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Hydrogen Generation by Water Electrolysis

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Abstract

Hydrogen is a promising energy vector for the future. Among the different methods of its production, the electrolysis of water has attracted great attention because it is a sustainable and renewable chemical technology. Thus, hydrogen represents a suitable energy vector for the storage of intermittent energies. This chapter is devoted to the hydrogen generation by water electrolysis as an important part of both existing and emerging industrial electrochemical processes. It aims to give an insight into the theoretical foundations of the operating principles of different types of electrolyzers. Also, it is developed in this chapter, the thermodynamic and kinetic aspects of the reactions taking place at the electrodes of water electrolysis. The evolution reaction of hydrogen has a rapid kinetics, and thus, the polarization of the cathode is not critical. On the other hand, the evolution reaction of oxygen is characterized by a very slow kinetics and is thus responsible for most of the overvoltage in the electrolysis of water. The most important technologies of water electrolysis are addressed: alkaline electrolysis, proton exchange membrane electrolysis, and solid oxide high-temperature electrolysis.

Keywords: hydrogen, oxygen, water electrolysis, catalyst, electrolyte, alkaline, polymer, solid oxide

1. Introduction

The United Nations (UN) published The Sustainable Development Program in 2015, which is an action plan for humanity, the planet, and prosperity. A total of 17 sustainable development goals and 169 targets are announced, which will stimulate action over the next 15 years in areas of critical importance for humanity and the planet (People, Planet, Prosperity, Peace, Partnership). The seventh goal is to ensure access to affordable, reliable, sustainable, and modern energy for all [1]. The hydrogen economy is seen as an instrument for the transformation of the energy system [2]. Hydrogen is the fuel most often used in fuel cells. It can have

several provenances (electrolysis of water, cracking or reforming of petroleum products), with obvious implications on its degree of purity and consequently on the choice of catalyst, electrolyte, and operating conditions. The production of hydrogen by the electrolysis technique is very interesting because it can use a non-greenhouse gas energy source (renewable or nuclear energy). In addition, it remains the basic technique for providing applications that require small volumes of high purity hydrogen, including the semiconductor and food industry.

Hydrogen is the lightest chemical element. Its molecules contain two hydrogen atoms. If this gas does not exist in its natural state, it is found in many molecules: water, sugar, proteins, hydrocarbons, and so on.

Hydrogen is a very light gas, colorless, odorless, and extremely flammable and reacts very easily in the presence of other chemicals. The properties of this gas are summarized in **Table 1** [3].

The advantages of using hydrogen as a fuel in fuel cells are:

- its high electrochemical reactivity,
- its high theoretical energy density,
- unlimited availability (as long as you can break down the water),
- its harmless combustion product (H_2O) for the environment.

Its low density under normal conditions, the difficulty of storage, and the risk of explosion can summarize the major drawbacks of the use of pure hydrogen in fuel cells.

Notwithstanding the increasing interest in hydrogen as an energy carrier, its main uses continue to be in petroleum refining, ammonia production, metal refining, and electronics fabrication, with an average worldwide consumption of about 40 million tons [4–8]. This large-scale hydrogen consumption consequently requires large-scale hydrogen production. Presently, the technologies that dominate hydrogen production include reforming of natural gas [9], gasification of coal and petroleum coke [10–12], as well as gasification and reforming of heavy oil [13, 14]. Although water electrolysis has been known for around 200 years [15, 16], it still contributes only a minor fraction of the total hydrogen production (4% of the worldwide hydrogen production) [17, 18]. When compared to other available methods, water electrolysis has the advantage of producing extremely pure hydrogen (>99.9%), ideal for some high value-added processes such as the manufacture of electronic components [4].

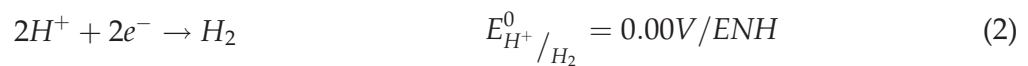
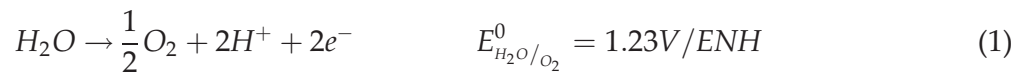
| Molecular weight | 2016 g/mol |
|---|--------------------------|
| Melting point | −259°C |
| Boiling point (1.013 bar) | −252.8°C |
| Evaporation heat (1.013 bar at boiling point) | 454.3 kJ/mol |
| Density in the gas phase (1.013 and at 21°C) | 0.0696 kg/m ³ |
| Solubility in water (1.013 bar and 0°C) | 0.0214 vol/vol |

Table 1. Characteristics of hydrogen [3].

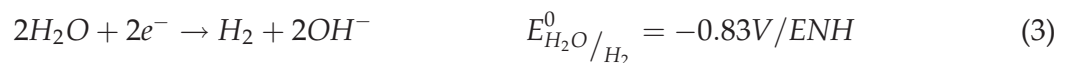
2. Principle of water electrolysis

Water electrolysis is the process whereby water is split into hydrogen and oxygen through the application of electrical energy, as in Eq. (6). Typically, a water electrolysis unit consists of an anode, a cathode separated with an electrolyte, and a power supply. The electrolyte can be made of an aqueous solution containing ions, a proton exchange membrane (PEM) or an oxygen ion exchange ceramic membrane. A direct current (DC) is applied from the negative terminal of the DC source to the cathode (seat of the reduction reaction), where the hydrogen is produced. At the anode, the electrons produced by the electrochemical reaction return to the positive terminal of the DC source.

