

# Hydrogen Production from Water Electrolysis: Current Status and Future Trends

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**Abstract**—This paper reviews water electrolysis technologies for hydrogen production and also surveys the state of the art of water electrolysis integration with renewable energies. First, attention is paid to the thermodynamic and electrochemical processes to better understand how electrolysis cells work and how they can be combined to build big electrolysis modules. The electrolysis process and the characteristics, advantages, drawbacks and challenges of the three main existing electrolysis technologies, namely alkaline, polymer electrolyte membrane and solid oxide electrolyte, are then discussed. Current manufacturers and the main features of commercially available electrolyzers are extensively reviewed. Finally, the possible configurations allowing the integration of water electrolysis units with renewable energy sources in both autonomous and grid-connected systems are presented and some relevant demonstration projects are commented.

**Index Terms**—Electric grid integration; electrolyzer; hydrogen; renewable energies; steam electrolysis; water electrolysis.

## I. INTRODUCTION

Massive utilization of fossil and nuclear fuels represents serious environmental threats such as natural resources exhaustion, pollutant gasses emission, waste generation and climate change. As a result of public awareness of this reality, an agreement has been reached in the sense that a novel, clean, sustainable and renewable resources-based energy system is needed [1].

In this context, the development of renewable energies, especially the ones dedicated to electric generation, has been spectacular in recent years. The existing worldwide renewable power capacity reached about 1230 GW in 2009, 7% more than in 2008, and about a quarter of the global power-generating capacity, estimated at 4800 GW. In 2009, these

energies supplied 18% of the global electricity production [2]. Moreover, renewable energies, others than large scale hydropower, rose to a total of 305 GW this year, a 22% increase over 2008, with China, United States, Germany, Spain and India as the top five countries [2].

Among all renewable energies, global wind power capacity increased the most in 2009, by 38 GW, bringing the global total to 158 GW. The most important wind energy producers this year were United States (35 GW), China (25.8 GW), Germany (25.7 GW) and Spain (19 GW) [3]. On the other hand, hydropower supplied 15% of the global electricity production in 2008. Approximately, 31 GW were added during 2009, the second highest increase in capacity after wind power. Global hydropower capacity reached an estimated 980 GW by the end of 2009, including 60 GW of small hydro [2]. Concerning photovoltaic solar energy, an estimated 7.2 GWp of grid-connected capacity were added in 2009, increasing the existing total by 53% up to about 21 GWp. Off-grid PV accounts for an additional 3–4 GWp. Germany, with 9.8 GWp of installed power capacity, topped the list, followed by Spain (3.5 GWp), Japan (2.6 GWp) and the United States (1.6 GWp) [2], [3].

An electric system based on renewable energies gives rise to new challenges concerning storing and utilization of the surplus energy, system operation, distributed generation management, energy supply reliability and future integration with an automotive sector based on the electric vehicle [4]–[6]. Renewable energies can take the grid to extreme situations. An example is Spain, where wind power reached on November 9<sup>th</sup> 2010, a penetration peak of 54% of the power demanded, while it decreased to 1% on June 26, 2010 [7].

Hydrogen technologies can help to cope with these challenges and to contribute to the new energy system development [1], [8]–[10]. In this respect, the so-called hydrogen economy considers a future scenario in which hydrogen is produced through low-cost environmentally clean processes by means of renewable energy sources. Final use technologies, especially fuel cells, will be widely spread [11]–[15]. Support policies and recent technological progress are contributing to the cost reduction, knowledge improvement and better social acceptance of these hydrogen technologies [1], [16]–[23].

Hydrogen is the simplest and lightest chemical element of the periodic table. Its density as a gas (0.0899 kg/Nm<sup>3</sup>) is 15

This work was supported by the Spanish Ministry of Science and Innovation under Grants DPI2010-21671-C02-01 and ENE2009-14522-C05-03.

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times lighter than that of air.<sup>1</sup> Hydrogen is a fuel with a wide inflammability range both in air, from 4 to 75 vol.%, and in oxygen, from 4 to 95 vol.%. It is also the fuel with the highest energy content per mass unit, being its higher heating value (HHV) 3.54 kWh/Nm<sup>3</sup> (39.42 kWh/kg), that is, 2.5 and around 3 times more energetic than methane and gasoline, respectively [24].

Even though hydrogen is the most abundant element in the universe, it cannot be found in its pure state in the nature. Actually, up to 96% of hydrogen is produced from fossil fuels and the other 4% from water [25]-[29]. The main methods to produce hydrogen are classified by the raw material used. Concerning fossil fuels, steam reforming and partial oxidation of hydrocarbons, especially natural gas (methane), stand out, although coal gasification is also used in those countries rich in this resource [1], [26], [27]. Renewable hydrogen might also be obtained from biomass through these same thermochemical processes. Furthermore, hydrogen can be produced from biomass by means of biological processes such as fermentation. Last but not least, water is another renewable resource of great interest for hydrogen production. In this case, the main production method is the electrolysis, although thermal and photocatalytic decompositions are also attracting some attention.

With a market share of 48%, steam reforming of methane (SRM) is at present the most commonly used process to produce hydrogen. The process low cost, between 1 and 3€ per kg of hydrogen including the cost of CO<sub>2</sub> sequestration, explains the SRM leadership. In addition, it is the less polluting option to obtain hydrogen from fossil fuels. Its efficiency ranges from 70 to 80% [25]-[27].

In the context of the hydrogen economy, hydrogen production methods based on fossil fuels are considered transitional technologies. Water is widely agreed to be the most interesting source of sustainable hydrogen of the future mainly because the process is easy to be integrated with renewable energy sources.

Thermal decomposition is based on the dissociation of the water molecule with heat. Since direct hydrogen production requires temperatures above 2500°C approximately [24], thermochemical cycles with different intermediate chemical reactions are used to produce hydrogen at lower temperatures, around 850-1000°C. These processes currently have several drawbacks related to the recombination of hydrogen and oxygen, the corrosion and heat exchange problems caused both by high temperatures and the chemicals used, and the difficulty to get the heat sources for the processes. Photoelectrolysis is a developing technology that has only been tested at a laboratory scale. It aims at obtaining hydrogen from the incidence of solar rays on semiconductors immersed in an aqueous solution that act as photocatalysts.

Electrolysis is the most important method to obtain hydrogen from water. It is a mature technology based on the

generation of hydrogen and oxygen by applying a direct electric current to water to dissociate it. The hydrogen obtained with this technology has a high purity that can reach 99.999 vol.% once the produced hydrogen has been dried up and oxygen impurities have been removed. Since electrolytic hydrogen is suitable for being directly used in low temperature fuel cells, such purity levels are of great advantage against both fossil fuels and biomass based processes. Depending on the size of the electrolysis system, the processing cost ranges between 3 and 15€ per kg of hydrogen. Traditionally, the largest electrolytic hydrogen production plants worldwide have been placed close to hydroelectric plants in order to profit from electricity supply during low-priced hours. Two examples are the 22000 Nm<sup>3</sup>/h plant that Asea Brown Boveri (ABB) installed in 1960 in Aswan (Egypt) and another one in Ryukan (Norway) with a capacity of around 27900 Nm<sup>3</sup>/h that Norsk Hydro (now incorporated to Statoil) installed in 1965. Large electrolysis plants were also installed in Trail (1939, Canada), Cuzco (1958, Peru), Nangal (1958, India) and Alabama (1971, USA) [30].

Water electrolysis hydrogen production systems supplied by renewable energies are now attracting an increasing interest since they are considered the only ones that may obtain large amounts of sustainable hydrogen with no emission of pollutant gasses nor consumption of fossil or nuclear resources [25], [31]-[39]. For the time being, these systems are nevertheless limited to some research and development projects.

