I^2) \\ & - (1.718 \times 10^{-5} \times I^3) + (0.167 \times T) \\ & - (7.051 \times 10^{-4} \times T^2) \end{aligned} \quad [6.13]$$



6.2 Current versus voltage curves for (a) a 20-cell PEM electrolyzer, and (b) a 24-cell alkaline electrolyzer. In each case, the voltage per cell is plotted.

In this equation I is the electrolyzer current and T is the electrolyzer cell temperature. Figure 6.3 shows the response surface of the efficiency as a function of the electrolyzer current and temperature based on Equation [6.13]. The operating efficiency increased for any given operating current as the temperature increased. Thus, to increase the electrolyzer efficiency



6.3 Three-dimensional plot of the regression model prediction of electrolyzer efficiency as a function of the electrolyzer current and the electrolyzer cell temperature. (Source: © International Association for Hydrogen Energy, Figure 12 in Kelly *et al.*, 2011, used with permission.)

it should be operated at as high a temperature as the electrode and membrane materials will allow, while maintaining a good service life for the electrolyzer.

6.6.1 Faradic efficiency

It is important that the electrons added to an electrolyzer are used to drive the water-splitting reactions and not side reactions such as corrosion of the electrodes or the production of hydrogen peroxide. The production of the desired products results in a high Faradic efficiency. In our earlier discussion of the energy or voltage efficiency, the overvoltages resulted in the production of heat rather than in the formation of the desired products. Losses that reduce the Faradic efficiency result in products other than hydrogen or oxygen. The Faradic efficiency is sometimes referred to as the Coulombic or current efficiency, while the efficiency in Equation [6.9] is referred to as the energy or voltage efficiency.

For good Faradic efficiency in water electrolysis, the electrodes must be stable against oxidation or reduction versus the HER and OER reactions. In commercial electrolyzers that must last for many years this problem has been very well addressed and the side reactions are very minor. Thus, the electrodes resist corrosion, and very pure hydrogen and oxygen are produced

as products. Typically, electrolysis produces hydrogen with a purity exceeding 99%, and gas purity issues are more associated with the cell membrane permeation issues than Faradic losses at the electrodes.

6.7 High-pressure water electrolysis

A high-pressure electrolyzer can be designed and used instead of the more commonly available low-pressure electrolyzers that produce hydrogen at outlet pressures typically less than approximately 15 bar (200 hundred psi). Hydrogen from such low-pressure electrolyzers must be compressed mechanically in a piston, diaphragm, or other type of compressor up to 700 bar for practical hydrogen storage and vehicle fueling applications. Motor-driven mechanical compressors have several limitations, including energy losses, noise, contamination, and maintenance of moving parts. Mechanical compressors typically operate in a regime approximating a non-reversible polytropic compression (Kelly and Girdwood, 2012). In contrast, electrolytic compression approximates a reversible isothermal compression that requires the minimum amount of work. The work for an isothermal compression from a starting pressure P_i to a final pressure P_f is:

$$W_{\text{isothermal}} = P_i \times V_i \times \ln(P_f \div P_i) \quad [6.14]$$

where V_i is the specific volume of hydrogen at a pressure P_i . The isothermal compression work is the minimum amount of work that is needed to compress a gas, and it can only be achieved in a system that changes in a so-called reversible fashion. In a reversible system the pressure differential is infinitesimally small, and in an isothermal process the heat of compression is instantaneously removed. Such a process would take forever, and it can only be approximated in the real world.

The Nernst equation prediction for the thermodynamic increase in the water electrolysis voltage with increasing product gas pressure is identical to the prediction of the work energy needed for a reversible isothermal gas compression. Thus, electrolysis is a very efficient way to compress gases (Kelly and Girdwood, 2012). Electrolysis forms small bubbles in a continuous fashion that approximates a reversible process

Furthermore, in a high-pressure electrolyzer, reduction in the bubble size can help to reduce the concentration polarization, η_c (Equation [6.10]). At high pressure the gas bubbles are squeezed to a lower volume, thereby increasing the electrode area and reducing η_c . For example, at a pressure of 10 atmospheres the bubble size is reduced by 90% from the value at one atmosphere. Reducing the kinetic overvoltage at high pressure could offset the small thermodynamic (Nernst) energy increase needed to produce

high-pressure hydrogen electrolytically. This could make electrolysis an even more efficient means to compress hydrogen and oxygen as compared to mechanical compression. An accurate determination of the energy used in high-pressure electrolysis is needed to test this hypothesis.