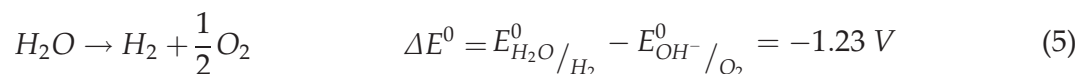
For the case of water electrolysis in an acid aqueous electrolyte, the processes that occur at the anode and the cathode are described, respectively, by Eqs. 1 and 2:



The half reactions occurring on the cathode and anode, respectively, can be written as:



The global reaction for the two cases is:



Electrolysis of water is not a spontaneous phenomenon because the standard global reaction potential is negative. Therefore, it needs an external intervention (power source) and the global reaction can be written as:



3. Thermodynamic

The equation of the German chemist Walther Nernst can be obtained from thermodynamics. The variation of Gibbs free energy is a function of the concentrations of the species participating in a chemical reaction ($aA + bB + \dots \rightarrow mM + nN + \dots$):

$$\Delta G = \Delta G^0 + RT \cdot \ln \left(\frac{a_M^m \cdot a_N^n \cdot \dots}{a_A^a \cdot a_B^b \cdot \dots} \right) \quad (7)$$

where $a_A^a, a_B^b, \dots, a_M^m, a_N^n, \dots$, are the activities of the species.

Some species involved in the electrode reaction are solids or pure liquids. For these pure substances, the activity is constant and its value is considered unitary. The activity of the gases is usually taken to be the partial pressure of the gases expressed in the atmosphere, and the activity of the ions in dilute solution is generally considered to be their molar concentration. By substituting in Eq. (7) the reactions, and dividing each member of the equation by $-nF$, we obtain the Nernst equation. Nernst's equation expresses the relationship between the potential of an electrochemical cell and the concentrations of its constituents at equilibrium. In the specific case of an electrochemical cell, it is written:

$$\Delta E_{npile} = (E_{Cathode}^0 - E_{Anode}^0) - \frac{RT}{nF} \ln \left(\frac{a_M^m \cdot a_N^n \dots}{a_A^a \cdot a_B^b \dots} \right) \quad (8)$$

3.1. Faraday's law

In 1832, Michael Faraday stated his two laws of electrolysis:

1. The weights of substances formed at an electrode during electrolysis are directly proportional to the quantity of electricity that passes through the electrolyte.
2. The weights of different substances formed by the passage of the same quantity of electricity are proportional to the equivalent weight of each substance.

The quantity of material (m) produced is:

$$m = k \cdot \int_0^t I \cdot dt \quad (9)$$

where k is a proportionality constant and I is the instantaneous current flowing through the cell. In a cell in which a continuous current circulates, the majority of this current is connected to chemical reactions (faradic current) and a small part, often negligible can be used for other purposes (non-Faradic current). Thus, the amount of material that forms or disappears at the electrodes is proportional to the intensity of the current and the duration of the electrolysis t . Knowing the number of moles is (m/M) , which corresponds to a quantity of electricity ($Q = \frac{m}{M} \cdot N \cdot F = I \cdot t$). Hence, Faraday's law:

$$m = \frac{I \cdot t \cdot M}{nF} \quad (10)$$

With: m is the mass of substances formed (g); M is the molar mass of substances formed (g/mol.); n is number of exchanged electrons, I is the current in amperes (A), $Q = I \cdot t$ is the quantity of electricity in coulomb (C), t is the time (s).

3.2. Cell voltage (difference of potential)

The potential difference for a cell of an electrolyzer, which is always $\Delta E = 1.8 \sim 2.0$ V at the current density of $j = 1000 \sim 300$ A/m² in industry water electrolysis [17], is an addition of four terms:

$$\Delta E = \Delta E_{\text{the}} + \eta_a + \eta_c + R \cdot I \quad (11)$$

with: η_a (V) is the anodic overvoltage; η_c (V) is the cathodic overvoltage; R (Ω) is the global resistance and I (A) is the current.

Figure 1 shows the relationship between the electrolyzer cell potential and operating temperature [19–22]. The cell potential-temperature plane is divided into three zones by the so-called equilibrium voltage line and thermo-neutral voltage line. The equilibrium voltage is the theoretical minimum potential required to dissociate water by electrolysis, below which the electrolysis of water cannot proceed. The equilibrium voltage decreases with increasing temperature. The thermo-neutral voltage is the actual minimum voltage that has to be applied to the electrolysis cell, below which the electrolysis is endothermic and above which, exothermic. The thermo-neutral voltage naturally includes the overpotentials of the electrodes, which are only weakly dependent on temperature. Thus, the thermo-neutral voltage only exhibits a slight increase with temperature. If water electrolysis takes place in the shaded area in **Figure 4**, the reaction will be endothermic.

3.3. Electrodes polarizations

As these electrochemical reactions are heterogeneous surface processes, it is convenient to relate the reaction rate to the electrode area, A , as $\frac{dm}{A \cdot dt} = \frac{I}{A \cdot n \cdot F}$. Therefore, the expression for current density, $j = \frac{I}{A}$, may be rewritten as $j = \left(\frac{nF}{A} \cdot \frac{dm}{dt} \right)$.