From a technological point of view, the advanced alkaline electrolyzers are at present sufficiently developed as to start the production of renewable hydrogen at significant rates. However, it is generally agreed that the massive hydrogen production required by the hydrogen economy will need electrolysis units with production capacities much higher than the ones existing now. Polymer electrolyte membrane (PEM) electrolyzers are commercially available, but their cost is high and the technology seems more suitable for low-scale applications. On the other hand, the solid oxide electrolyzers (SOEs) for hydrogen production from steam are at a R&D stage. They show great potential since the use of high-temperature heat reduces their electricity usage.

This paper reviews the current status and future trends of the production of hydrogen from water electrolysis. Emphasis is placed in the potential for using renewable energies as the primary energy source. First, the fundamentals of the electrolysis process and the configuration of the electrolysis cells are presented. Next, a section is devoted to each of the main water electrolysis technologies: alkaline, PEM and SOEs. Afterwards, the integration of hydrogen production units with renewable energies in both autonomous and grid-connected systems is discussed. Finally, some of the most relevant demonstration projects worldwide on renewable hydrogen produced from water electrolysis are described.

<sup>1</sup>Nm<sup>3</sup> means normal cubic meter, that is, 1 m<sup>3</sup> of gas at 273.15 K and 1 atm.

## II. FUNDAMENTALS OF WATER ELECTROLYSIS

### A. The principle

Water electrolysis consists of circulating a direct current through water to separate its molecules into hydrogen and oxygen [30]. The current flows between two electrodes separated and immersed in an electrolyte to raise the ionic conductivity. The electrodes have to be resistant to corrosion, have a good electric conductivity, exhibit good catalytic properties and show a suitable structural integrity. The electrolyte has to be prevented from having any change during the process, therefore it is important for it not to react with the electrodes.

The electrolysis process requires the implementation of a diaphragm or separator to avoid the recombination of the hydrogen and the oxygen generated at the electrodes. The electrical resistance of the diaphragm prevents short-circuiting the electrodes. Nevertheless, the diaphragm should have a high ionic conductivity. Finally, diaphragms have to show a high stability both physical and chemical.

The electrodes, the diaphragm, and the electrolyte are the elements that configure the electrolytic cell. The global electrolysis reaction taking place is:



In the electrolysis process, the electrons are taken or released by the ions at the electrodes surface, generating a multiphase gas-liquid-solid system. The reduction half-reaction takes place at the cathode. The electrons flow to this electrode from the outside circuit and polarize it negatively. The oxidation half-reaction occurs at the other electrode, called anode. The electrons leave the anode to the outside circuit, polarizing it positively. Hydrogen is hence generated at the cathode and oxygen at the anode.

### B. Thermodynamics

A water electrolyzer is an electrochemical device that converts electric and thermal energy into chemical energy stored in a fuel (hydrogen). The processes that happen in an electrolysis cell can be described according to the fundamentals of thermodynamics [40], [41].

When an electrolytic cell operates at constant temperature and pressure, the required energy for the water electrolysis reaction is determined by the process enthalpy change ( $\Delta H$ ). For this reaction to take place, part of the energy has to be electric. This part corresponds to the Gibbs' free energy change ( $\Delta G$ ). The rest is thermal energy ( $Q$ ) and equals the product of the process temperature ( $T$ ) and the entropy change ( $\Delta S$ ). The following expression shows the relation among these thermodynamic magnitudes:

$$\Delta G = \Delta H - Q = \Delta H - T \cdot \Delta S. \quad (2)$$

The electrolysis process is an endothermic ( $\Delta H > 0$ ) and non-spontaneous ( $\Delta G > 0$ ) chemical reaction. The reverse process occurs in fuel cells, and is exothermic ( $\Delta H < 0$ ) and spontaneous ( $\Delta G < 0$ ).

The reversible cell voltage,  $V_{rev}$ , is the lowest required

voltage for the electrolysis to take place. This voltage can be expressed as a function of  $\Delta G$  by means of:

$$V_{rev} = \frac{\Delta G}{z \cdot F} \quad (3)$$

where  $z$  is the number of electron moles transferred per hydrogen mole ( $z = 2$ ) and  $F$  is the Faraday constant, which represents the charge on one mole of electrons (96485 C/mol). If the thermal energy,  $T \cdot \Delta S$ , is provided by means of electricity, as it is the case in most commercial electrolyzers, the minimum voltage for water electrolysis to occur is known as the thermo-neutral voltage ( $V_m$ ). In an ideal electrolysis process,  $V_m$  is equal to the enthalpy voltage ( $V_{\Delta H}$ ) since the total energy required is equal to the enthalpy change ( $\Delta H$ ). In this case, both  $V_{\Delta H}$  and  $V_m$  can be obtained from the following expression:

$$V_{\Delta H} = \frac{\Delta H}{z \cdot F} \xrightarrow{\text{ideal process}} V_m = V_{\Delta H}. \quad (4)$$

However, in a real electrolysis process,  $V_m > V_{\Delta H}$ . The reason is the additional energy consumption, both electric and thermal, caused by thermodynamic irreversibilities that are mainly related to the water vapor contained in the hydrogen and oxygen flows, the lower temperature and pressure of the supply water with respect to the operation set-points, and the fact that the process is not actually adiabatic, hence entailing thermal losses due to convection and radiation [42].

At standard temperature and pressure (298.15 K and 1 atm),  $\Delta G^\circ = 237.21$  kJ/mol,  $\Delta S^\circ = 0.1631$  kJ/mol K and  $\Delta H^\circ = 285.84$  kJ/mol [43]. By substituting  $\Delta G^\circ$  and  $\Delta H^\circ$  in (3) and (4), the reversible and thermo-neutral voltages of an electrolytic cell at standard conditions are obtained:  $V_{rev}^\circ = 1.229$  V and  $V_m^\circ = 1.481$  V.

The energy consumption of the electrolysis process depends, nevertheless, on temperature and pressure. Changes in these magnitudes have an influence on the characteristic voltages ( $V_{rev}$  and  $V_m$ ). Fig. 1(a) shows the evolution of the process energy consumption at standard pressure for a temperature range from 298 to 1273 K (from 25 to 1000°C). The electric energy demanded by the electrolysis reaction,  $\Delta G$ , decreases as temperature increases; on the other hand, the thermal demand,  $T \cdot \Delta S$ , increases. In the liquid state, the total energy consumption,  $\Delta H$ , decreases slightly (between 298 and 373 K) as the temperature increases, while in the gaseous state it increases a little. It should be noted that above 373 K the latent heat of water vaporization (approximately, 40.8 kJ/mol) has to be accounted for in the total energy demand of the process. The electric energy consumption is significantly lower at high temperatures. That is the reason why steam electrolysis has such a great potential. For instance, when temperature increases from 25 to 1000°C,  $\Delta G$  decreases from 237.2 to 177.5 kJ/mol, which means a 25.1% reduction. However, a heat source with a temperature high enough is required in order to cover the thermal demand of the process. From 25 to 1000°C,  $T \cdot \Delta S$  increases from 48.6 to 112.9 kJ/mol, that is 132.3%.

