

Chapter 16

Hydrogen From Water Electrolysis

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1 INTRODUCTION

Renewable power cannot be stored yet the global growth of renewable energy sources and integration into the energy mix continues at a significant pace (Fig. 16.1) [1].

Despite great technological advancements, it is not possible to match the fairly predictable peaks and troughs of energy demand with the unpredictable peaks and troughs of energy supply from renewable sources. This issue necessitates the continued use of conventional and rapidly responding energy sources predominantly based on the combustion of hydrocarbon-based fuels to maintain energy supplies. As a result this approach can lead to scenarios wherein demand is low and is being met by conventional power sources coinciding with a peak in renewable energy production due to a particular weather pattern. While it could be instinctively assumed that the conventional power plant could simply be switched off, or at least turned down and energy demands met from renewable sources, in practice this is not possible as conventional fossil fuel power plants and nuclear plants cannot be quickly shut down and restarted, thus it is the renewable energy source that often must be curtailed such that all the energy they are capable of producing is not exploited. For example, in the United States up to 4% of wind power was curtailed in 2013 [2]. Integration of energy storage with renewable energy sources would enable all energy produced by a renewable energy source to be exploited, thus reducing the dependency on conventional, polluting sources of power. Indeed, it appears that flexible energy storage is the barrier to greater penetration and development of renewables.

Energy storage is already a fundamental concept in the global energy economy. Hydrocarbons are currently the most exploited source of energy, accounting for more than 85% of global energy production [3]. What we consider our most familiar fuels: gasoline, coal, and natural gas, to name but a few, are energy storage media themselves. Many millions of years ago, the energy of the

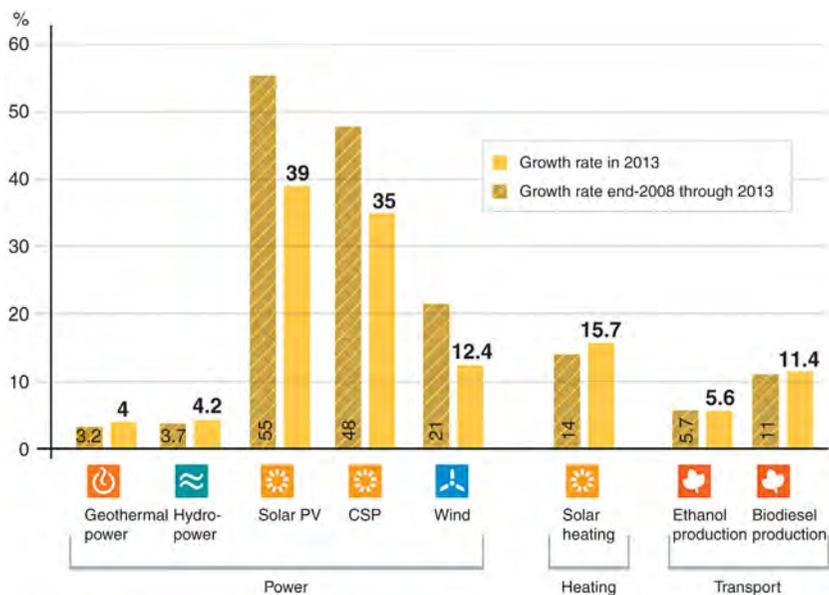


FIGURE 16.1 Average annual growth rates of renewable energy capacity and biofuels production, end 2008–2013.

Sun was consumed by plants enabling their growth and proliferation across the prehistoric Earth. These plants provided a rich and plentiful food source for our dinosaur ancestors and as these prehistoric plants and animals died and were covered by millennia of new growth, they were slowly transformed into the fossil fuels we exploit today. Thus energy storage is a concept that has existed for many millennia, but the fuels are literally fossils.

The challenges facing scientists and engineers developing new technologies for energy storage are twofold. First, one must consider the environmental impact of the energy storage medium. While hydrocarbons provide a rich source of energy the products of the combustion processes required to release the stored energy contribute to climate change, unless the carbon could be captured to produce a closed carbon cycle. Second, one must consider timescale. As stated earlier, the lifecycle of organic life and its subsequent decomposition into a usable fuel source is extremely slow, taking many millions of years. Thus when selecting a new energy storage medium the ideal candidate should be able to release stored energy without producing any pollutants or harmful side-products and should be able to store energy on an instantaneous timescale. Considering the fundamental requirements of energy storage, namely nonpolluting and quickly responding, hydrogen is a perfect medium for energy storage.

Hydrogen is not found in appreciable or exploitable concentrations freely on Earth and instead must be produced from other compounds. There are two principal routes to the production of hydrogen. Most commonly hydrogen is

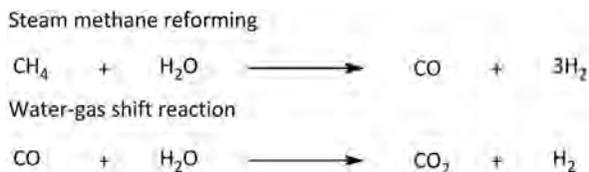
produced from natural gas via a process known as steam reforming. In addition to hydrogen, this process also produces carbon dioxide and is not a viable solution to the pollution-free production of hydrogen from excess renewable energy. Hydrogen may also be produced via electrolysis of water. In this process electricity (electro-) is used to break down (-lysis) water (H_2O) into its component parts of oxygen and hydrogen with no harmful or polluting side-products. If the electricity required to carry out this process is provided by a renewable source then a nonpolluting sustainable source of hydrogen is obtained. Release of the energy stored in hydrogen is an extremely clean process, producing only water as a byproduct and releasing large quantities of energy in doing so. Indeed on a weight-by-weight basis hydrogen produces almost four times more energy than the equivalent weight of gasoline [4].

2 HYDROGEN AS AN ENERGY VECTOR AND BASIC PRINCIPLES OF WATER ELECTROLYSIS

2.1 Hydrogen as an Energy Vector

Hydrogen is a gaseous element occurring as its diatomic gas H_2 . For clarity when the chapter refers to hydrogen, unless otherwise noted, this is in reference to the diatomic molecule H_2 . Since hydrogen does not naturally occur on Earth it must be formed by the decomposition of other molecules. Approximately 95% of the hydrogen produced around $50 \times 10^6 \text{ t a}^{-1}$ (around 50 million tonnes per annum) [5] is produced via steam reforming of natural gas and subsequent water-gas shift reaction (Scheme 16.1) with the remainder being formed via electrolysis. As can be seen from Scheme 16.1, the formation of hydrogen from natural gas results in the production of carbon dioxide. Given the finite supplies of natural gas and the greenhouse effect of carbon dioxide, production of hydrogen from this route does not address the needs of renewable energy storage. The production of hydrogen from water via electrolysis is a clean process, resulting in only oxygen being produced as a byproduct. If the electricity required to split the water into hydrogen and oxygen is supplied via a renewable energy source then the process is environmentally benign.

Hydrogen has two main applications as an energy vector. First, it may be combusted in a similar manner to natural gas. This is an extremely clean combustion process with water being the only product. A subset of this



SCHEME 16.1 Production of hydrogen from natural gas.

application is the storage of hydrogen in a conventional natural gas network, in a so-called power-to-gas process. This natural gas/hydrogen mixture is then combusted in an identical manner to unadulterated natural gas. It is worth noting that the coal gas that is used to supply gas to many homes and industries could contain up to 50% hydrogen. Natural gas supplies now largely supplant coal gas. In addition to combustion, hydrogen may also be exploited as an energy vector via catalytic recombination with oxygen. In contrast to the thermal energy produced in a combustion process, the catalytic reaction with oxygen produces electrical energy. This process is exploited by fuel cells to produce electrical energy.