For a general electrochemical reaction:

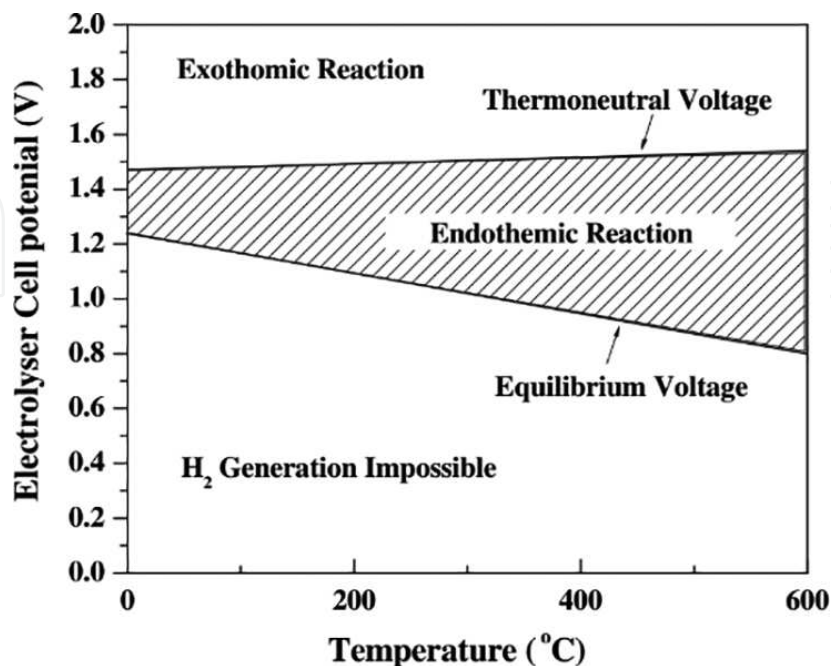
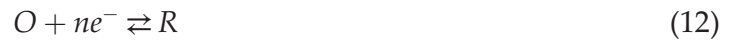


Figure 1. Cell potential for hydrogen production by water electrolysis as a function of temperature [19].

Under nonequilibrium potential conditions, the equation that best describes the current density versus potential is the Butler-Volmer expression:

$$j = \vec{j}_a + \overleftarrow{j}_c = nF\overleftarrow{k}_0 C_R(0, t)e^{\left(\frac{\alpha_a nF(E-E^0)}{RT}\right)} - nF\vec{k}_0 C_O(0, t)e^{\left(\frac{\alpha_c nF(E-E^0)}{RT}\right)} \quad (13)$$

where \vec{j}_a and \overleftarrow{j}_c are, respectively, the anodic and cathodic current density; \overleftarrow{k}_0 and \vec{k}_0 are, respectively, the rates constants of the anodic and cathodic reaction; α_a and α_c are, respectively, the anodic and cathodic exchanges coefficients; E^0 is the standard potential.

Under the control of electron transfer rate, (the concentration of the electrodes' surface is equal to the concentration in the bulk), this equation can be expressed as current density versus overpotential ($\eta = E - E_{eq}$):

$$j = j_0 \left(e^{\left(\frac{\alpha_a nF\eta}{RT}\right)} - e^{\left(\frac{\alpha_c nF\eta}{RT}\right)} \right) \quad (14)$$

The anodic and cathodic exchanges coefficients (α_a , and α_c) are related ($\alpha_a + \alpha_c = 1$), and generally, $\alpha \approx \alpha_a \approx \alpha_c \approx \frac{1}{2}$. For a given single-step reaction at a constant temperature, the j versus η characteristics will depend on j_0 , α_a , and α_c .

For large η values, the Butler-Volmer equations can be simplified to give the Tafel equation ($|\eta| = a \cdot \log |j| + b$):

$$\text{For } \eta \ll 0 : \log(j) = -\log(j_0) - \frac{\alpha_c nF}{2.3RT} \cdot \eta \quad (15)$$

$$\text{For } \eta \gg 0 : \log(j) = -\log(j_0) + \frac{\alpha_a nF}{2.3RT} \cdot \eta \quad (16)$$

For the hydrogen evolution reaction (HER), the Volmer-Tafel and Volmer-Heyrovský mechanisms are often proposed and well known [16, 23, 24]. The first step (Eq. 17) involves the formation of adsorbed hydrogen, which is then followed by either chemical desorption (Eq. 18) or electrochemical desorption (Eq. 19), where H_{ads} is an adsorbed hydrogen atom.



For the hydrogen evolution reaction (HER), the overpotential, η_{H_2} , is generally calculated by the Tafel equation. Hydrogen formation is intrinsically determined by the strength of the bond between hydrogen and the electrode surface. Pd has the lowest heat of adsorption of hydrogen

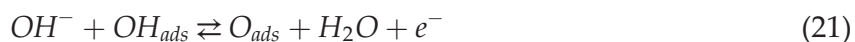
($\Delta H_{ads, Pd, 298}(H_2) = 83. kJ\ mol^{-1}$); for Ni, the heat of adsorption is $\Delta H_{ads, Ni, 298}(H_2) = 105\ kJ\ mol^{-1}$ [25]. Electrode properties, type and concentration of the electrolyte, and temperature are parameters that also influence hydrogen formation. If hydrogen adsorption is the rate-determining step, electrode materials with more edges and cavities in their surface structure will favor electron transfer and create more centers for hydrogen adsorption. If hydrogen desorption is the rate-determining step, physical properties such as surface roughness or perforation will prevent bubbles from growing and increase electron transfer by adding reaction area, consequently increasing the rate of electrolysis [26]. When the overpotential is low, electron transfer is not as fast as desorption and hydrogen adsorption will be the rate-determining step. In contrast, when the potential is high enough, hydrogen desorption will be the rate-determining step.