In addition to the efficiency of electrolytic compression, electrolyzers have few moving parts and are virtually silent. Thus, it is very desirable to use electrolysis to increase the hydrogen pressure to levels needed for hydrogen storage. We will give an example of this in the next section.

Thermally-powered hydrogen compressors offer another way to compress hydrogen that is very inefficient, but that may be viable if waste heat could be used to power the process (Kelly and Girdwood, 2012). Thus, efficiency is not the sole criterion that should be used to choose a compression method.

6.8 Coupling electrolyzers with solar energy for vehicle hydrogen fueling

The attractive environmental features of hydrogen-powered fuel-cell vehicles powered by renewable energy led General Motors Research and Development to design, build, and test a solar-powered, high-pressure, hydrogen fueling system based on water electrolysis (Birnie, 2009; Ipsakis *et al.*, 2009; Kelly *et al.*, 2008). In that system, a PV solar-powered system was directly coupled to a high-pressure electrolyzer. This was a proof-of-concept for a single-vehicle fueling system for home use that could serve as a starting point for enabling the sale of hydrogen-powered FCEV without building an expensive centralized hydrogen fueling network. The system design is described in detail elsewhere (Kelly *et al.*, 2008) and only the major relevant details will be given here.

The design of the system began with a high-pressure electrolyzer: an Avalence LLC (Milford, CT) Hydrofiller high-pressure electrolyzer that could produce H_2 at pressures up to 450 bar (6500 psi) without the use of a compressor was chosen. The electrolyzer design used a monopolar alkaline (KOH) electrolyte system with cylindrical steel electrolysis cells and a novel system for balancing the H_2 and O_2 gas pressures so that only a very small differential pressure could occur across the cell membrane. The design also maintained a nearly constant electrolyte level and included a gas/liquid separation system. The system was designed to produce approximately 0.5 kg of hydrogen per day using solar energy with the average solar insolation for Southeastern Michigan. This required using two banks of 24 electrolysis cells in series (48 cells total). The electrolyzer output was fed to a high-pressure storage tank. The storage tank was connected to a dispenser for fueling FCEV. The complete system was referred to as the electrolyzer storage and dispensing system (ESD).

A solar PV system was designed to directly power the electrolyzer. No power conversion was incorporated between the electrolyzer and the solar power system. In order to operate the electrolyzer at high current, and high hydrogen production, approximately 50 V was needed across the banks of 24 electrolysis cells. We chose Sanyo HIP-190BA3 modules with a maximum power point (MPP) of about 55 V under standard PV test conditions. This allowed for some losses due to reduced PV system output at real-world operation temperatures that are higher than those at standard PV test conditions. The complete PV system used 40 Sanyo modules wired in parallel to power the electrolyzer. The measured hydrogen output from the system was very near the 0.5 kg per day design value.

A picture of the PV-ESD system is shown in Fig. 6.4. After a brief test period during a particularly harsh portion of the winter season, one of the high-pressure elastomer hoses, used in the electrolyzer, failed. The failure was traced to heating in the hose, caused by the reaction between high-pressure oxygen and small amounts of hydrogen that permeated through the cell membrane and into the oxygen. The electrolyzer required extensive repair and some parameter changes. New membranes were installed with lower hydrogen permeation rates and the pressure output was reduced to approximately 140 bar (2000 psi). The electrolyzer was returned to service and run on solar power over a period of 109 days without incident. Even with the daily and seasonal changes in the PV system solar irradiance, PV system



6.4 Picture of the General Motors solar hydrogen fueling system and an FCEV that was fueled with high-pressure hydrogen produced by the system. (Source: © International Association for Hydrogen Energy, Figure 1 in Kelly *et al.*, 2011, used with permission.)

temperature, and the electrolyzer temperature, the solar to hydrogen efficiency (where the electrolyzer efficiency is based on 1.245 V as in Equation [6.9]) averaged 8.2%. This efficiency was computed as the average of the PV solar to electric efficiency of 13.7% and an electrolyzer electric to hydrogen efficiency of 59.7%. In particular, the 8.2% solar to hydrogen efficiency was higher than previous PV-electrolysis test systems, and the earlier work on solar-powered electrolysis did not use a high-pressure electrolyzer (Kelly *et al.*, 2012).