2.2 History of Water Electrolysis

Water electrolysis was first demonstrated in 1789 by the Dutch merchants Jan Rudolph Deiman and Adriaan Paets van Troostwijk using an electrostatic generator to produce an electrostatic discharge between two gold electrodes immersed in water [6]. Later developments by Johann Wilhelm Ritter exploited Volta's battery technology and allowed separation of the product gases (Fig. 16.2) [7].

Almost a century later, in 1888 a method of industrial synthesis of hydrogen and oxygen via electrolysis was developed by the Russian engineer Dmitry Lachinov [8] and by 1902 more than 400 industrial water electrolyzers were in operation [9]. Early electrolyzers utilized aqueous alkaline solutions as their electrolytes, and this technology persists to this day. A more recent development in water electrolysis is the proton exchange membrane process, first described in the mid-1960s by General Electric as a method for producing electricity for the Gemini Space Program [10], and later adapted for electrolysis. Today a number of companies are active in the manufacture and development of electrolysis technologies with Proton, Hydrogenics, Giner, and ITM Power being leaders in the field.

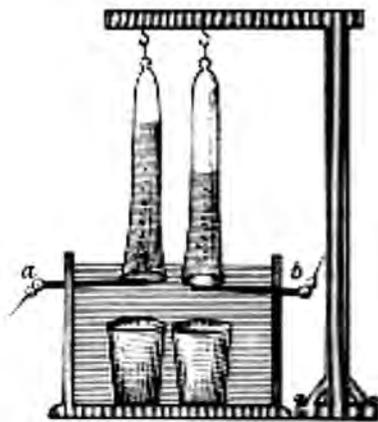


FIGURE 16.2 Ritter's electrolysis apparatus.

2.3 Electrochemistry and Thermodynamics

The electrolysis of water is thermodynamically disfavored and as such requires an input of energy to drive the process. In the case of the electrolytic splitting of water into hydrogen and oxygen, this energy input comes in the form of a potential difference between the anode and cathode of an electrochemical cell. By application of Gibbs energy equation (Eq. 16.1) and knowledge of the standard enthalpy of formation (286.03 kJ mol⁻¹) and ideal gas entropy (0.163 kJ mol⁻¹ K⁻¹) of gaseous water we can calculate the Gibbs energy of water at 298 K (25 °C):

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ \Delta G^\circ / (\text{kJ mol}^{-1}) &= 286.03 - (298 \times 0.163) \\ \Delta G^\circ / (\text{kJ mol}^{-1}) &= 237.46\end{aligned}\quad (16.1)$$

Gibbs energy

Using this Gibbs energy we can calculate the reversible voltage required to split water electrolytically (Eq. 16.2), where n is the number of electrons transferred and F is Faraday's constant. Two electrons are required to produce a single molecule of hydrogen, hence $n = 2$.

$$\begin{aligned}V_{\text{rev}} &= -\frac{\Delta G^\circ}{nF} \\ V_{\text{rev}} / \text{V} &= -\frac{237\,460}{2 \times 96\,485} \\ V_{\text{rev}} &= -1.23 \text{ V}\end{aligned}\quad (16.2)$$

Calculation of V_{rev}

This value of 1.23 V requires that all components be in the gaseous state, that is, that the water which is consumed in the reaction be vaporized. In a conventional electrolyzer where water is at atmospheric pressure and temperatures are typically below 80 °C, there is an additional energy input required as illustrated in Eq. 16.3. This gives rise to the thermoneutral potential of 1.48 V. The potential at which water splitting occurs can approach the reversible potential by carrying out the electrolysis at high temperature and pressure and approaches to this will be discussed in Section 3.

$$\begin{aligned}V_{\text{tn}} &= -\frac{\Delta H^\circ}{nF} \\ V_{\text{rev}} / \text{V} &= -\frac{286\,030}{2 \times 96\,485} \\ V_{\text{rev}} &= -1.48 \text{ V}\end{aligned}\quad (16.3)$$

Calculation of V_{tn}

Two further concepts are required to understand the electrochemistry of an electrolyzer: overpotential and efficiency. While the electrolysis of water is thermodynamically feasible at 1.48 V, in reality the reaction will occur prohibitively slowly and further potential must be applied to accelerate the reaction to a practical rate. This extra potential is known as overpotential and minimizing this additional potential is fundamental in producing efficient electrolytic cells. Overpotential is due to a combination of the very low conductivity of water and the high activation energy required to split water. The former may be addressed by incorporating salts, acids, or bases into the water to improve its conductivity. This is the case with an alkaline electrolyzer where the electrolyte is aqueous sodium hydroxide solution. The latter is addressed by the addition of suitable electrocatalysts, a concept considered in more detail in [Section 3](#).

The efficiency of an electrolysis process can be considered in two ways. We can consider the Faradaic efficiency—the ratio of the number of moles of hydrogen produced versus the charge passed. If the process has a 100% Faradaic efficiency then every electron produced by the oxidation of water is transferred to a corresponding proton to produce hydrogen. Note that two electrons are required to produce a single mole of hydrogen ($n = 2$, [Eq. 16.2](#)). The actual Faradaic efficiency may approach 100%, but is always slightly lower due to parasitic electrochemical processes, for example, degradation of components of the electrochemical cell, and the crossover of hydrogen to the oxygen-producing side of the cell.

The energy efficiency of the cell or stack is measured by calculation of the energy available from the hydrogen produced by the cell, using the higher heating value of hydrogen (HHV) [[11](#)] and dividing this by the energy consumed by the cell as shown in [Eq. 16.4](#), where I is the cell current, V is the voltage, and t is the time over which the hydrogen production was measured; η_{eff} is expressed as a percentage.

$$\eta_{\text{eff}} = \frac{\text{moles of hydrogen produced} \times \text{HHV}_{\text{H}_2}}{I \times V \times t} \times 100 \quad (16.4)$$

Calculation of cell energy efficiency

Commercial electrolyzers often express their energy efficiency in terms of the whole system η_{sys} , including parasitic loads due to pumps, heaters, etc. In addition commercial systems are characterized by their specific energy consumption, that is, the energy required to produce 1 cubic meter of hydrogen under normal conditions. This is commonly expressed in $\text{kW h (Nm}^3\text{)}^{-1}$. Some typical values and the corresponding η_{sys} are given in [Table 16.1](#).

The individual reactions taking place during electrolysis differ depending on the nature of the process taking place and will be discussed in full in [Section 3](#).

TABLE.16.1 Efficiency Comparisons

Manufacturer	Product	System efficiency/ (kW h) (N m ³) ⁻¹	$\eta_{\text{sys}}/\%$	References
Hydrogenics	HyLYZER™	6.7	53%	[12]
Proton OnSite	Hogen® S-series	6.7	53%	[13]

3 HYDROGEN PRODUCTION VIA WATER ELECTROLYSIS

3.1 Water Electrolysis

The basic principles, chemistry, and thermodynamics of water electrolysis have been described in [Section 2](#). Herein we discuss the device architectures, their advantages and disadvantages, and materials of construction. There are three main routes to the electrolysis of water: alkaline electrolysis, proton exchange membrane (PEM) electrolysis, and solid oxide electrolysis. Of these only alkaline and PEM electrolysis have been commercialized and while solid oxide electrolyzers show great technological promise, they are still the subject of considerable development [14]. The technological parameters defining the main types of commercial electrolyzers are shown in [Table 16.2](#) [15,16]. Comparable information on solid oxide electrolyzers is not available due to the lack of commercial devices.