Fig. 1(b) shows the influence of pressure on the energy

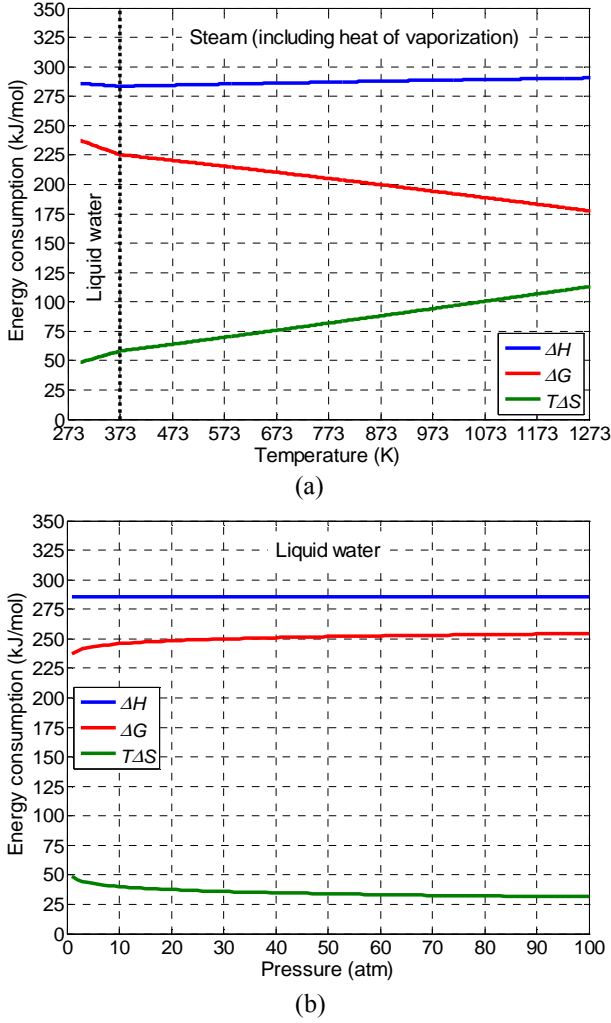


Fig. 1. Evolution of the energy consumption of an ideal electrolysis process: (a) as a function of the temperature at standard pressure (1 atm); (b) as a function of the pressure at standard temperature (298.15 K) [44].

consumption when operating at standard temperature (298.15 K). At this temperature and within the pressure range (1-100 atm), the reaction takes place in the liquid state. The electric energy demand,  $\Delta G$ , increases with a logarithmic tendency as pressure increases; more precisely, it increases 7.3% when the pressure goes from 1 to 100 atm. Contrary to the electric demand, the reaction thermal consumption,  $T\Delta S$ , decreases as the pressure rises. From 1 to 100 atm, it decreases 35.5%. The net energy consumption of the electrolysis reaction,  $\Delta H$ , remains practically constant despite the pressure increment. It hardly decreases a 0.03% if the pressure rises from 1 to 100 atm. In this respect, the increment of electric demand within the pressure range analyzed, about 17.2 kJ/mol, is compensated by the decrease in thermal demand.

### C. Electrochemistry

When a DC electric current is supplied to an electrolysis cell to produce hydrogen, the cell voltage ( $V_{cell}$ ) increases with respect to  $V_{rev}$ . This is due to the cell irreversibilities, mainly overvoltages and parasitic currents, which generate energy

losses and limit the cell efficiency.

The electrolysis cell voltage,  $V_{cell}$ , can be expressed as the sum of the reversible voltage and the additional overvoltages that appear in the cell:

$$V_{cell} = V_{rev} + V_{ohm} + V_{act} + V_{con}. \quad (5)$$

The term  $V_{ohm}$  in (5) is the overvoltage caused by the so-called ohmic losses. These losses are caused first by the resistance of several cell elements (electrodes, current collectors, interconnections, etc.) to the electrons flow. They are also consequence of the opposition to the ions flow of the electrolyte, the gas bubbles, and the diaphragm. Voltage  $V_{ohm}$  is mainly proportional to the electric current that flows through the cell. The term,  $V_{act}$ , known as the activation overvoltage, is due to electrode kinetics. The charge transfer between the chemical species and the electrodes demands energy. This energy barrier that the charge has to overcome to go from the reactants to the electrodes and vice versa highly depends on the catalytic properties of the electrode materials. It causes an overvoltage across the electrodes ( $V_{act}$ ). The anodic half-reaction produces a much higher activation overvoltage than the cathodic half-reaction.  $V_{act}$  is highly non-linear and behaves with a logarithmic tendency with respect to the electric current flowing through the cell [45].

The term  $V_{con}$ , known as concentration overvoltage, is caused by mass transport processes (convection and diffusion). Transport limitations reduce reactant concentration while increasing the concentration of the products in the interface between the electrode and the electrolyte. Usually,  $V_{con}$  is much lower than  $V_{ohm}$  and  $V_{act}$ , especially in the case of alkaline electrolysis.

The relationship between cell voltage ( $V_{cell}$ ) and current ( $I_{cell}$ ) is given by the  $I$ - $V$  characteristic curve, which characterizes the electrochemical behavior of an electrolytic cell. The  $I$ - $V$  curve is highly dependent on the electrolysis process temperature. For a given current, reversible, ohmic and activation voltages decrease as temperature increases, and so does the cell voltage. On the other hand, changes in the process pressure hardly influence on the  $I$ - $V$  curves [44], [46].

Two  $I$ - $V$  characteristic curves of an alkaline electrolysis cell for operation temperatures of 25 °C and 65°C are provided in Fig. 2 [44]. The pressure set-point is 20 bar for both curves.  $I$ - $V$  curves are commonly represented in terms of current density to make it possible to compare cells of different surface area. Reversible and thermo-neutral voltages are also shown for the same working conditions. Both  $V_{rev}$  and  $V_{tn}$  decrease as temperature increases, being  $V_{rev}$  more sensitive than  $V_{tn}$ . At the beginning, the evolution of the cell voltage with the current is logarithmic, while it becomes linear as the current increases. In the low current range of the curve, activation phenomena are predominant, while for high currents, ohmic and, to a lesser extent, concentration phenomena are also considerable. The cell voltage for any current, and consequently the cell power consumption, is lower at 65°C than at 25°C.

The  $I$ - $V$  curves show that, when the cell voltage is lower than  $V_{rev}$ , the cell current is null and the electrolysis reaction does not take place. When the cell voltage lies between  $V_{rev}$  and  $V_{in}$ , heat must be supplied for the electrolysis to occur. This thermal power is equal to the product of the voltage difference between  $V_{in}$  and  $V_{cell}$ , and the cell current  $I_{cell}$  (corresponding to the cell voltage  $V_{cell}$ ). When the cell voltage is greater than  $V_{in}$ , the power supplied to the cell is always greater than the minimum required by the process ( $V_{in} \times I_{cell}$ ) and then the electrolysis reaction takes place. Now, the cell consumes an extra power equal to the product of the difference between  $V_{cell}$  and  $V_{in}$ , and the current  $I_{cell}$ . This extra power is due to the cell losses, and becomes apparent as heat thus increasing the process temperature until the cooling system evacuates this energy.

From Faraday's law, the hydrogen production rate in an ideal electrolysis cell is proportional to the charge transfer flow, that is, to the electric current  $I_{cell}$ . Assuming that the same current flows through every electrolyzer cell, the hydrogen production rate ( $f_{H_2}$ ) in  $\text{Nm}^3/\text{h}$  can be expressed as:

$$f_{H_2} = \eta_F \frac{N_{cell} I_{cell}}{z F} \frac{22.41}{1000} 3600 \quad (6)$$

where  $\eta_F$  is the Faraday efficiency,  $N_{cell}$  is the number of cells that constitute the electrolysis module and  $I_{cell}$  is the cell current in A.

The Faraday efficiency, also known as current efficiency, can be defined as the ratio between the ideal electric charge required for the production of a given amount of hydrogen, and the real electric charge that is consumed by the electrolysis module. A Faraday efficiency lower than 1 is caused by the parasitic currents that appear in the real electrolysis process and that do not contribute to the generation of useful hydrogen. Part of the parasitic currents flows between the cells either without taking part in the oxidation and reduction half-reactions or participating in non-desired electrochemical reactions. The rest of the parasitic currents generates hydrogen but it is lost through the diaphragms of the cells.  $\eta_F$  reaches its maximum value, which is usually above 0.95, when the electrolyzer operates at rated production conditions [44], [47].