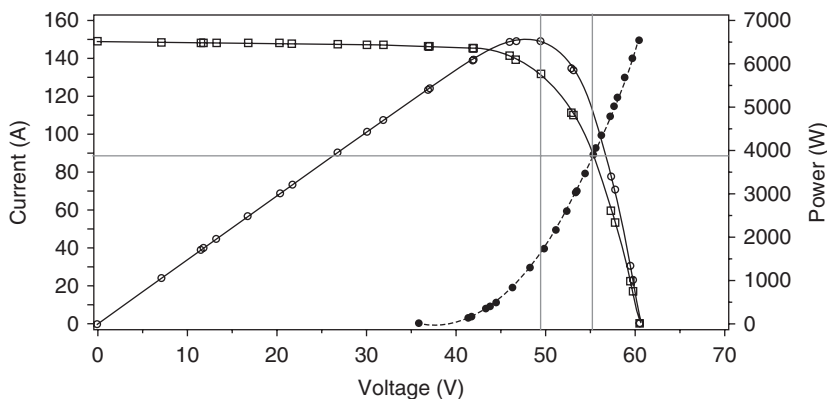
One other significant development from this study was the derivation of a new metric for describing the quality of the power transfer from a solar system to a load, such as an electrolyzer. The metric was called the coupling factor (Kelly, 2013). The coupling factor varies from 0 for no power transfer from the PV power system to the load, to 1 for transfer of all of the PV power to the load.

The coupling factor is computed from the actual PV power achieved when a solar power system is electrically attached to a load, and the maximum PV power achievable by the PV system under the ambient conditions. It is given by:

$$\text{Coupling factor} = \text{PV power achieved, W} / \text{Maximum PV power, W} \quad [6.15]$$

In Equation [6.15] the PV power achieved is the measured solar voltage times the measured solar current when the PV system is electrically connected to a load. The maximum PV power is the power that the PV system could make if it was at the MPP on its current versus voltage (I–V) curve.

This is illustrated for a single condition in Fig. 6.5 by super positioning the I–V curve measured for the PV system and the electrolyzer system on the same graph. The maximum PV efficiency occurred at 49.5 V and was 14.1%. At that MPP the PV system could generate 6550 W. The PV and ESD I–V curves intersected at 55.3 V; at this voltage, the ESD electrical to hydrogen efficiency, computed using Equation [6.9], (for an electrolyzer with 24 cells in series) is 54.4%. At that point the PV system would be providing 4910 W of power to the electrolyzer. The coupling factor is the ratio of the actual PV power used by the load divided by the maximum PV power that could be generated by the system under the ambient conditions, and for the example above it equals 0.75 (4910 W divided by 6550 W). As discussed elsewhere (Kelly, 2013), a model that predicts the PV MPP as a function of the solar irradiance and PV module temperature can be used, along with the measured PV efficiency when it is connected to a load, to compute the coupling factor without having to measure the PV I–V curve. This increases the utility of the coupling factor as a real-time metric for the efficiency of PV power utilization.



6.5 Superimposed current-voltage (I-V) curves for a PV solar system (\square) and an electrolyzer system (\bullet) to illustrate how the systems would be coupled when they are connected electrically with the PV system powering the electrolyzer load. The curve connecting the open circles is the power-voltage curve for the solar PV system (power = $I \times V$). The vertical lines identify the voltage for two important points: (1) the PV MPP, and (2) the intersection of the PV and electrolyzer I-V curves. The horizontal line is the system current at the PV-electrolyzer I-V curve intersection. (Source: © International Association for Hydrogen Energy, Figure 3 in Kelly *et al.*, 2011, used with permission.)

6.9 Educational aspects of water electrolysis

A vitally important, and often overlooked, aspect of water electrolysis is the task of motivating and educating the next generation of scientific researchers and engineers at an early age. Water electrolysis is a very easy experiment to integrate into a science class using the technique of active learning where students perform experiments and observe the results. To begin, all that is needed is a battery, some paper clips, baking soda and a container. Students will see bubbles forming at the two electrodes and learn that electricity can be used to drive chemical reactions and store the energy in chemical bonds. More advanced versions of this simple experiment can use electrolyzers that are specifically designed for educational purposes, in which voltage, current, and the volume of the hydrogen and oxygen produced are measured. Even if the student does not pursue a technical career, as an adult, he or she will be more willing to adopt a new technology, such as a hydrogen-powered FCEV, by having some hands-on experience with the electrolysis process in the classroom.