3.2 Alkaline Water Electrolysis

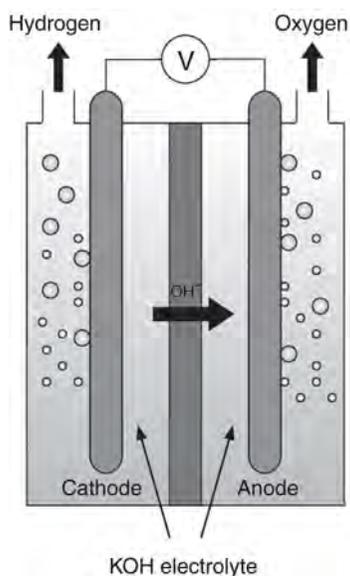
The first commercialized water electrolysis system was based on the principles of alkaline water electrolysis, and alkaline-based systems remain the most ubiquitously utilized water electrolysis systems [17]. A schematic of an alkaline water electrolyzer is given in [Fig. 16.3](#). The cathode and anode are often manufactured from nickel [18] and the separator between the anodic and cathodic chambers is a polymer which is permeable to hydroxide ions and water molecules, for example, Zirfon Perl from Agfa. Alkaline electrolyzers have the advantage of technological maturity and relatively low cost compared with PEM electrolyzers.

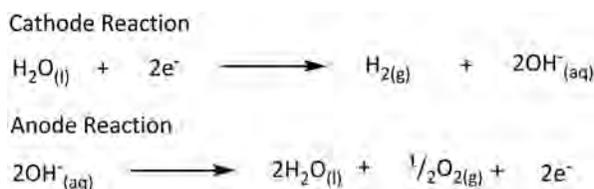
The reactions taking place in an alkaline electrolyzer are given in [Scheme 16.2](#).

There are a number of technological disadvantages associated with the alkaline electrolysis system: namely, low current density, limited ability to operate at low loads, and the inability to operate at high pressure. The latter two limitations are due to the crossover of gases possible through the separator. This will increase both with increasing pressure of hydrogen at the cathode and will also increase with reduced load where the oxygen production rate decreases and the hydrogen concentration in the oxygen stream can increase to dangerous levels (H_2 lower explosion limit >4%) [19].

TABLE 16.2 Comparison of Water Electrolysis Methods

	Alkaline electrolyzer	Proton exchange (PEM) electrolyzer
Cell temperature/(°C)	60–80	50–80
Cell pressure/(10 ⁵ Pa) (bar)	<30	<30
Current density/(mA cm ⁻²)	0.2–0.4	0.6–2.0
Cell voltage/V	1.8–2.4	1.8–2.2
Power density/(mW cm ⁻²)	<1	<4.4
Efficiency (HHV)/(%)	62–82	67–82
Specific energy consumption stack/(kW h) (Nm ³) ⁻¹ H ₂	4.2–5.9	4.2–5.6
Specific energy consumption system/(kW h) (Nm ³) ⁻¹ H ₂	4.5–7.0	4.5–7.5
Partial load range/(%)	20–40	5–10
Cell area/(m ²)	>4	<0.03
H ₂ production rate/(Nm ³ h ⁻¹)	<760	<10
Lifetime stack/h	<90 000	<20 000
Lifetime system/a (years)	20–30	10–20
Degradation rate/(μV h ⁻¹)	<3	<14

**FIGURE 16.3** Alkaline water electrolyzer.



SCHEME 16.2 Alkaline water electrolysis.

3.3 Proton Exchange Membrane Electrolysis

A schematic of a PEM electrolyzer is given in Fig. 16.4. Central to the operation of the PEM electrolyzer is the proton-conducting membrane. This membrane is made of a sulfonated fluorinated polymer. The most commonly used membrane is Nafion manufactured by DuPont. Various thicknesses of Nafion may be employed ranging from (25 to 250) μm . The exact thickness of membrane required for any specific application is determined by the conditions to be employed in the electrolyzer. Higher pressures and conditions likely to degrade the membrane at a greater rate, for example, low-load operation or frequent stop-starts tend to require a thicker membrane either to withstand the high differential pressure and minimize gas crossover or to provide a suitable margin for material loss due to degradation. The thinner the membrane the greater the efficiency of the electrolysis process. This is due to a reduction in the resistance of the membrane with decreasing thickness [20,21]. Thus a balancing act must be struck between the optimal electrochemical properties of the membrane and its suitability for a given set of process conditions. There is considerable ongoing research into the development of new membranes with improved properties including greater proton conductivity and improved mechanical strength [22,23].

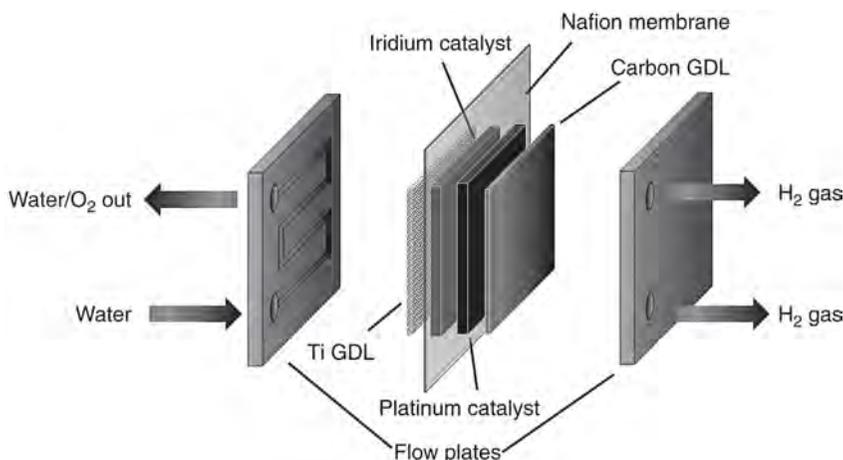
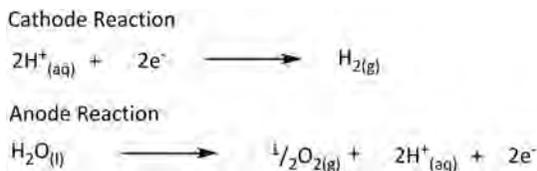


FIGURE 16.4 Cell layout diagram for a PEM Electrolyzer.



SCHEME 16.3 Proton exchange membrane water electrolysis.

As discussed in [Section 2](#), the kinetics of water oxidation is extremely slow without the addition of suitable electrocatalysts. Due to the highly acidic nature of the PEM electrolysis process the choice of catalysts is limited to rare transition metals that are stable under acidic conditions, for example, rhodium, ruthenium, platinum, iridium, and their oxides [24]. The current state of the art for electrocatalysts in PEM water electrolysis is platinum at the cathode for proton reduction and iridium oxide at the anode for water oxidation. There has been a large amount of research undertaken to prepare new electrocatalysts for both water oxidation and proton reduction [25–28] to increase the efficiency of the process and to reduce cost. The combination of the membrane and the electrocatalysts is collectively known as membrane electrode assembly (MEA).