The hydrogen adsorption energy is a good parameter to identify the most promising materials for the HER. If the activities for the HER of the coinage metals (I_B metals: Au, Cu, Ag), the platinum group (Pt, Ir, Ru) metals and the valve metal (Ti) in 0.1 M HClO₄, are plotted as a function of the $M-H_{ads}$ binding energy, a volcano relationship is established (**Figure 2**) with Ir and Pt at the apex of the volcano curve [27].

Further analysis of **Figure 2** reveals that the I_B group elements are positioned on the ascending slope of the volcano with the order activity increasing from Au < Cu < Ag. **Figure 1** also shows that the elements that interact strongly with H_{ads} (such as Ru and Ti) are positioned on the descending slope of the volcano, supporting previous suggestions that the $M-H_{ads}$ binding energy can be used as a descriptor for the HER. Not in passing, given that recent analysis has demonstrated that neither Ru nor Ti are bare metals in the HER region, it is suggested that, in fact, experimentally it is very difficult (impossible) to determine unambiguously solely based on the $M-H_{ads}$ energetics what would be the correct position of these two elements in the observed volcano relationship. This is most likely also true for the HER in alkaline solutions, when the rates of the reaction are much slower than in acidic environments [22].

The HER exchange current of Pt in acid media is at least two orders of magnitude higher than that in alkaline electrolytes, including KOH. This is due to the shorter $Pt - H_{ads}$ distance in alkaline media, as suggested by theoretical estimates. It has been claimed that Ni(OH)₂ nanoclusters on Pt surface enhance HER rates in 0.1 M KOH by one order of magnitude [26], although no theoretical explanation for this synergistic effect has been attempted. The long-term stability of Ni(OH)₂ in the strongly reducing environment occurring at the cathode is also not discussed.

The mechanism of the oxygen evolution reaction (OER) is more complex than that suggested for HER. The most generally accepted mechanism for the OER is that described by Cappadonia et al. [29]:



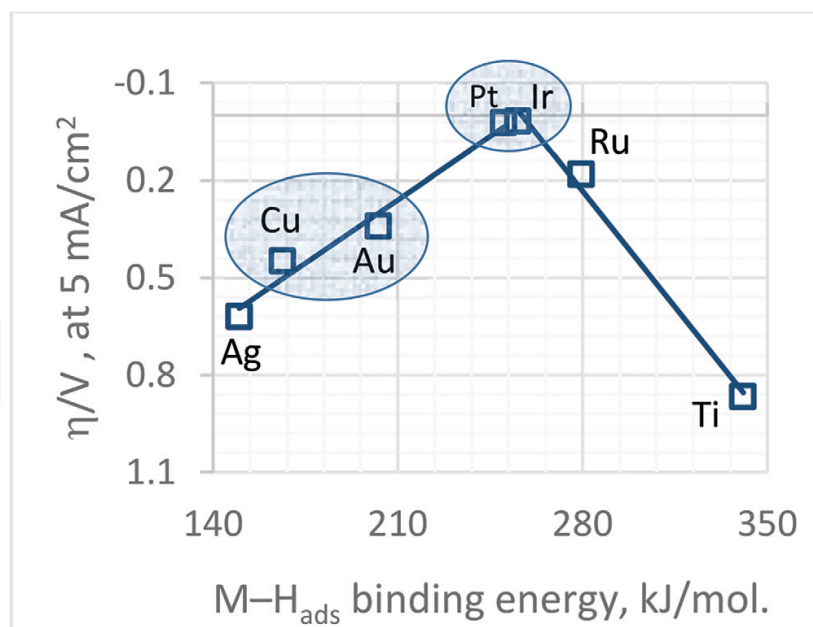


Figure 2. HER activity, overpotential (η) at 5 mA cm^{-2} , measured in 0.1 M HClO_4 ($\text{pH} = 1$) as a function of calculated M-H binding energy for several metals (volcano plot) [20].

The mechanism is controlled by the charge transfer (step 20 or 21) at low temperatures. On the other hand, at high temperatures, the recombination step (Eq. 22) controls the reaction on Ni electrode [22–30].

Generally, acid solutions or PEMs are used as electrolytes in water electrolyzers because acidic media show high ionic conductivity and are free from carbonate formation, as compared with alkaline electrolytes. Consequently, noble metals are used as electrocatalysts for OER in acidic media. Ruthenium and iridium have shown strong activity for OER, but they were passivated at very high anode potentials [31–36]. Bifunctional electrocatalysts, which can work for both oxygen evolution and oxygen reduction, have also been proposed for water electrolysis. A typical bifunctional electrocatalyst is composed of a noble metal oxide such as IrO_2 . For unsupported bifunctional electrocatalysts, Pt-MOx ($\text{M} = \text{Ru}, \text{Ir}, \text{Na}$), bimetallic (e.g., Pt-Ir), and trimetallic (e.g., $\text{Pt}_{4.5}\text{Ru}_4\text{Ir}_{0.5}$) materials have been developed [37–40].

At high current densities, are added to the polarization of the electrodes other resistances: ohmic losses in the electrolyte, resistances from bubbles, diaphragm, and ion transfer.