6.10 Major issues facing the use of water electrolysis for hydrogen production

There are some major issues that are currently preventing the widespread use of electrolysis as a source of hydrogen. As well, there are some impor-

tant reasons why hydrogen could be the most important energy carrier in the future, and why electrolysis may provide much of that hydrogen.

6.10.1 The cost of electrolytic hydrogen

The cost of electrolytic hydrogen is directly tied to the cost of electricity. For example, consider someone who owns an FCEV and who buys a home-fueling system that uses water electrolysis to make hydrogen at their home. If they pay \$0.10 kWh for electricity and the electrolyzer is 60% efficient, then it will require 33.3 kWh per kg times \$0.10 per kWh divided by 0.60, which equals \$5.50 per kg. This does not consider the cost of the electrolyzer and other items needed for storage and dispensing. To compare this to the cost of a conventional ICE system, one typically assumes that the FCEV gets twice as many miles per kg of hydrogen as the conventional vehicle gets miles per gallon of gasoline. Thus, this is comparable to \$2.75 per gallon gasoline and it seems like it could be attractive, providing the cost of a home hydrogen fueling system is not too high.

Simulations of much larger-scale systems, including those using solar electricity, have been performed (Mason and Zweibel, 2008). Depending on the solar-to-electrical efficiency, and how long the system lasts, the levelized cost of hydrogen ranged from \$2.73 to \$6.48 per kg (gallon of gasoline equivalent price). The biggest uncertainty in that analysis was that the actual PV costs would indeed be reduced as much as the authors assumed.

6.10.2 Needed electrolyzer developments

A major facilitator for the use of water electrolysis to produce hydrogen is an efficient, low-cost and robust electrolyzer that can produce high-pressure hydrogen. For PEM electrolyzers this will require thriftiness of the Pt. For both PEM and alkaline electrolyzers it will require low-cost and robust membranes that minimize the permeation of hydrogen, especially if the high-pressure oxygen is stored. It should also be remembered that an efficient way to store hydrogen in a small volume without using compression would circumvent the need for electrolysis at high pressure.

As discussed earlier, the major obstacle to electrolyzer efficiency is the overvoltage of the OER occurring at the electrolyzer anode. For the large scale use of hydrogen, both the production of hydrogen in electrolyzers and the use of hydrogen in fuel cells need to be greatly improved by catalyzing the OER and ORR at the electrolyzer anode and fuel-cell cathode, respectively. If significant improvements could be made to these processes, the use of hydrogen could become an efficient way to store electrical energy in the form of hydrogen chemical energy and generate electricity as needed using the hydrogen in fuel cells. This could be an enabler in using solar

energy and hydrogen to address the terawatt challenge as discussed in the next section.

At the present state of the art, electrolyzers are about 65% efficient, and fuel cells are about 50% efficient. Thus, the round trip efficiency in using hydrogen for storage of electrical energy is only 30%. Presently Li-ion batteries have round trip efficiencies of over 80%, well more than twice that of hydrogen.

6.10.3 Hydrogen and the terawatt challenge

The hydrogen economy and FCEV seem further away today than they did at the beginning of the twenty-first century, but it is very likely that by mid-century there will be a major change in the sources and storage of energy. The forecast for the amount of additional energy needed and the environmental consequences of obtaining that energy from fossil fuels will begin to favor the installation of more renewable energy. Solar is the one energy source that can supply 14–20 terawatts (TW) of additional continuous power needed by midcentury. However, it cannot supply that power in a controlled manner like a fossil-fueled power plant. Rather, solar power is intermittent, so even with large solar installations some form of storage is needed. That is where water electrolysis to produce hydrogen becomes attractive. Hydrogen can store solar power and integrate it over time to store solar energy that can be used in response to energy demands, i.e., fueling FCEV, making electricity and as feedstock for the chemical industry.

The goal for solar electricity is to become cost competitive with the current fossil-fueled system. If the cost of installed PV power can be reduced from the present cost of about \$5 per watt installed to about \$1 per watt installed, the cost of solar electricity is predicted to reach \$0.10 kWh. Of course, there are assumptions on the cost of borrowing money and the solar system lifetime, but this seems like an achievable goal without any breakthrough technologies. At first, the power grid can absorb the added solar power and it can be directly used as electricity. Perhaps the first 20% of solar or other renewable and intermittent power can be added directly to the grid without any storage. In particular, the fact that solar power is produced during the day when the electrical demand is greatest is a good thing for using solar power directly on the electrical grid. However, at some point a system for storage of renewable energy will be needed, and hydrogen can fill that role, provided some improvements in the efficiency of electrolysis can be achieved.