The water is fed into the anode of the electrolyzer and the product gases are conducted away from the reactive sites on the MEA via the flow channels of the bipolar flow plates. These flow plates are typically manufactured from titanium as this gives the mechanical strength and resistance to corrosion required. Stainless steel and graphite are also used in some systems though their application is limited by relatively poor corrosion properties and the poor mechanical strength of graphite compared with titanium. Despite titanium's near ubiquitous use, it is not the perfect material for bipolar plates. It is subject to oxidation and is very difficult to machine, adding to its cost. There is limited research into alternative materials. A recent publication described the use of three-dimensional printing to prepare flow plates though the difficulty of rendering these plates suitably conductive limits their current use to prototyping [29].

Between the flow fields of the bipolar plates and the MEA a conductive layer is added. This layer is known as the gas diffusion layer (GDL) and is added to improve the electrical connection between the bipolar plates and the MEA and also to insure the effective mass transport of both the reactant water and the product gases. The cathodic GDL is often made of carbon paper. This material is not suitable for use at the anode as the highly oxidative conditions at this electrode would quickly decompose the carbon paper. Instead, a titanium or similar inert metal mesh is inserted between the flow fields and the MEA.

The reactions taking place in a PEM electrolyzer are given in [Scheme 16.3](#).

3.4 Solid Oxide Water Electrolysis

Solid oxide electrolysis differs from both alkaline and PEM systems in that the operating temperature is typically an order of magnitude greater in a solid

Cathode Reaction



Anode Reaction



SCHEME 16.4 Solid oxide electrolyzer water electrolysis.

oxide electrolyzer (SOE) spanning the range 800–1000 °C. At this temperature it should be apparent that the feed cannot be water and in this case the electrolyzer is fed with steam. The chemical reactions taking place in the SOE are given in [Scheme 16.4](#).

Intuitively, the high operating temperatures of the SOE system would suggest that the efficiency of operation would be poor; however, this is not the case. The increase in thermal energy demand is compensated for by the decrease in the electrical energy demand and the overall energy demand of the system is largely insensitive to increasing the temperature. This is illustrated in [Fig. 16.5](#) [30].

In the solid oxide electrolysis process, water in the form of high-pressure steam is reduced at the cathode to give hydrogen gas and oxygen anions. These anions migrate through the solid oxide electrolyte, where they are oxidized on the anode to produce oxygen gas. The electrons produced from the oxidation travel around the external circuit and supply the electrons for the water reduction. The product gases diffuse through the porous electrodes. A schematic of the SOE is given in [Fig. 16.6](#) [31].

The SOE utilizes a solid electrolyte separating the anode and the cathode. In this regard the system has some similarity with the PEM system, where a solid

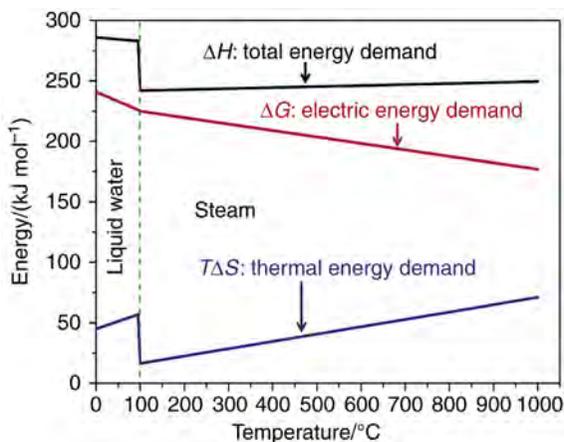


FIGURE 16.5 Electrolysis energy demand. (Reproduced from Ref. [30] with permission from The Royal Society of Chemistry.)

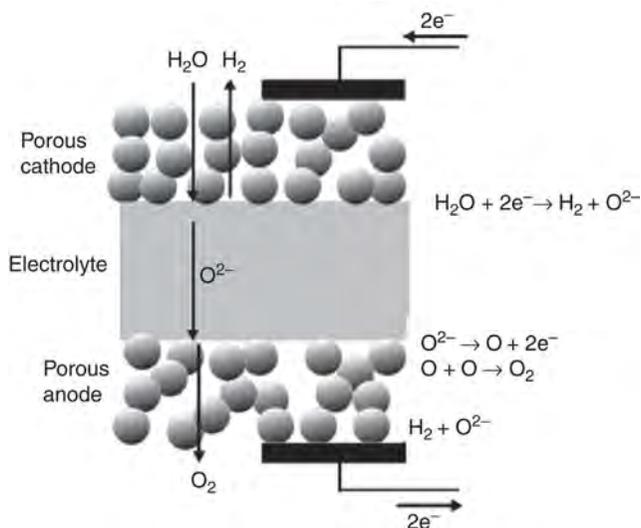


FIGURE 16.6 SOE operation.

electrolyte is also employed to provide ionic conductivity to the system. The current state-of-the-art electrolyte in a solid-oxide system is yttria-stabilized zirconia (YSZ) [30]. This material only has sufficient ionic conductivity at high temperatures, hence the requirement to operate at temperatures approaching 1000°C . At this high temperature, there are numerous problems with cell integrity including poor long-term cell stability, interlayer diffusion, and fabrication and materials problems [32]. In addition to oxygen anion conductivity, it is also possible to operate an SOE on the principle of proton conductivity in a manner similar to a PEM electrolyzer [33]. In this system a different electrolyte must be adopted. Doped BaCeO_3 shows good conductivity in this system [34].

4 STRATEGIES FOR STORING ENERGY IN HYDROGEN

4.1 Properties of Hydrogen Related to Storage

Hydrogen was first identified as an element by Henry Cavendish in 1766 during a series of experiments wherein he added various metals to strong acids. He described the gas produced as inflammable air. The primitive apparatus used by Cavendish to first isolate and store hydrogen gas is shown in Fig. 16.7 [35]. Since this first isolation of hydrogen, considerable effort has gone into the development of suitable storage technologies for containing this gas. Storage by compression or via cryogenic liquefaction are the most developed technologies and form the basis of the technologies used in current automotive demonstration projects. A significant challenge associated with both pressurized and cryogenic storage is that the storage vessel itself contributes at least 90% to total system weight [36].

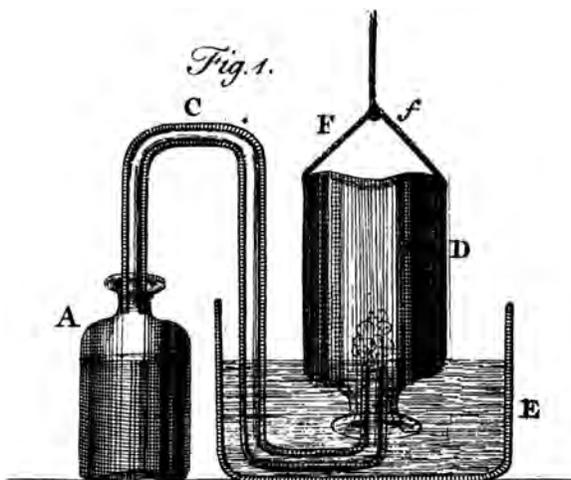


FIGURE 16.7 Cavendish apparatus for isolation of hydrogen gas.

Basic properties of hydrogen are given in [Table 16.3](#).

Hydrogen has the highest energy density by weight of any fuel; however, due to its very low density, its volumetric energy density is very poor. Thus storage of large quantities of energy in the form of uncompressed hydrogen gas would require impractically large storage facilities. This requirement may be addressed by compression or liquefaction of the hydrogen, thus increasing its volumetric energy density.