The specific energy consumption,  $C_E$ , relates the energy consumed to the hydrogen produced. It is commonly expressed in  $\text{kWh}/\text{Nm}^3$  and usually increases with the production rate [44]. Concerning only the electrolysis process,  $C_E$  can be calculated, for a given time interval  $\Delta t$ , as follows:

$$C_E = \frac{\int_0^{\Delta t} N_{cell} \cdot I_{cell} \cdot V_{cell} dt}{\int_0^{\Delta t} f_{H_2} dt} \quad (7)$$

Since the previous expression is referred to the electrolysis process, it does not consider the energy consumption of the peripherals and auxiliary equipment that may incorporate a complete hydrogen production system, such as magnetic valves, sensors, microprocessors, electrolyte cooling systems and purification units used to remove oxygen and moisture from the generated hydrogen. It does not include the losses in

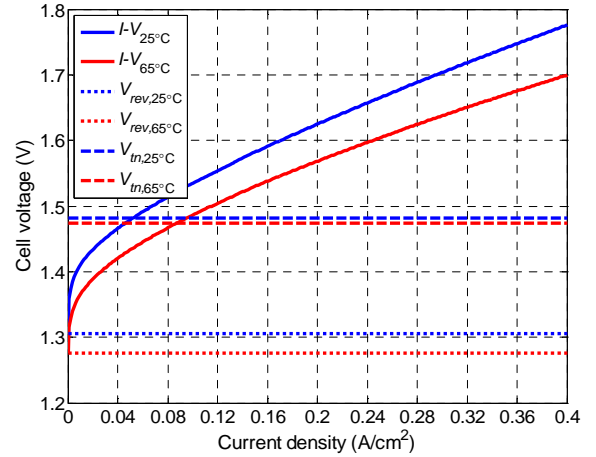


Fig. 2.  $I$ - $V$  characteristic curves of an alkaline electrolysis cell for temperatures of 25 and 65°C at 20 bar [44].

the electric power supply either. There can be also additional hydrogen losses such as the hydrogen derived to the purity sensors, the hydrogen lost in the electrolyzer water feeding system and the hydrogen leaks in valves and in the gas manifold. These additional energy consumptions and losses must be taken into account to calculate  $C_E$  for the global hydrogen production system.

Finally, another important parameter of an electrolyzer is its efficiency,  $\eta_E$ . It represents the ratio between the energy contained in the hydrogen produced and the energy needed to electrolyze the water consumed during the process. Consequently,  $\eta_E$  can be easily calculated as the ratio between the HHV of hydrogen ( $3.54 \text{ kWh}/\text{Nm}^3$ ) and the energy consumption  $C_E$  in  $\text{kWh}/\text{Nm}^3$ :

$$\eta_E = \frac{\text{HHV of } H_2}{C_E} \cdot 100. \quad (8)$$

Obviously, the efficiency can be calculated either for the electrolysis process or for the global hydrogen production system.

#### D. General characteristics of the electrolyzers

The electrolysis cell is the basic element of the electrolytic hydrogen production system. The cells are connected in parallel or in series to form the electrolysis module. This is shown in Fig. 3, where  $V_{cell}$  and  $I_{cell}$  are the voltage and current of each cell, and  $V_M$  and  $I_M$  the voltage and current of the module. When the electrolysis module is constituted by cells connected in parallel, the electrodes of each cell are connected to the corresponding power supply terminals. This configuration, in which each electrode has a single polarity, is named monopolar or unipolar. On the other hand, when the module consists of cells connected in series, the same current flows through the cells. In this case, each electrode, except for the initial and the final ones, has two polarities, positive and negative, with respect to the two cells it belongs to. This configuration is named as bipolar, and the module is also known as cell stack [30]. It is important to clarify that each bipolar electrode actually consists of two electrodes, anode (+)

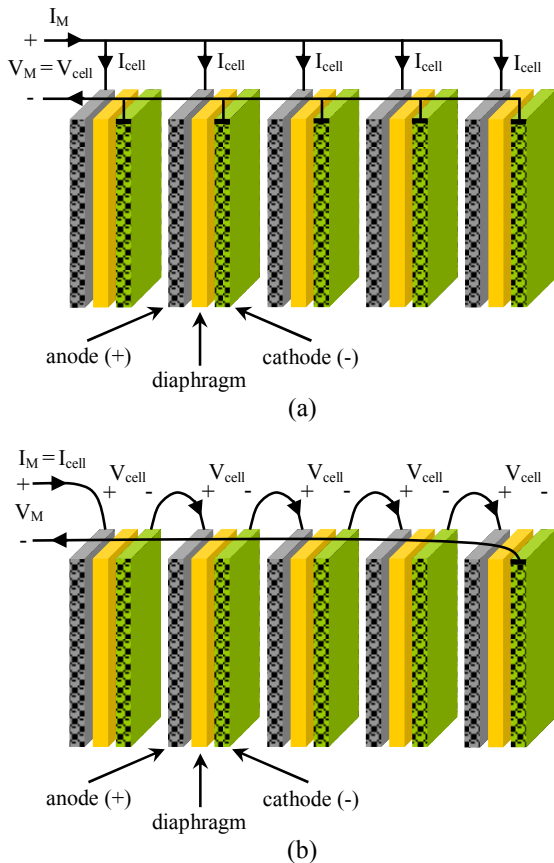


Fig. 3. Configuration of an electrolysis module: (a) unipolar module or parallel connection of cells; (b) bipolar module or series connection of cells [44].

and cathode (-), physically joined by means of a current collector, which is usually made up of wire mesh or plates (not included in the figure) of materials such as graphite and stainless steel. Finally, the electrolysis module can also have a mixed connection, with cells in series forming branches that are, in turn, connected in parallel. This connection is nevertheless hardly adopted by the manufacturers.

Assuming that all the cells of a module are the same, the voltage at the module terminals,  $V_M$ , is the sum of the voltages of the cells connected in series, and the module current,  $I_M$ , is the sum of currents flowing through the cell branches connected in parallel. Therefore, in a monopolar module,  $V_M = V_{cell}$ , while in a bipolar one,  $I_M = I_{cell}$ .

The electrolyzers that include a monopolar electrolysis module are known as tank or monopolar electrolyzers. When the module is bipolar, they are named as filter-press or bipolar electrolyzers [24], [30], [48]-[51]. Each type of electrolyzers has its own advantages and drawbacks. Monopolar electrolyzers are more simple and robust, although they require considerable space. Bipolar electrolyzers have a more complex configuration due to the joining and sealing of the cells in series, but their compact design allows them to reduce the space. Monopolar configuration requires doing several external connections that result in additional losses. In this respect, bipolar electrolyzers achieve greater current densities

per cell with respect to the monopolar ones. In addition, they have several channels, in general four per cell, where liquid electrolyte can be supplied through and flow. All these electrolyte channels as well as the series connected cells offer many paths that make flowing of internal (parasitic) currents easier. Hence, these losses are much lower in electrolyzers with monopolar module and liquid electrolyte.

Monopolar electrolyzers require a low voltage electric supply, about 1.9 to 2.5 V, and very high currents that can reach some thousand amps depending on the hydrogen production range. The voltage levels in bipolar electrolyzers depend on the number of cells connected in series. They can reach several hundred volts from cell voltages between 1.7 and 1.9 V. On the contrary, the current for the same hydrogen production rate is much lower than in monopolar electrolyzers. Besides, monopolar ones have a greater chance of having a non-uniform current distribution through each cell due to differences in the cell internal ohmic resistance. Monopolar configuration is fully modular and allows carrying out maintenance and reparation works of a cell while the others keep on operating normally. However, in the bipolar configuration, the production process has to be stopped in these situations, and in general the complete module has to be replaced. Most of the manufacturers have developed their electrolyzers from bipolar electrolysis modules since they are considered more suitable than monopolar ones for hydrogen production.