3.4. Electrical resistance

The electrical resistance in a water electrolysis system has three main components: (1) the resistance in the system circuits; (2) the mass transport phenomena including ions transfer in the electrolyte; (3) the gas bubbles covering the electrode surfaces and the diaphragm [15].

The nature and the dimensions of the materials used in the electrodes and the connections and the electric circuit, the methods of their preparations are responsible for the electrical resistance of the system. It can be expressed as follows:

$$R = \sum_i \frac{l_i}{A_i \cdot \chi_i} \quad (23)$$

where χ_i ($\Omega^{-1}m^{-1}$) is the electrical conductivity for each component of the circuit, including wires, connectors, and electrodes. This part of the resistance can be reduced by reducing the length of the wire, increasing the cross-section area and adopting more conductive wire material.

The ionic solution conductivity χ is a function of concentration and temperature. For an ionic solution containing ions (i), charged $+z_i$ or $-z_i$ and at the concentration C_i in $mol \cdot m^{-3}$, the conductivity of the solution, noted χ ($\Omega^{-1}m^{-1}$), is:

$$\chi = \sum_i \lambda_i \cdot z_i \cdot C_i \quad (24)$$

with: λ_i is the equivalent conductivity of the ion (i) in, $S \cdot m^2 \cdot mol^{-1}$.

The presence of bubbles in the electrolyte solution and on the electrode surfaces causes additional resistances to the ionic transfer and surface electrochemical reactions. One of the accepted theoretical equations to study the bubble effect in the electrolyte is given as follows [41]:

$$\kappa_g = \kappa(1 - 1.5f) \quad (25)$$

where κ is the specific conductivity of the gas-free electrolyte solution; f is the volume fraction of gas in the solution [42].

3.5. Transport resistances

Convective mass transfer plays an important role in the ionic transfer, heat dissipation and distribution, and gas bubble behavior in the electrolyte. The viscosity and flow field of the electrolyte determines the mass (ionic) transfer, temperature distribution and bubble sizes, bubble detachment and rising velocity, and in turn influence the current and potential distributions in the electrolysis cell. As the water electrolysis progresses the concentration of the electrolyte increases, resulting in an increase in the viscosity. Water is usually continuously added to the system to maintain a constant electrolyte concentration and thus the viscosity.

4. Alkaline electrolysis

The conductivity of the solution is enhanced by the use of strong electrolytes that deliver ions with high mobility [43], such as sodium, potassium for positive ions, and hydroxide or chlorides as negative ions. During electrolysis, the water molecules move to the cathode by diffusion as they are consumed, and the hydroxide ions move to the anode by migration because they have an opposite charge and diffusion because they are consumed. A diaphragm

separates the two anode and cathode compartments and the gases formed are thus collected: hydrogen at the cathode and oxygen at the anode as shown in **Figure 3**.

Concentrated solutions of potassium hydroxide are generally used as the electrolytic solution because they have very high conductivities and fewer corrosion problems compared with other alkaline electrolytes. The electrode materials often used are based on nickel because of its low cost, high activity [44].

Electrolysis cells can be of two types of configurations: monopolar and bipolar [14]. **Figure 4(a)** gives a schematic of the monopolar configuration. The electrodes are altered in the electrolyzer and are all directly connected to the terminals of the DC power supply: the anodes at the positive terminal and the cathodes at the negative terminal. The total voltage applied to the entire electrolysis cell is essentially the same as that applied to the individual pairs of the electrodes in the cell ($U_{tot} = U_i$), but the current is subdivided between the different unit cells ($I_{tot} = n \times I_i$). **Figure 4(b)** depicts conflation in bipolar mode. Only the two end electrodes are connected directly to the DC power source. The other inner electrodes have a dual role: one side acts as the cathode for a unit cell and the other side acts as the anode for the adjacent unit cell. These cells are electrically linked thanks to their electrodes which are bipolar and ionically via the electrolytic solution. The total voltage of the cell is the sum of the individual voltages of