4.2 Gaseous Hydrogen Storage

When considering a storage strategy for hydrogen it is important to consider the final application of the hydrogen and to match the pressure of the storage medium to that required by the application. The compression of hydrogen to a

TABLE 16.3 Hydrogen Properties

Property	Value
Melting point/K	13.99
Boiling point/K	20.27
Density/(g L ⁻¹)	0.0899
Higher heating value/(MJ kg ⁻¹)	141.80
Lower heating value/(MJ kg ⁻¹)	119.96
Gravimetric (specific) energy density/(MJ kg ⁻¹)	141.80
Volumetric energy density at STP/(MJ L ⁻¹)	0.0107

TABLE 16.4 DoE Hydrogen Storage Targets

Target	2009	2015	Ultimate
System gravimetric density/(mass%)	4.5	5.5	7.5
System volumetric density/(g L ⁻¹)	28	40	70
System fill time for 5 kg fill/(min)	4.2	3.3	2.5

suitable storage pressure consumes energy and consequently incurs an efficiency penalty. Compression of hydrogen to $(350\text{--}700 \times 10^5)$ Pa (350–700 bar) consumes energy equal to (5–20)% of the lower heating value of hydrogen. These pressure ranges are considered the optimum for transport applications using compressed hydrogen as they represent a balance between compression energy consumption, driving range of the vehicle being fueled, and the investment required in refueling stations and associated infrastructure [37]. Research and development into the storage of pressurized gaseous hydrogen is largely predicated on the emergence of a hydrogen vehicle and refueling sector. The US Department of Energy (DoE) has produced a series of targets for the storage of hydrogen (Table 16.4) [38].

The “ultimate” target represents the performance that is anticipated to be required for full penetration of hydrogen-powered vehicles into the light-duty market. In addition to the energy density requirements outlined earlier, there are also technical requirements related to the small size of the hydrogen molecule. This gives hydrogen a high diffusivity in many materials. In the case of storage of high-pressure hydrogen in steel containers, this diffusivity can result in embrittlement of the container leading to failure of the material [39–43]. The targets set by the DoE and the challenges of embrittlement have driven a great deal of research in the storage of hydrogen as a high-pressure gas.

In vehicular applications, two storage vessel technologies known as Type III and Type IV have grown to a dominant position in vehicular applications [44]. Type III storage vessels are composed of a pressure vessel made of a metallic liner fully wrapped with a fiber–resin composite [45,46]. Type IV storage vessels differ from type III vessels in that the pressure vessel is made of a polymeric liner as opposed to a metallic liner, and is again fully wrapped with a fiber–resin composite [45,46]. Type III storage vessels are considered to be the technically superior design due to the metallic liner. This liner gives the storage vessel a higher thermal conductivity which minimizes the temperature rise associated with the filling of the storage vessel with compressed hydrogen. High cost remains the most significant barrier to successful implementation of this technology, though public perception of the safety of compressed hydrogen storage may also need to be overcome [47,48].

4.3 Cryogenic Liquid Hydrogen Storage

Conversion of hydrogen to a cryogenic liquid requires a large input of energy to condense the gas. This energy input amounts to (30–40)% of the lower heating value of hydrogen and results in a corresponding loss of efficiency in any system relying on cryogenic hydrogen [49]. On this basis, it compares poorly with storage of hydrogen as a pressurized gas despite the increase in volumetric energy density to 8 MJ L^{-1} . In addition, storage containers for cryogenic hydrogen must be insulated and refrigerated to maintain the low temperature required and require frequent venting to allow evaporated hydrogen gas to escape.

4.4 Cryocompressed Hydrogen Storage

Cryocompression of hydrogen refers to several different storage methods that combine elements of compressed and cryogenic storage and includes liquid hydrogen, cold compressed hydrogen, or hydrogen stored as a mixture of saturated liquid and vapor. Common between methods is the storage of hydrogen in its cryo state and at pressures of $(250\text{--}350 \times 10^5) \text{ Pa}$ (250–350 bar) [50]. Storage of hydrogen as a cryocompressed fluid serves to overcome the limitations of both compressed gas and cryogenic liquid storage allowing both an increase in volumetric energy density versus compressed gaseous hydrogen and also minimizing the evaporative losses associated with cryostorage at atmospheric pressure [51].

4.5 Hydrogen Storage by Physisorption

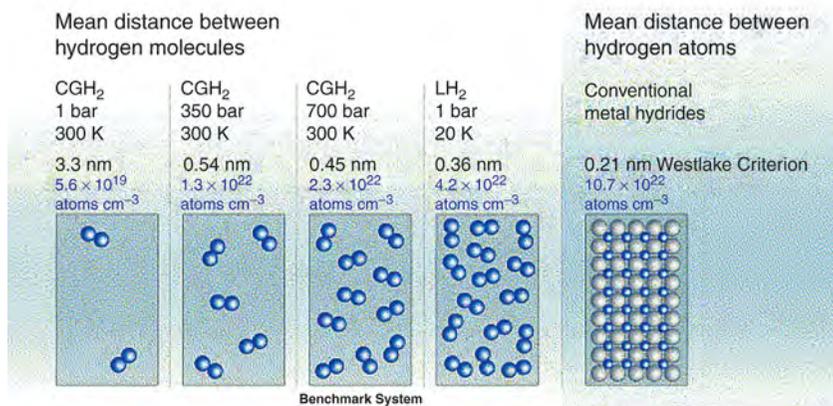
Nonmechanical means can be used to store hydrogen, for example, by physisorption onto porous supports. This process is reversible and the hydrogen may be adsorbed and desorbed over multiple cycles. The hydrogen is physically attached to the adsorbent via Van der Waals interactions and is limited to a monolayer of hydrogen. Sorbents with high surface areas therefore have the greatest capacity for hydrogen storage [52]. Cryogenic hydrogen absorption at temperatures below $-195 \text{ }^\circ\text{C}$ can profoundly increase the level of physisorption of hydrogen [53,54]. The adsorbent properties of various materials are given in Table 16.5 [55].

4.6 Hydrogen Storage by Chemisorption

In contrast to hydrogen storage by physisorption, chemisorption of hydrogen requires that the hydrogen undergo a chemical transformation and become chemically bonded to another species e.g. in a hydride. The increased energy density in chemisorbed hydrogen is attributed to the shorter mean distance between hydrogen atoms in the hydride compared with the hydrogen molecules in a compressed or liquefied state (Fig. 16.8) [37]. The advantage of this approach is the very high energy density achievable compared with storage of hydrogen in compressed or liquefied form. In common with other hydrogen

TABLE 16.5 Properties of Selected Physisorption Media

Storage medium	Temperature/(°C)	Pressure/ (10 ⁵ Pa) (bar)	Capacity/ (mass%)	Reference
Carbon nanotubes	27	1	0.2	[56]
	25	500	2.7	[57]
	-196	1	2.8	[58]
Graphene oxide	25	50	2.6	[59]
Polymers of intrinsic microporosity	-196	10	2.7	[60]
Hyper crosslinked polymers	-196	15	3.7	[61]
Covalent organic frameworks	-196	70	7.2	[62]
Zeolites	25	100	1.6	[63]
	-196	16	2.07	[64]
Metal organic frameworks	25	50	8	[65]
	-196	70	16.4	[66]
Clathrate hydrates	-3	120	4	[67]

**FIGURE 16.8** Mean distance between hydrogen molecules [37].

storage methods, storage via chemisorption has its share of technical challenges; namely, ease and cyclability of charging and discharging, storage capacity, and stability of the material after charging [55]. In particular, from a practical perspective if one was to consider a system wherein pressurized hydrogen was pumped at pressure onto a discharged hydrogen precursor, formation of

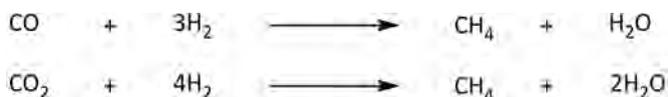
the hydride would have a given heat of formation ΔH associated with it. If the tank is to be filled with hydrogen in the 150 s (2.5 min) filling time proposed by the DoE (Table 16.4) a great deal of heat would be required to dissipate in a very short time requiring a prohibitively large heat exchanger to be installed into the storage tank.