Electrolyzers can also assemble series, parallel and mixed connections of modules. Many manufacturers use a basic electrolysis module and then configure their commercial electrolyzers with several of them in order to achieve the desired production rate [30], [51]-[53].

An electrolyzer, or in general an electrolytic hydrogen production plant, includes additional equipment. The hydrogen and oxygen generated are cooled, purified, compressed and stored. In many installations, the oxygen is not stored but vented to the atmosphere instead. There are also electrolyzers that produce hydrogen at very high pressure, thus avoiding the compression stage and its economic and energy cost. Small units evacuate the excess heat generated in the electrolytic process by means of an air cooling system, whereas larger units use a water one. Water coming into the unit is previously treated so as to fulfill purity requirements to avoid mineral deposition in the cells, fast deterioration of the cell elements, and non-desired electrochemical reactions.

In general, electrolyzers are reliable devices that do not require continuous maintenance since they hardly include mobile elements. In addition, they are silent and have a high degree of modularity, what makes them suitable for decentralized applications in residential, commercial and industrial areas.

Although electrolyzers have been used for a long time, their future applications will probably often require them to be coupled to renewable energy sources in order to generate clean hydrogen and contribute to the electric grid operation. In this



respect, there is still a long way to go in many aspects such as:

- Reduction of manufacturing, distribution and installation costs.
- Efficiency improvement: electrolysis module, power supply, peripherals, control system, etc.
- Operation under variable electric supply profiles.
- Increase of the operating temperature and pressure.

### III. ALKALINE WATER ELECTROLYZERS

Alkaline water electrolysis is recognized as a mature technology; the number of units in operation by 1902 was above 400 [54]. Alkaline water electrolyzers are reliable and safe, and exhibit lifetimes that can reach up to 15 years [29], [55]; as a result, they constitute the most extended technology at a commercial level worldwide. The investment costs have been estimated to be in the range of 1000 to 5000 \$/kW depending on the production capacity [24], [56]. The main manufacturers of alkaline water electrolyzers have been compiled in Table I [52], [58], [68], [62]-[65], [57]-[69]. Most of them fabricate the bipolar modules except for the companies Avalence [58] and Sagim [68], which use monopolar cells. Alkaline electrolyzers allow significantly efficient operation with usual values in the range of around 47-82%.

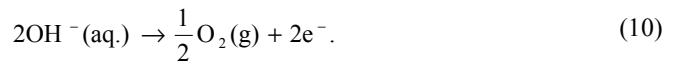
In the last years, significant advances have been achieved regarding water alkaline electrolysis mainly in two directions [30], [50], [70], [71]. On the one hand, the efficiency of the electrolyzers has been improved with the aim of reducing the operating costs associated to the consumption of electricity; on the other hand, the operating current densities have been increased in order to reduce the investment costs. It should be noted that for big units, the investment costs are almost proportional to the electrolysis cells surface area. Owing to the recent improvements, modern alkaline water electrolyzers are also known as advanced alkaline electrolyzers; some of these improvements are:

- 1) Minimization of the space between the electrodes in order to reduce the ohmic losses and allow working with higher current densities. At present, distances among the electrodes below 1 mm are typical, what is referred to as zero-gap configuration. Some manufacturers fabricate the cells with the electrodes and the diaphragm as a sole element, thus achieving a true zero gap [50], [72].
- 2) Development of new advanced materials to be used as diaphragms replacing the previous ones made of asbestos. In this regard, the use of ion exchange inorganic membranes has become widespread. Some examples are the membranes based on antimony polyacid impregnated with polymers [73], a porous composite composed of a polysulfone matrix and  $ZrO_2$  (Zirfon<sup>®</sup>) [74], and separators based on polyphenyl sulfide (Ryton<sup>®</sup>) [24].
- 3) Development of high-temperature alkaline water electrolyzers. Working temperatures up to 150°C increase the electrolyte conductivity and promote the kinetics of the electrochemical reactions on the electrodes surface.
- 4) Development of advanced electrocatalytic materials to

reduce the electrode overvoltages. The anode is specially challenging because the oxidation half-reaction is most demanding; cobalt oxides are being considered for this electrode.

The operating principle of an alkaline water electrolysis cell is illustrated in Fig. 4. The cell consists of 2 electrodes separated by a gas-tight diaphragm. This assembly is immersed in a liquid electrolyte that is usually a highly concentrated aqueous solution of KOH, of the order of 25-30 wt.%, to maximize its ionic conductivity. Typical operating temperatures range from 65 to 100°C [75]. Other possible electrolytes such as solutions of NaOH or NaCl are less commonly used. The main and obvious drawback of the alkaline electrolyte is its corrosive character.

Hydrogen gas evolves from the cathode, where water is reduced according to (9) yielding hydroxide anions that circulate across the diaphragm to the anode within the electric field established by the external power source. The hydroxide anions recombine on the surface of the anode according to (10) to produce oxygen that bubbles towards the gas manifold liberating electrons that close the electric circuit.



The evolution of the gaseous products from the electrodes is critical because a significant overvoltage concentration can be originated that reduces the electrolysis efficiency. In order to facilitate gas bubbling, the electrodes should be carefully designed to maximize the interfacial contact area with the liquid electrolyte. To this end, it is important that the electrodes have a porous texture and show many perforations. As concerns the electrolyte, it is shown under working conditions that a convective recirculation is established, as illustrated in Fig. 4, by virtue of the internal gradients of temperature and the liquid conveyed by the evolving gases. The movement of the liquid has beneficial effects. First, it helps the homogenization of the concentrations of the chemical species inside the pores of the electrodes. It facilitates, moreover, the evolution of gaseous products, and increases the heat transfer rate allowing an effective refrigeration of the electrolysis module. Advanced alkaline electrolyzers are the most suitable for large-scale hydrogen production. Some manufacturers (see Table I) fabricate units with very high production capacities in the 500-760 Nm<sup>3</sup>/h range, corresponding to electric power consumptions of about 2150-3534 kW [62]-[65]. The production rate is in practice limited to 25-100% of the nominal range in order to prevent operating at conditions that could potentially lead to the formation of flammable gas mixtures [76], [77]. On the other hand, the maximum allowable current density is about 0.4 A/cm<sup>2</sup>. As concerns the temperature, the operating range is typically between 5 and 100°C depending on the model, although some prototypes can reach 400°C [78]. Regarding the electrolysis pressure, there are models operating at atmospheric pressure [62], [66], whereas others can reach up to 448 bar [58].