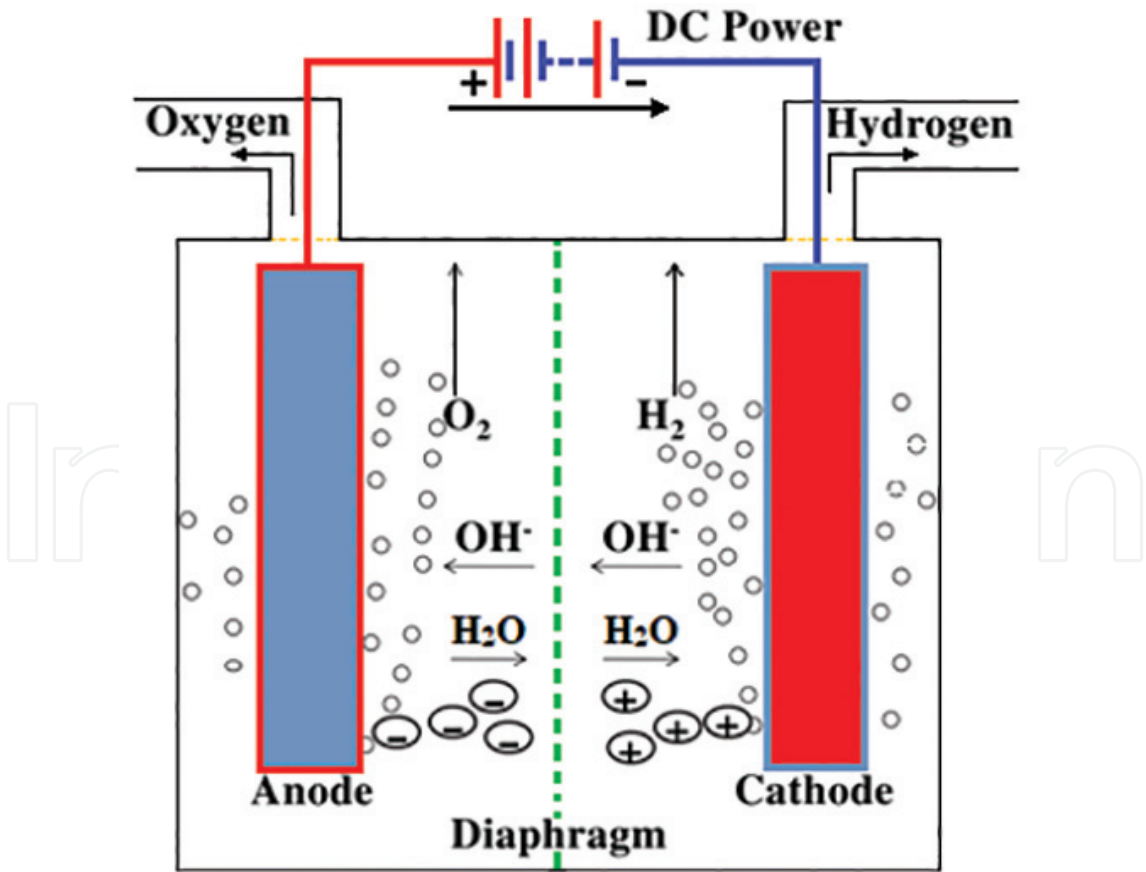


Figure 3. Principle of an alkaline water electrolysis.

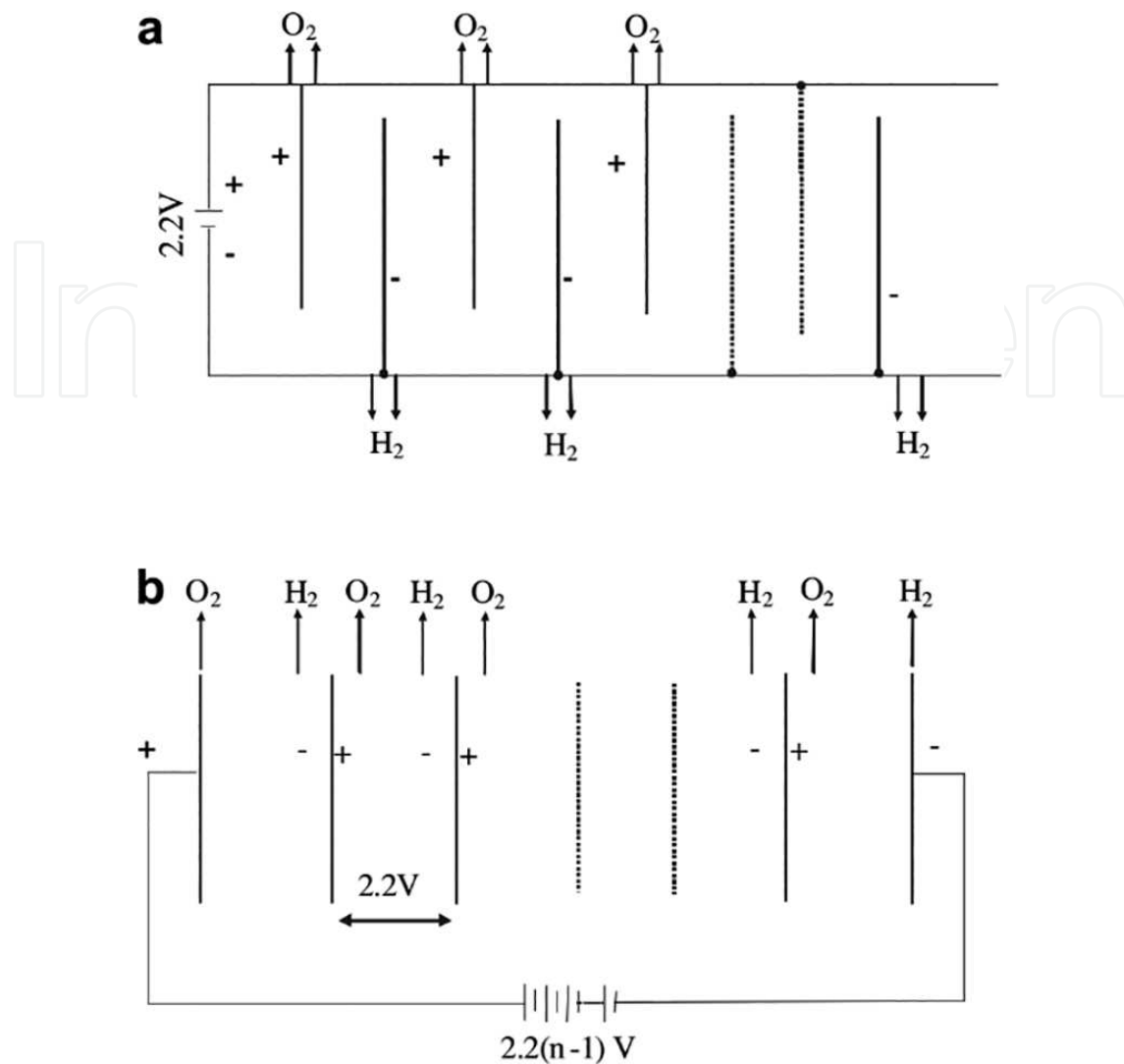


Figure 4. Schematics of cell configurations of monopolar (a) and bipolar (b) electrolyzers [14].

the unit cells ($U_{tot} = n \times U_i$), but the current for each unit cell is equal to the output current of the generator ($I_{tot} = I_i$). The electrical energy consumed is the same in the two configurations.