While there are clearly a number of technical challenges to be overcome in relation to the use of hydrides as a hydrogen storage medium, there are a number of candidates undergoing detailed development in an attempt to overcome these limitations. Current research is focused on metal hydrides based on alkali and alkaline earth elements such as MgH_2 [68] and complex hydrides such as NaAlH_4 [69], the borohydrides LiBH_4 and NaBH_4 [70], and LiNH_2 [71].

4.7 Power-to-Gas

Power-to-gas describes the injection of either hydrogen directly produced via electrolysis and suitably purified if required or methane produced via methanation of hydrogen into the natural gas network. This topic is described in more detail elsewhere in this volume (chapter 18) and is considered here only briefly for completeness. The adulteration of methane with hydrogen gas is well known historically. “Town gas” derived from coal comprising a mixture of hydrogen, carbon monoxide, and methane was supplied to industrial and domestic properties from the 1840 s and was only phased out in the United Kingdom with the introduction of natural gas sourced from the North Sea. The potential of the natural gas network, ubiquitous in all developed countries, has tremendous potential as a storage medium for energy. In the United Kingdom alone, more than 836 000 GW h of energy were consumed in the form of natural gas in 2011 [72]. Even small quantities of hydrogen gas stored in this network deliver a large amount of energy storage.

There are limitations to the storage of hydrogen in the natural gas network. Due to the potential for hydrogen embrittlement as discussed in relation to pressurized hydrogen storage mentioned previously, and the different burning characteristics of methane/hydrogen mixtures compared with pure methane [73], limitations are placed on the quantity of hydrogen in natural gas, for example, 0.1% by mole in the United Kingdom [74]. This limitation in the quantity of hydrogen that can be stored in the gas network can be overcome by conversion of the hydrogen to methane via reaction with carbon dioxide or carbon monoxide (Scheme 16.5) [75,76] in a process known as methanation.



SCHEME 16.5 Methanation of hydrogen.

5 TECHNOLOGY DEMONSTRATIONS UTILIZING HYDROGEN AS AN ENERGY STORAGE MEDIUM

5.1 System Engineering

A block diagram of a generic energy storage system using hydrogen as the energy storage medium is given in Fig. 16.9.

The energy source for such an energy storage system is typically a renewable source such as wind or photovoltaics, though in principle any source of electrical energy may be used, even grid electricity if the economics are appropriate, for example, if very cheap grid electricity can be sourced during off-peak periods. The power-conditioning section of the system is of paramount importance and will determine whether electricity is taken from the energy source, the voltage of that electricity, and whether it should be sent directly to the electrolyzer or whether it should be stored in an intermediate energy store, for example, a battery. The use of a battery in the power-conditioning step can help to overcome limitations in the performance of an electrolyzer at low loads and to minimize start–stop cycling which can decrease the lifetime of the electrolyzer. Alkaline electrolyzers, in particular, have minimum loads typically around (20–40)% of full load [15]. PEM electrolyzers have much better low-load performance but at low loads gas crossover increases [77] as well as the degradation rate of the membrane [21]. The choice of electrolyzer type—alkaline, PEM, or SOE—will be based on the economic and technical aspects of the project. The characteristics of each type of electrolyzer are discussed in Section 3.

Hydrogen gas produced by an electrolyzer can be of varying purity depending on both the type of electrolyzer and the operating conditions employed. The two significant impurities found in the hydrogen gas stream from an electrolyzer are water and oxygen. Water is often removed by passage of the gas through a desiccant, for example, silica gel, or by pressure swing adsorption or a combination of both. Removal of oxygen is via a catalytic recombination process wherein the oxygen is recombined with hydrogen to produce water. This process is

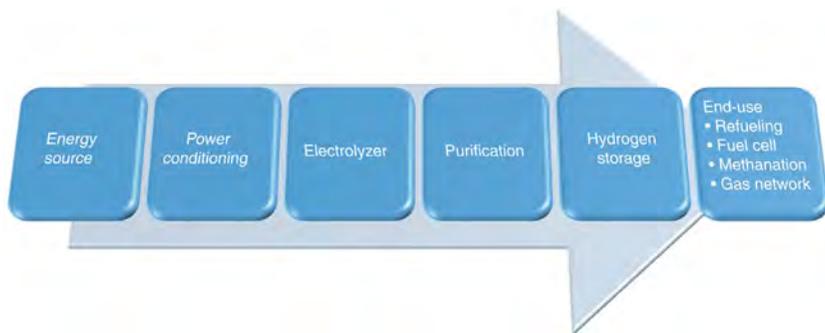


FIGURE 16.9 Block diagram of hydrogen-based renewable energy storage.

carried out by passage of the product gas through a palladium filter heated to (300–600) °C depending on the exact composition of the filter [78]. It goes without saying that this should be placed upstream of the final drying process to prevent reintroducing water to the product gas. The parasitic load from this balance of plant will reduce overall system efficiency. Contamination of the hydrogen with oxygen is typically at a lower level than the opposite case due to the greater size and lower mobility of the oxygen molecule within the membrane and the differential pressure between the hydrogen- and oxygen-producing sides of the membrane; however, despite being at a low level, oxygen contamination can reduce the purity of the product gas to a level where further purification is required, particularly for applications requiring high purity, for example, LED device manufacturing, silicon carbide epitaxy, and polysilicon manufacturing [79]. Hydrogen can be contaminated by up to 2.7% oxygen at high pressure [77]. While still outside the flammability limit for hydrogen/oxygen mixtures (3.9–95.8%), a safety margin must be considered and any reading greater than 2% is likely to lead to an alarm condition. In addition, this crossover of gases increases the likelihood of recombination of oxygen and hydrogen within the membrane of the electrolyzer which can lead to a reduction in the lifetime of the membrane and reduces the efficiency of the electrolyzer [80].

5.2 Renewable Energy Storage

The largest of the current renewable energy storage projects utilizing hydrogen that are currently in operation are facilities located in Germany at Grapzow [81] in the province of Mecklenburg-Vorpommern and in Falkenhagen [82] in Brandenburg. Both systems are coupled to a wind farm and utilize electrolyzers supplied by Hydrogenics and are in collaboration with the utility company E.ON. The 1 MW Grapzow electrolyzer is capable of producing 210 Nm³ of hydrogen per hour. This hydrogen can be directed to either an internal combustion engine to generate electricity or injected into the local gas network. The Falkenhagen system consists of a 2 MW electrolyzer and can supply up to 360 Nm³ of hydrogen for storage in the gas network. There are a number of comprehensive reviews of the coupling of electrolysis systems to renewable energy sources which give further details on a number of additional projects [83,84]. All projects at this stage can be considered as demonstration projects—showcasing technology and enabling further understanding of operational parameters in a live environment prior to scaleup to full commercial status.

The first hydrogen-based system for storing renewable electricity by means of electrolysis and subsequent hydrogen storage was realized in 1991 [85]. This project was based in Nuenberg vorm Wald in Germany and marked the beginning of that country's leadership in the adoption and demonstration of technologies essential for realization of hydrogen economy. This pilot plant operated from 1991 to 1999 and utilized electrical power generated from an array of photovoltaic panels with a capacity of 266 kWp (kilowatt-peak) (Fig. 16.10).