Table I: Main Electrolyzer Manufacturers and Performance Data

Manufacturer	Technology (configuration)	Rated production (Nm <sup>3</sup> /h) <sup>a</sup>	Rated power (kW) <sup>b</sup>	Specific energy consumption (kWh/Nm <sup>3</sup> ) <sup>c</sup>	Efficiency (%) <sup>d</sup>	Maximum pressure (bar)	Hydrogen purity (vol.%)	Location	Ref.
AccaGen	alkaline (bipolar)	1-100	6.7-487	6.7-4.87 <sup>e</sup>	52.8-72.7	10 (optional 30 and 200 <sup>f</sup> )	99.9 (99.999 <sup>g</sup> )	Switzerland	[57]
Avalence	alkaline (monopolar)	0.4-4.6 (139 <sup>f</sup> )	2-25 (750 <sup>f</sup> )	5.43-5 <sup>h</sup>	65.2-70.8	448	n.a.	USA	[58]
Claind	alkaline (bipolar)	0.5-30	n.a.	n.a.	n.a.	15	99.7 (99.999 <sup>g</sup> )	Italy	[59]
ELT	alkaline (bipolar)	3-330	13.8-1518	4.6-4.3 <sup>h</sup>	76.9-82.3	atmospheric	99.8-99.9	Germany	[60]
ELT	alkaline (bipolar)	100-760	465-3534	4.65-4.3 <sup>h</sup>	76.1-82.3	30	99.8-99.9	Germany	[60]
Erredue	alkaline (bipolar)	0.6-21.3	3.6-108	6-5.1 <sup>e</sup>	59-69.8	2.5-4	99.3-99.8 (99.999 <sup>g</sup> )	Italy	[61]
Giner	PEM (bipolar)	3.7	20	5.4 <sup>i</sup>	65.5	85	n.a.	USA	[82]
Hydrogen Technologies, division of Statoil	alkaline (bipolar)	10-500	43-2150	4.3 <sup>h</sup>	82.3	atmospheric	99.9 (99.999 <sup>g</sup> )	Norway	[62]
Hydrogenics	alkaline (bipolar)	10-60	54-312	5.4-5.2 <sup>e</sup>	65.5-68.1	10 (optional 25)	99.9 (99.998 <sup>g</sup> )	Canada	[52]
Hydrogenics	PEM (bipolar)	1	7.2	7.2 <sup>e</sup>	49.2	7.9	99.99	Canada	[52]
H2 Logic	alkaline (bipolar)	0.66-42.62	3.6-213	5.45-5 <sup>e</sup>	64.9-70.8	4 (optional 12)	99.3-99.8 (99.999 <sup>g</sup> )	Denmark	[63]
Idroenergy	alkaline (bipolar)	0.4-80	3-377	7.5-4.71 <sup>h</sup>	47.2-75.2	1.8-8	99.5	Italy	[64]
Industrie Haute Technologie	alkaline (bipolar)	110-760	511.5-3534	4.65-4.3 <sup>h</sup>	76.1-82.3	32	99.8-99.9	Switzerland	[65]
Linde	alkaline (bipolar)	5-250	n.a.	n.a.	n.a.	25	99.9 (99.998 <sup>g</sup> )	Germany	[66]
PIEL, division of ILT Technology	alkaline (bipolar)	0.4-16	2.8-80	7-5 <sup>e</sup>	50.6-70.8	1.8-18	99.5	Italy	[67]
Proton OnSite	PEM (bipolar)	0.265-30	1.8-174	7.3-5.8 <sup>h</sup>	48.5-61	13.8-15 (optional 30)	99.999	USA	[53]
Sagim	alkaline (monopolar <sup>e</sup> )	1-5	5-25	5 <sup>h</sup>	70.8	10 <sup>j</sup>	99.9	France	[68]
Teledyne Energy Systems	alkaline (bipolar)	2.8-56	n.a.	n.a.	n.a.	10	99.999	USA	[69]
Treadwell Corporation	PEM (bipolar)	1.2-10.2	n.a.	n.a.	n.a.	75.7	n.a.	USA	[83]

n.a.: not available.

<sup>a</sup>Gas production rates are commonly given in normal cubic meters per hour (Nm<sup>3</sup>/h) and kilograms per hour (kg/h): 1 Nm<sup>3</sup>/h = 0.0899 kg/h.

<sup>b</sup>Rated power has been obtained either directly from the manufacturers, when the data is available, or as the product of third and fifth columns (rated production and specific energy consumption, respectively).

<sup>c</sup>Specific energy consumption has been obtained either directly from the manufacturers, when the data is available, or as the ratio between fourth and third columns (rated power and rated production, respectively).

<sup>d</sup>Efficiency has been calculated as the ratio between the HHV of hydrogen (3.54 kWh/Nm<sup>3</sup>) and the specific energy consumption (fifth column).

<sup>e</sup>Module configuration by series-connected monopolar cells.

<sup>f</sup>In development.

<sup>g</sup>The manufacturer indicates that the specific energy consumption refers to the global hydrogen production system.

<sup>h</sup>The manufacturer does not indicate if the specific energy consumption is exclusively of the electrolysis process (module) or it refers to the global hydrogen production system.

<sup>i</sup>The manufacturer indicates that the specific energy consumption refers only to the electrolysis process (module).

<sup>j</sup>Pressurization with internal compressor, not by isothermal process inside the electrolysis module.

<sup>k</sup>With an additional purification system (to remove oxygen and water vapor from the produced hydrogen gas).

Nevertheless, the maximum electrolysis pressure is typically close to 25-30 bar. Interestingly, this pressure is sufficiently high to avoid one of the compression stages when hydrogen is to be stored as compressed gas. Higher pressures do not offset because the investment costs increase significantly as well as the risks of formation of hazardous gas mixtures [77].

The purity levels of hydrogen and oxygen can reach 99.9 and 99.7 vol.%, respectively, without auxiliary purification equipment [29], [55], [71]. On the other hand, the water fed to the electrolyzer has to be significantly pure, with an electric conductivity below 5 μS/cm in order to protect the electrodes and operate safely [52].

#### IV. PROTON EXCHANGE MEMBRANE ELECTROLYZERS

The use of ion exchange polymers in electrochemical applications dates back to the end of the '50s in the USA coinciding with the aerospace race. By 1966, General Electric developed the first water electrolyzer based on the proton conducting concept using a polymer membrane as the

electrolyte; in 1978 it began to commercialize the first water electrolyzers of this type [79], [80]. This technology is also referred to as polymer electrolyte membrane (PEM), proton exchange membrane, and, less frequently, as solid polymer electrolyte (SPE) [80], [81]. At present, there are very few companies manufacturing PEM electrolyzers, as can be noticed in Table I [52], [53], [82], [83]. This is mainly due to their limited production capacity, short lifetime and comparatively high investment cost [24], [55], [56], [84].

In PEM electrolyzers, the electrolyte is a gas-tight thin (below 0.2 mm in thickness) polymeric membrane with a cross-linked structure and strongly acid character due to the presence of functional groups of the sulfonic acid (–SO<sub>3</sub>H) type. These groups are responsible for the proton (H<sup>+</sup>) conducting ability of the materials through an ion exchange mechanism [85]. As for the PEM fuel cells, the most commonly used membrane for water electrolysis is Nafion (a DuPont trademark [86]).

The modules of the PEM electrolyzers almost invariably



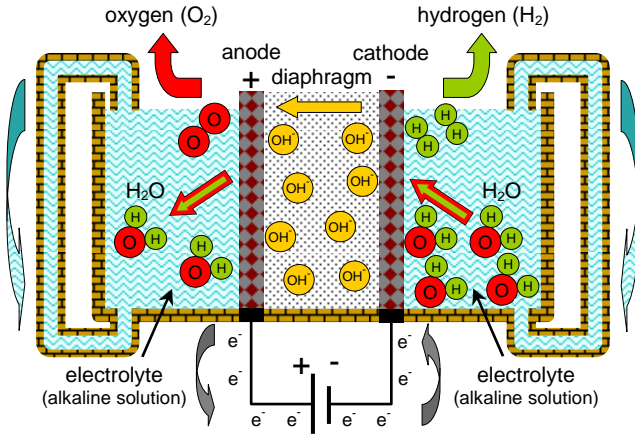
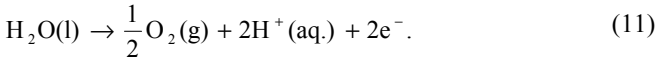


Fig. 4. Scheme of the operating principle of an alkaline electrolysis cell [44].

adopt a bipolar configuration in which the electrical connection between cells is carried out by means of bipolar plates that also play an important role in the evacuation of the generated gases. The anode, cathode and membrane set constitute the so-called membrane electrode assembly (MEA). The electrodes typically consist of noble metals such as platinum or iridium [79].