6.11 Future trends

There are several important research and development areas that must be addressed in the future to make water electrolysis an important source of

hydrogen and that would push mankind toward the so-called hydrogen economy. Perhaps the most important is the move toward solar energy, and in particular solar electricity. To store that energy, so it can be used when needed, and especially aboard vehicles, electrolytic hydrogen is not resource limited. Second, high-pressure electrolyzers are needed unless some means for energy-efficient low-pressure hydrogen storage is developed. Third, the overvoltage of the OER in electrolyzers and the ORR in fuel cells need to be reduced, or over 60% of the electrical energy will be wasted in the round trip when using hydrogen as the energy carrier. Fourth, an efficient means to store hydrogen safely at low pressure needs to be found. Finally, photoelectrolysis should be developed to deliver low-cost solar-powered hydrogen on a large scale.

6.12 Conclusions

We have reviewed the chemistry, including the thermodynamics and kinetics, of water electrolysis. Water electrolysis can potentially be a very important process for producing hydrogen as an energy carrier as our energy needs keep increasing for a growing population with higher lifestyle aspirations. However, this transition to a hydrogen economy is hindered by inefficiencies in both splitting the water into its elements and as the hydrogen utilization in fuel cells. The fundamental chemical mechanism for the reactions OER in an electrolyzer and the ORR in a fuel cell need to be understood, and a better catalyst must be developed. The seemingly simple process of splitting water is very complex at the molecular level. Nonetheless, the potential of hydrogen produced from water for storing vast amounts of renewable energy, and the fact that hydrogen can produce electricity, will naturally lead to increased use of hydrogen as an energy carrier in the future.

6.13 Sources of further information and advice

For the last 20 years hydrogen production, storage and use in fuel cells has been a very active research topic. The International Journal of Hydrogen Energy has been at the forefront of publishing research on hydrogen. The US Department of Energy has a website devoted to hydrogen, and has a conference every year with published proceedings. In addition, the US Department of Energy (DOE) has a National Renewable Energy Laboratory that publishes work on hydrogen in addition to renewable energy. The European Union has an extensive amount of information available on hydrogen research and assessment. Several recent textbooks discuss the major aspects of hydrogen production delivery, and usage in anticipation of a future hydrogen economy. Some of these resources are listed in the

specific reference list at the end of the chapter. For convenience, a short list of general references is given below.

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- U.S. Department of Energy, Energy Efficiency and Renewable Energy. <http://www1.eere.energy.gov/hydrogenandfuelcells/>

6.14 Acknowledgements

I want to especially thank Thomas L. Gibson, my teammate on hydrogen work for 10 years at General Motors Research and Development Center, for his ideas and hard work that contributed to our publications and patents on electrolytic hydrogen. I also thank Lawrence D. Burns, Alan I. Taub, James A. Spearot, Steven H. Cadle, Mei Cai and David B. Ouwerkerk, all of General Motors, for their leadership and support of the solar hydrogen research. Finally, I thank John A. Turner of the National Renewable Energy Laboratory for his guidance in the initial stages of our research.

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6.16 Appendix: nomenclature

DC	direct current
E°	standard potential, V
ESD	electrolyzer, storage, dispensing system; mainly refers to the electrolyzer component
F	Faraday's constant (96 485 coulombs/equivalent)
FCEV	fuel-cell electric vehicles
HER	hydrogen evolution reaction
HOR	hydrogen oxidation reaction; the reverse of the HER
HHV	hydrogen higher heating value, 39.4 kWh kg ⁻¹
ΔG^0	standard change in Gibbs free energy
ΔH^0	standard change in enthalpy
η	overvoltage
η_a	activation overvoltage
η_c	concentration overvoltage
η_{ir}	ohmic overvoltage
I	current, amperes
I–V curve	current versus voltage plot
ICE	internal combustion engines
LHV	hydrogen lower heating value, 33.35 kWh kg ⁻¹
MPP	PV maximum power point

OER	oxygen evolution reaction
ORR	oxygen reduction reaction; the reverse of the OER
PEM	proton exchange membrane
PV	photovoltaic cells, modules, or arrays
ΔS^0	standard change in entropy
Solar energy	product of solar insolation and the array area, kWh
Solar insolation	solar irradiance integrated over time, kWh m ⁻²
Solar irradiance	solar flux, power per unit area, kW m ⁻²
T	temperature, K
$W_{\text{isothermal}}$	work in a constant temperature compression