FIGURE 16.10 Overhead view of the Nuenberg vorm Wald Plant [85].

Over the lifetime of the project this demonstration plant utilized both alkaline (low and high pressure) and PEM electrolysis technologies (Fig. 16.11). This plant tested a number of subsystems connected to the electrolysis system including hydrogen and oxygen purification and storage systems, fuel cells, gas-fired boilers fueled with a hydrogen/methane mixture, and a liquid hydrogen-fueling

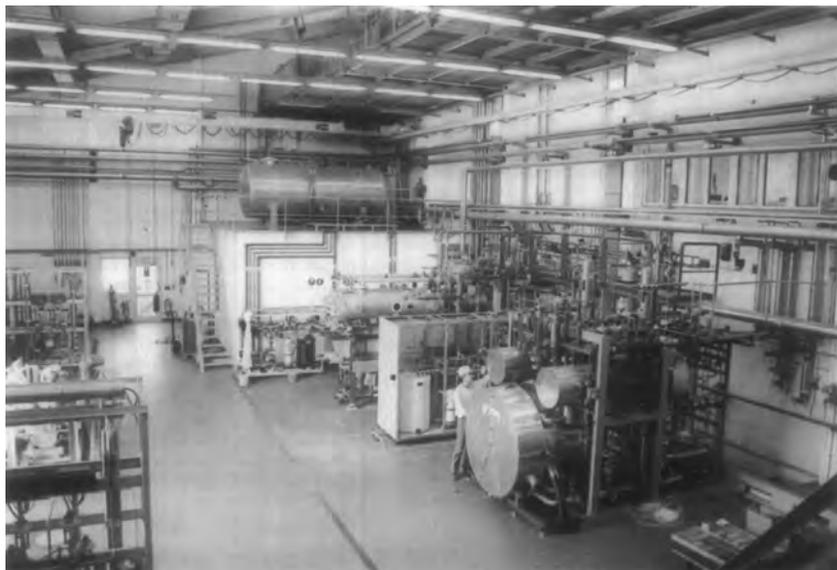


FIGURE 16.11 Interior of the Neunberg Plant—DI Water tank and low pressure electrolyzers (top right) and high pressure electrolyser (bottom right).

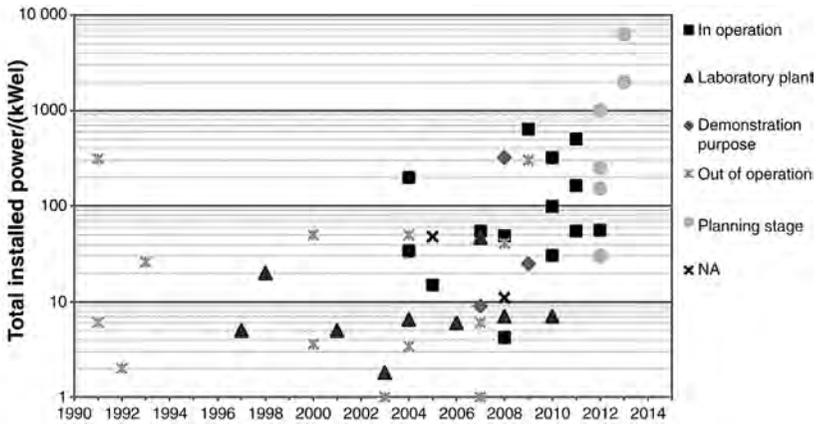


FIGURE 16.12 Installed power of hydrogen storage demonstration plants.

station used to fuel prototype liquid hydrogen–fueled cars. With regard to the latter, liquid hydrogen is no longer considered the technology of choice for exploiting hydrogen in transportation applications and has now been largely supplanted by pressurized hydrogen gas.

Since the pioneering work at Nuenberg (Fig. 16.10), many demonstration plants have followed. These were comprehensively reviewed by Gahleitner [84] in 2013. From this work it can be seen that the number of demonstration projects both planned and in operation has not only increased in number but has increased in capacity (Fig. 16.12). Both are essential criteria for the eventual rollout of full-scale plants for the storage of energy as hydrogen gas.

6 EMERGING TECHNOLOGIES AND OUTLOOK

6.1 Electron-Coupled Proton Buffers and Decoupling of Hydrogen Gas Generation

An unavoidable consequence of electrolysis in a conventional electrolyzer is that the production of oxygen and hydrogen takes place in the same device separated only by a membrane. This in turn defines a number of limitations on the operation of a conventional system; namely, (1) extremely high levels of gas purity (>99.999%), specifically for electronic applications, cannot be directly obtained from the electrolyzer without requiring further purification [86]; (2) operation at low loads and at frequently changing loads reduces the lifetime of the membrane and further increases the potential for gas crossover [77]; and (3) production of hydrogen at high pressure requires high differential pressure across the membrane [87]. To maintain the integrity of the membrane a thicker membrane is used in these circumstances resulting in higher cell resistance and consequently lower efficiency. In this respect, it is interesting to see if water

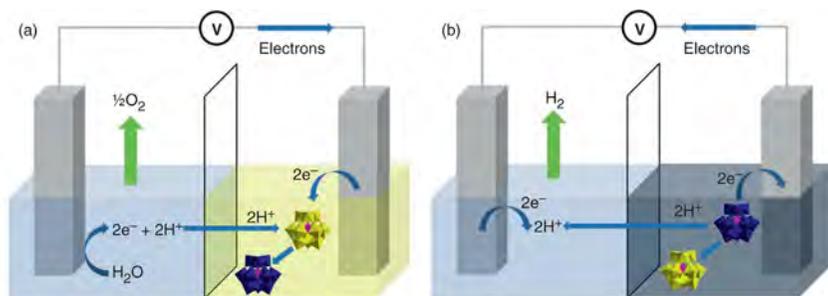


FIGURE 16.13 ECPB mediated (a) oxygen and (b) hydrogen generation. (Reprinted with permission from McMillan Publishers Ltd: Symes MD, Cronin L. *Nat Chem* 2013;5:403–9, Copyright 2013.)

electrolysis could be done in a fundamentally different way, perhaps mirroring the activation of water in photosynthesis which has two sets of coupled processes, that is, a light reaction which results in oxygen evolution and a dark reaction which harnesses the proton gradient and electrons for organic activation.

Recent work by Cronin et al. [88–90] has demonstrated that a new route to water splitting is possible and the limitations described earlier can be circumvented by decoupling the hydrogen and oxygen production via the introduction of a redox mediator, known as an electron-coupled proton buffer (ECPB) into the cathode of the electrolyzer cell. This mediator effectively intercepts the electrons formed by water oxidation, being itself reduced, and the consequent increase in negative charge is balanced by the protons formed (Fig. 16.13a) which are associated with the reduced mediator. The hydrogen evolution reaction can then be carried out in a separate device (Figure 16.13b) regenerating the oxidized ECPB ready for reuse.

The ability to act as an ECPB is determined by the position of the redox waves associated with the oxidation and reduction of the ECPB. To function as an ECPB the oxidations and reductions must occur at potentials between the oxygen- and hydrogen-evolving reactions. This allows the ECPB to “intercept” the electrons at a more positive potential than that required to combine with the protons to form hydrogen. This is illustrated in Fig. 16.14. The ECPB, in this case phosphomolybdic acid (solid line), demonstrates its electrochemical activity in the window between the oxidation of water and the reduction of protons (dashed line).