The operating principle of a PEM water electrolysis cell is shown in Fig. 5. At the anode, water is oxidized according to (11) to produce oxygen, electrons, and protons that circulate across the membrane to the cathode where they are reduced according to (12) closing the circuit and producing hydrogen that bubbles towards the cathodic gas manifold:



As indicated in Table I, PEM electrolyzers are commercially available for low-scale production applications. Maximum hydrogen throughput is in the order of 30 Nm<sup>3</sup>/h with a power consumption of 174 kW [53]. In contrast with alkaline electrolyzers, the practical production rate of PEM electrolyzers covers practically the full nominal range [52], [53]. These devices can operate at current densities that are quite higher than their alkaline counterparts, achieving values even above 1.6 A/cm<sup>2</sup> [24]. Their efficiencies range from 48 to 65%, approximately. The presence of the polymeric membrane limits the electrolysis temperatures to values usually below 80°C. Some models reach pressures up to 85 bar [82]. This is due to the compact character of the electrolysis modules as well as the structural properties of the MEAs, which can endure big pressure differences between the electrode compartments. This enables e.g. production of hydrogen at 35 bar and oxygen at atmospheric pressure thus avoiding the hazards of handling high-pressure oxygen [24], [87].

The hydrogen purity, higher than in alkaline electrolyzers, is typically above 99.99 vol.% (in some cases up to 99.999 vol.%) without the need of auxiliary equipment [88]. Moreover, the very low gaseous permeability of the polymeric

membranes lowers the risk of formation of flammable mixtures; hence to operate at very low current densities is permissible. The electric conductivity of the water fed to the electrolyzer has to be below 1 μS/cm [53].

An interesting feature of PEM electrolyzers is their ability to work under variable power feeding regimes. This is due to the fact that the proton transport across the polymeric membrane responds quickly to power fluctuations. This is in contrast with alkaline electrolyzers, where the ionic transport in liquid electrolytes shows a greater inertia [24].

Although commercially available, PEM electrolyzers have some drawbacks that require special attention in the short-term. The main problem is perhaps their high investment costs, mainly associated to the membranes and the metal noble-based electrodes. PEM electrolyzers exhibit, moreover, shorter lifetimes than the alkaline technology. Finally, their hydrogen production capacity will have to increase significantly in the future [79].

## V. SOLID OXIDE ELECTROLYZERS

Solid oxide electrolyzers (SOEs) constitute an advanced concept enabling water, or rather, steam electrolysis at high temperatures (600-900°C), which results in higher efficiencies compared to alkaline or PEM electrolyzers [89]. Nevertheless, this concept is not new; pioneering work on solid oxide electrolyte steam electrolysis dates back to the end of the '60s mainly in the USA and Germany [90]. It is also relevant that much of the information available on SOEs has been obtained working with solid oxide fuel cells (SOFCs) operated in the reverse mode [89], [91].

The operating principle of a SOE cell is shown in Fig. 6. Both steam and recycled hydrogen are fed to the cathode, where water is reduced to produce hydrogen according to (13). The oxide anions generated in the cathode pass through the solid electrolyte to the anode, where they recombine according to (14) forming oxygen and closing the circuit with the released electrons:

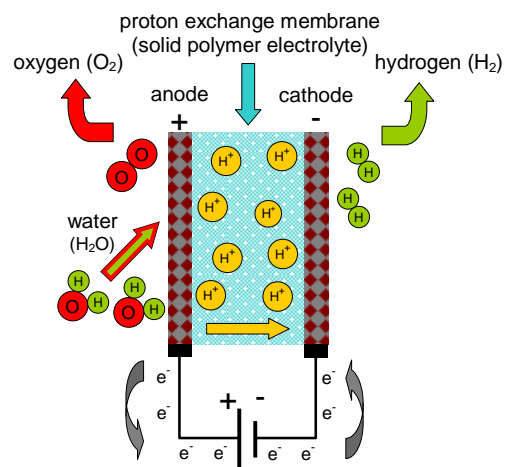
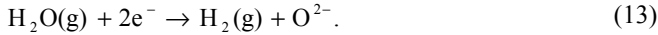


Fig. 5. Scheme of the operating principle of a proton exchange membrane (PEM) electrolysis cell [44].



These reactions evolve with the electrodes in contact with a gas or vapor phase, which is in clear contrast with the processes taking place on the electrodes of the alkaline or PEM electrolyzers and makes the issue of maximizing the interfacial area in contact between the electrodes and the gaseous chemical species challenging [92]. This is the reason of the porous character of the SOEs' electrodes. As for SOFCs, a gas-tight thin film of yttria ( $\text{Y}_2\text{O}_3$ )-stabilized zirconia ( $\text{ZrO}_2$ ) (YSZ) is typically used as the solid oxide electrolyte. This material exhibits good ionic conductivity at the prevailing high operating temperatures through a mechanism that involves the oxygen vacancies present in the mixed oxide lattice. The cathode is a cermet usually consisting of nickel and YSZ. The anode is commonly a composite of YSZ and perovskites such as lanthanum manganites ( $\text{LaMnO}_3$ ), ferrites ( $\text{LaFeO}_3$ ) or cobaltites ( $\text{LaCoO}_3$ ) partially substituted with strontium in order to promote structural and electronic defects that increase the electrocatalytic activity [93]-[96].

Steam electrolysis emerged with the aim of reducing the energy intensiveness, and so, the operating costs of conventional liquid water electrolysis [97]. This fact can be understood on the basis of thermodynamic considerations as explained in section II.B. Indeed, whereas the total energy demand of the water splitting reaction increases only very slightly as the temperature increases, the electrical energy demand decreases significantly. This means that the proportion of the required energy that can be supplied in the form of heat increases with electrolysis temperature. To give an idea, the thermo-neutral cell voltage ( $V_m$ ) increases from 1.48 to 1.52 V if the temperature goes from 25 to 1000°C. However, within that temperature range, the reversible cell voltage ( $V_{rev}$ ) decreases from 1.23 to 0.91 V. As a result, theoretically up to 40.1% of the energy required to produce hydrogen from steam electrolysis at 1000°C can be supplied as heat at that temperature [89].

The features of the SOEs operation make this technology very attractive to produce hydrogen when a high-temperature heat source is available. This is the reason of the interest of the nuclear energy sector on steam electrolysis in view of the capability of the high-temperature gas cooled nuclear reactors to act as a heat source at temperatures up to 950°C [98]-[101]. Interestingly, it has been shown that renewable sources such as geothermal energy have potential as a heat source for steam electrolysis [102].

Whereas high-temperature operation reduces the cell voltages and increases the rate of the electrochemical reactions, it implies remarkable challenges as concerns thermal stability of the materials and sealing issues. Moreover, the stream leaving the cathode is a mixture of hydrogen and steam that requires further processing which results in significantly higher capital costs of SOEs compared to conventional liquid

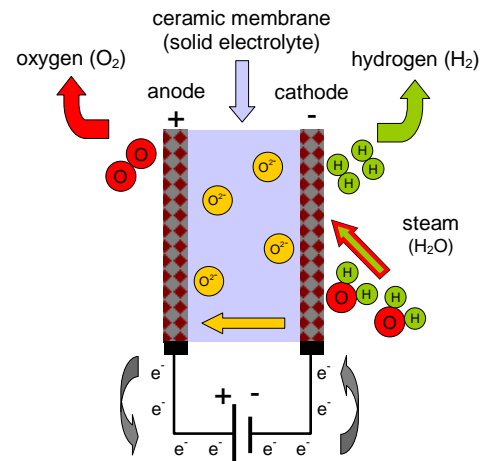


Fig. 6. Scheme of the operating principle of a solid oxide (SOE) electrolysis cell [44].

water electrolysis. As a matter of fact, although the target value established by the Department of Energy of the US for the investment cost of an electrolyzer is 170 \$/kW, values of up to 1000 \$/kW are considered in current economic models because large scale production of SOEs is still not mature [103]. It has been reported that it will take at least 10 years until SOEs are fully available [104]. As regards the reduction of the investment costs, it is noteworthy the advancements made on the use of proton-conducting ceramics such as some strontium zirconates instead of the oxide-conducting YSZ. These ceramics exhibit protonic conductivity at intermediate temperatures, in the order of 700°C, and advantageously pure hydrogen is obtained from the cathode, thus simplifying the steam electrolysis plant [105]. In this case, the electrochemical reactions at the electrodes are the same than in the PEM electrolyzers. This new concept is considered to have a great long-term potential.