The wide range of flammability limits of the mixture of hydrogen and oxygen requires a careful design of the electrolyzer system. The separator diaphragm (or membrane) must avoid the mixing of the two gases inside the cell. Furthermore, the corrosive nature of the electrolyte does not allow leaks that are often likely to take place at the connections and seals of the electrolyzer. The bipolar configuration is more risky in mixing oxygen and hydrogen because of their simultaneous productions on the same bipolar electrode (on each side) and also electrolyte leakage as the monopolar design.

Obviously, the life of the system is an important criterion. It is extremely linked to the quality of the materials used. Indeed, these materials must be resistant to high concentrations of the alkaline electrolyte and operating conditions of the electrolyzer (pressure and temperature). In particular, connections and seals are subject to corrosion, which is why it is recommended to use sealing materials that are also stable in this environment [14].

5. PEM electrolyzer

PEM electrolyzers are characterized by their very simple construction and their compactness. The operating principle of electrolysis of water with an electrolyte protons exchange membrane (PEM) is simple. When operating in electrolysis, the water decomposes at the anode into protons and molecular oxygen. The oxygen is evacuated by the water circulation, and the protons migrate to the cathode under the effect of the electric field. There, they are reduced to molecular hydrogen. Each proton carries with it a procession of several molecules of solvation water: it is the electro-osmotic flow.

During the twentieth century, several major innovations have significantly increased the energy and faradic efficiencies of electrolyzers. The concept of zero-gap cells has been developed in order to overcome the disadvantages of the electro-osmotic flow. It consists of pressing porous electrodes against the solid separator in order to reduce the interpolar distance and to reject the gas production at the rear of the interpolar space.

The zero-gap concept with immobilized electrolyte goes even further: it consists of maintaining the electrolyte (acid) in the separator so as to be able to electrolyze the water in the acidic medium while avoiding corrosion problems. Of course, this interesting approach was practically limited by the leakage of electrolyte pushed back into the circuit of the electrolyzer.

The membrane thus serves both electrolyte and separator of electrodes and gases. Therefore, the membrane must have certain physicochemical properties, such as:

- High ionic conductivity to promote proton migration and reduce ohmic drop;
- No electrical conductivity to avoid short-circuits;
- Good chemical stability;
- Low permeability to oxygen and hydrogen;
- Good mechanical and dimensional stability, especially resistance to pressure;
- Good thermal stability, operating temperature up to 80–100°C.

Compared to a liquid electrolyte, we can note some behavioral difference resulting from the properties of this assembly:

- The anionic charges of the membrane are fixed; there can be no concentration gradient in their case.
- The gas evolution is done by the back of the electrodes, the ohmic drop is not disturbed by the reactions to the electrodes, in return, it is necessary to make laying electrodes to allow gas release.
- The nature of the ions also intervenes, but the water content of the membrane, different according to the nature of the ions carried and according to the conditions of preparation and use of the membrane, will condition both its thickness, its mechanical strength, and especially its conductivity.

The appearance of the first ion exchange membranes in the 1940s made it possible to seriously consider industrial applications for this zero-gap concept with immobilized electrolyte. Notably, as early as 1953, at the dawn of the American space program, the US General Electric Company suggested for the first time the use of cation exchange membranes as a solid polymer electrolyte for the production of acid fuel cells. The US solid polymer electrolyte (SPE) concept was born. Applied to the electrolysis of water, it was hoped to be able to operate at a high current density (of the order of an ampere per cm^2). This possibility was interesting for minimizing investment costs and increasing the volume density of production. Unlike fuel cells, the electrolysis of water SPE requires a polymeric material that is very resistant to the oxidizing potential of the anode under the release of native oxygen.

6. Solid oxide electrolyzer

Solid oxide fuel cells are electrochemical devices that can operate reversibly in the electrolysis mode. In the solid oxide electrolyzer, water vapor is reduced to H_2 .

Electrolysis at high temperature allows decreasing the electric consumption because with the increase of the temperature offers an additional part of the global energy; which allows high operational efficiencies in the solid oxide electrolyzer.

The main advantage is that a substantial part of the energy required for the electrolysis process is added in the form of heat, which is much cheaper than electrical energy. In addition, the high temperature promotes the conduction of the electrolyte and accelerates the kinetics of the reaction, reducing the energy loss due to the polarization of the electrode. Thus, the efficiency of the electrolysis at high temperature is higher than that obtained at low temperature. The typical high-temperature electrolyzer can achieve an electrical efficiency of 92% while the electrolyzers at low temperature reach a maximum of 85% efficiency.