Cronin and coworkers have identified three different redox mediator types which show great promise in decoupling hydrogen and oxygen production. In the first example, the polyoxometalate, phosphomolybdic acid is used to decouple hydrogen and oxygen production resulting in two separate electrochemical steps [88]. In the second example the properties of the inorganic ECPB were extended to an organic system composed of potassium hydroquinone sulfonate [90]. The position of the redox waves of the ECPB defines whether or not the splitting of the voltages is largely symmetric, as with phosphomolybdic acid and potassium hydroquinone sulfonate, or asymmetric as in the final example

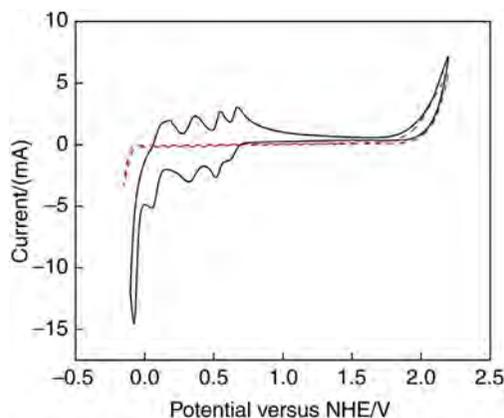


FIGURE 16.14 Comparison of ECPB reduction potentials with water electrolysis potentials.

of this technology. By choosing the polyoxometalate, silicotungstic acid, highly asymmetric behavior was discovered wherein only a single electrochemical input was required [89]. This electrochemical step produced the reduced form of the silicotungstic acid; however, it was found that, instead of a second electrochemical input to oxidize the acid and produce the hydrogen, this step could be successfully carried out by contact of the reduced ECPB with a suitable catalyst with no further electrical input (Fig. 16.15).

By separating the production of hydrogen from oxygen, devices based on ECPBs have the potential to overcome the low-load, high-pressure/efficiency, and purity limitations of conventional electrolyzers.

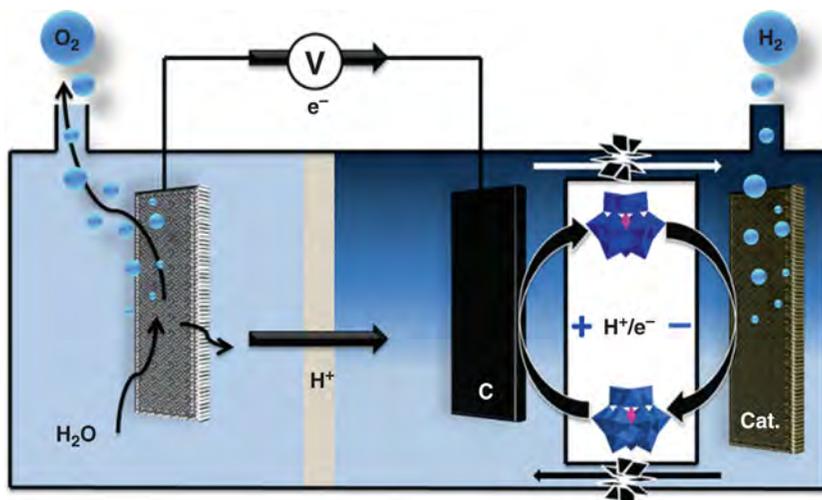


FIGURE 16.15 ECPB Mediated electrolysis using a single electrochemical input. (Reprinted with permission from AAAS: Rausch B, Symes MD, Chisholm G, Cronin L. *Science* (80) 2014;345:1326–30.)

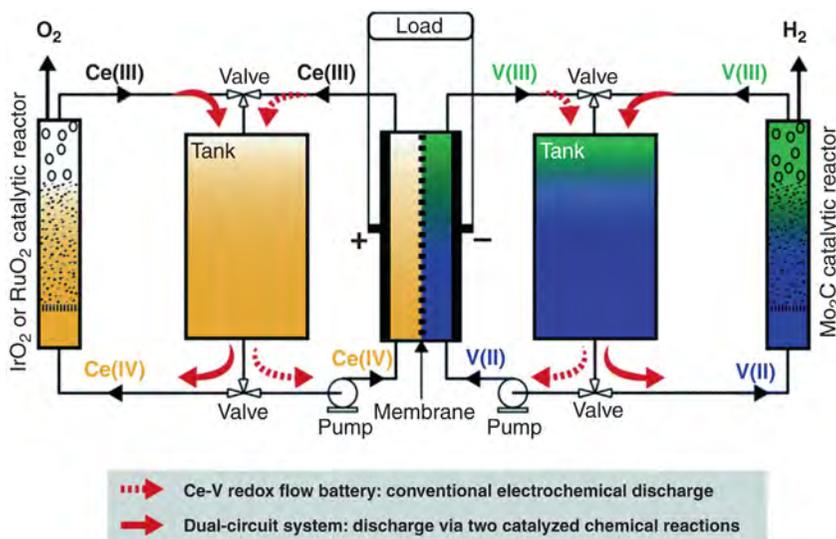


FIGURE 16.16 Ce–V Dual circuit flow battery, reproduced from reference [91] with permission from The Royal Society of Chemistry.

6.2 Flow Battery/Electrolyzer Hybrids

Redox flow batteries (see chapter 12) are a potential competitor technology to electrolysis as a route to economic and flexible energy storage and are discussed at length elsewhere in this volume. There is, however, a promising technology which serves to exploit elements of both flow batteries and electrolyzers to produce hydrogen from water. Amstutz et al. have recently developed a system based on indirect water electrolysis [91]. This system shares some commonalities with the ECPB concept described earlier in that the water-splitting reactions occur in two distinct liquid circuits of the device. This allows the water oxidation reaction to address a limitation of the flow battery wherein the flow battery has a fixed capacity and once this is reached no further energy can be stored. In having an additional water oxidation capability, hydrogen can be produced as an adjunct to the electrochemical energy storage of the flow battery. The system described is a cerium–vanadium (Ce–V) flow battery (Fig. 16.16).

Electrochemical charging of the flow battery proceeds via the following reactions during charging (Scheme 16.6).

Once charging is complete, or simultaneously with charging, the reduced V(II) species can be passed through a catalytic bed wherein it is oxidized to V(III) providing further V(II) for charging and also producing hydrogen gas via the following overall reaction (Scheme 16.7).

As previously noted the electrocatalyst most commonly used for hydrogen evolution in a conventional electrolyzer is platinum. The catalyst which is used in this system is molybdenum carbide (Mo₂C). It should also be noted that the

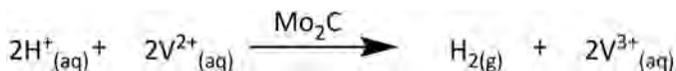
Cathode Reaction



Anode Reaction



SCHEME 16.6 Cerium–vanadium (Ce–V) flow battery reactions.



SCHEME 16.7 Hydrogen production from Cerium–vanadium (Ce–V) flow battery.

production of hydrogen via the oxidation of V(II) does not require additional electrochemical input to produce the hydrogen gas.

The increase in renewable penetration in electricity generation and the increasing recognition that such penetration can only be managed via energy storage offer tremendous potential for the exploitation of established and nascent electrolysis processes in providing a solution to the energy storage dilemma. In addition, when one considers the slow but steady emergence of the hydrogen-fueled vehicle market the signs are extremely positive for a hydrogen economy and thus for the electrolysis industry required to support this.

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