The high-temperature system uses oxygen ion conducting ceramics as an electrolyte (ZrO_2 stabilized by Y_2O_3 , MgO or CaO). The water is brought to a temperature of 200°C to supply steam in the cathode. The electrolysis cell operates at a temperature of $800\text{--}1000^\circ\text{C}$, which ensures the conduction of the solid electrolyte. The water vapor is decomposed into hydrogen gases and oxygen ions (O^{2-}). The oxygen ions are transported through the ceramic solid electrolyte to the anode, where they are oxidized to form gaseous oxygen.

7. Hydrogen station

Hydrogen has a low carbon footprint. It could thus significantly reduce energy-related CO_2 emissions and help limit climate change. Fuel cell electric vehicles (FCEVs) can provide the mobility service of today's conventional cars with potentially very low carbon emissions. Although the potential benefits of hydrogen and fuel cells in end-use applications are promising in terms of environment and energy security, the development of hydrogen production,

| Country or region | Existing hydrogen refueling stations | Planned stations | |
|-------------------|--------------------------------------|------------------|------|
| | | 2015 | 2020 |
| Europe | 36 | ~80 | ~430 |
| Japan | 21 | 100 | >100 |
| Korea | 13 | 43 | 200 |
| United States | 9 | >50 | >10 |

Table 2. Existing public hydrogen refueling stations and targets announced by hydrogen initiatives [46].

transport, and distribution are difficult. Although the first VECFs were developed in the 1960s, it is only in the last 10 years that the technology of using hydrogen as an energy carrier has begun to develop. Also, some automakers announce the launch of FCEV.

Generally, hydrogen station consists of hydrogen production process including desulfurizer, reformer, water gas shift (WGS) reactor and pressure swing adsorption (PSA) apparatus, and post-treatment process including a compressor, storage, and distributor [45]. Research on the development of the hydrogen station is actively conducted in advanced countries such as the United States, Canada, Japan and Europe. An overview of existing and planned hydrogen refueling stations is given in **Table 2** [46].

Currently, more than 79 hydrogen stations are operating worldwide and others are planned in the future. **Table 3** summarizes the current status of hydrogen station research and development programs and demonstration experiments at home and abroad [45].

| Nation | Program | H ₂ station | Hydrogen production method |
|--------|--|---|--|
| USA | SCAQMD project, CaFCP & freedom CAR etc. | CA, IL, MI, NV, AZ, eastern, etc. [25] | <ul style="list-style-type: none">• Electrolysis, liquid H₂, LNG & biomass reforming, photocatalyst, etc.• Compressed H₂ & LH₂• Air Product Co., Stuart Energy Co. etc. |
| Japan | WE-NET program, JHFC project, and new H ₂ project, etc. | Tokyo & Yokohama, etc. [14] | <ul style="list-style-type: none">• Reforming of naphtha, gasoline, LPG, LNG, diesel & methanol, COG, electrolysis, LH₂, etc.• Compressed H₂• Tokyo gas, Nippon Sanso, Cosmo oil, etc. |
| Canada | Hydrogenics & Canadian, Transportation FC Alliance, etc. | Toronto, etc. [6] | <ul style="list-style-type: none">• Electrolysis of H₂O (alternative energy)• Compressed H₂• Hydrogenics |
| EU | CUTE and ECTOS Projects, etc. | Framework (FP5) [32] | <ul style="list-style-type: none">• Electrolysis [4], LNG reforming [3], LH₂ [2]• Alternative energy, bus• Compressed H₂ & LH₂• BP Co., Linde Co. |
| Korea | MOCIE, H ₂ & FC Project MOST, 21C Frontier Project | Goal of MOCIE 1stage (03-05):1 2stage (06-08):10 3stage (09-12):50 | <ul style="list-style-type: none">• Production by reforming of LNG, LPG & naphtha• Compressed H₂• SK Co., KIST, KIER, KOGAS, GS Caltex |

Table 3. R&D situation of hydrogen station in worldwide [45].

8. Conclusion

Hydrogen economy is a promising instrument for the transformation of the energy system. Hydrogen, ideal fuel for fuel cells, can have several provenances (electrolysis of water, cracking or reforming of petroleum products). The production of hydrogen by the water electrolysis technique gives the concept renewability because it can use a non-greenhouse gas energy source (renewable or nuclear energy). This technique provides applications that require small volumes of high purity hydrogen, including the semiconductor and food industry.

Acid solutions are good electrolytes in water electrolyzers because acidic media show high ionic conductivity and are free from carbonate formation, as compared with alkaline electrolytes. But the acid needs the use of noble metals as electrocatalysts for OER. Consequently, potassium hydroxide is most commonly used in water electrolysis, avoiding the huge corrosion loss caused by acid electrolytes, and the use of noble metals as catalysts. Nickel is a popular electrode material due to its high activity and availability as well as low cost.

PEM electrolyzers are characterized by their very simple construction and their compactness with an electrolyte protons exchange membrane (PEM) is simple. During the twentieth century, several major innovations have significantly increased the energy and faradic efficiencies of electrolyzers.

Solid oxide electrolyzer, operating at high temperature, allows decreasing the electric consumption because with the increase of the temperature offers an additional part of the global energy; which allows high operational efficiencies in the solid oxide electrolyzer. Thus, the efficiency of the electrolysis at high temperature is higher (92%) than that obtained at low temperature (85%).

Research on the development of the hydrogen station is actively conducted in advanced countries such as the United States, Canada, Japan, and Europe. Currently, 70 hydrogen stations are operating worldwide, and demand is expected to increase rapidly in the future.

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