At present, SOEs are at the R&D stage. Work is being carried out at several centers such as the Japan Atomic Energy Agency (JAEA), Idaho National Laboratory (INL, USA), European Institute for Energy Research (EIFER, Karlsruhe, Germany), and Institute of Nuclear and New Energy Technology (INET, Beijing, China). Companies as Westinghouse Electric Co. (USA), Dornier System GmbH (Germany), Lurgi GmbH (Germany), Toshiba Corporation (Japan), and Ceramatec Inc. (USA) are also active in this field. Much of the data reported have been obtained with tubular cells either as single cells or stacks formed by several cells connected in series. In this cell configuration, a ceramic tube of *e.g.* calcia ( $\text{CaO}$ )-stabilized zirconia (CSZ) is used as support. Typical dimensions of the tube are 12-13 mm in inner diameter, 1-1.5 mm in thickness, and up to 1 m in length. A thin (below 0.25 mm) porous layer of a lanthanum perovskite is applied on the outer surface of the support to act as the anode. The anode is covered with a very thin layer of electrolyte (YSZ, about 0.04 mm in thickness) which in turn is finally coated with a layer (0.1 mm thick) of Ni/YSZ cermet acting as the cathode. This cell configuration has allowed

obtaining 17.6 NI/h of hydrogen at 1000°C, 0.4 A/cm<sup>2</sup> and 39.3 W of applied power. A stack consisting of 1000 electrolysis cells produced up to 600 NI/h of hydrogen [99]. This steam electrolysis technology is characterized by high overvoltages produced by the high ohmic losses prevailing at interconnections between cells. Concentration overvoltages due to diffusional transport limitations of steam are also high. In recent years, self-supporting planar steam electrolysis cells are attracting great attention [89], [106]. Contrary to tubular cells, the planar ones enable the fabrication of more compact stacks resulting in improved hydrogen production rates [99].

The main current obstacle for the industrial application of SOEs is the limited long-term stability of the electrolysis cells [89]. Solid oxide cell degradation is faster in electrolyzers than in fuel cells. Some of the problems that have been identified are electrolyte aging and electrode deactivation. The R&D efforts should focus on this issue in the short term.

## VI. RENEWABLE HYDROGEN PRODUCTION AND DEMONSTRATION PROJECTS

### *A. Integration of hydrogen production units with renewable energies in both autonomous and grid-connected systems*

Hydrogen can be produced from the electric energy generated by wind and photovoltaic systems in many different applications [88], [107]. They can be divided into autonomous and grid-connected applications, denoted in what follows off-applications and on-applications, respectively. Off-applications are those in which electrolyzers and renewable systems are not connected to the main electric grid. In these applications, the produced hydrogen is completely renewable. Depending on the elements of the autonomous system, two main configurations, denoted here as off-1 and off-2, can be adopted for these applications.

In the off-1 configuration, wind and photovoltaic systems are coupled with the electrolyzers to produce only hydrogen. In this configuration, the operating conditions of the electrolyzers are highly fluctuating since they are imposed by the variability of the wind and solar resources. The connection to the renewable systems can be carried out by means of a DC/DC power conditioning stage in the photovoltaic case and an AC/DC or DC/DC for the wind systems. These conversion stages make it possible to condition the currents and voltages generated by the renewable systems into proper values for the electrolyzers. In addition, the maximum power of the renewable systems can be tracked at each moment. However, the high currents and low voltages at which electrolyzers operate, as well as the intermittency of renewable resources, reduce the efficiency of the power conversion stages at values as low as 70%. In order to avoid this, a direct connection of the electrolyzer to the renewable system, without power conditioning, is sometimes adopted. As regards photovoltaic systems, this involves designing the photovoltaic generator in such a way that its  $I$ - $V$  characteristic curves fit in with those corresponding to the electrolyzer. In wind systems, a DC electric machine is required to make a direct coupling possible.

Research on the off-1 configuration has been carried out mainly theoretically and by simulation, and has focused primarily on photovoltaic systems [55], [108]-[116].

The second configuration (off-2) that can be adopted for autonomous systems incorporates hydrogen storage tanks and fuel cells in order to supply energy to loads connected to small grids placed in remote areas where the main grid is not accessible. In these systems, the surplus renewable energy not consumed by the loads is used to produce hydrogen. This hydrogen is stored and later used to feed the fuel cells when the loads demand more energy than the one provided by the renewable sources. The surplus hydrogen can also be used in other applications, such as house heating, fuel cell vehicles, etc. The power conditioning system has to be able to control the energy flow between the renewable sources, the loads, the electrolyzers and the fuel cells. In general, this configuration includes a hybrid combination of wind and photovoltaic generators, thus achieving a higher utilization factor of the complete system. The off-2 configuration has been studied in the scientific literature mainly by simulation and in combination with other energy storage means such as batteries, ultracapacitors and flywheels [117]-[126].

Unlike the off-applications, the on-applications are characterized by the fact that the electrolyzers and renewable systems are both connected to the grid [127]-[133]. Three main configurations can be adopted in on-applications, denoted here as on-1, on-2 and on-3. In the on-1 configuration, the electric energy generated by the renewable system is directly injected into the grid at every moment. The electrolysis system is driven with a constant operating profile which is related to the average electric energy supplied by the renewable system and then does not include its variations. This way the electrolyzer can operate at steady-state with no dependence on the wind speed or solar radiation variability. The electric grid acts as a virtual storage tank that smoothes the electricity generated by the renewable system. The capacity factor of the electrolysis system can come close to 100%, thus decreasing the hydrogen production costs. The main drawback is that, strictly speaking, the hydrogen generated is not completely renewable since the electrolyzer is allowed to operate when the energy supplied by the renewable system is lower than the permanent operating point or even zero.

In the second configuration (on-2) of grid-connected applications, the electrolysis system is only fed with the energy generated at each moment from the wind farm or photovoltaic plant. The hydrogen produced is therefore completely renewable. The electric energy exceeding the electrolysis system capacity is injected into the grid. The operation of the electrolyzers is subject to the intermittency of the renewable systems, what decreases the capacity factor. An electrolyzer facility, having been sized to process the anticipated electricity of a particular renewable system, will be underutilized much of the time, and its capacity factor will be inescapably low. However, this is not necessarily unacceptable. Low capacity factors are commonplace wherever there are supply

intermittencies, such as many installations processing perishable commodities.

Increasing penetration of wind especially, but also photovoltaic energy, arises new problems partly related to the grid integration of a highly variable energy source. From the point of view of the integration of renewable energies, hydrogen production systems and electric grid, the third configuration (on-3) is perhaps the most interesting one. In this configuration, the electrolysis system helps the grid operation by participating in the instantaneous adjustment between the energy produced by the renewable plants and the energy demanded by the loads connected to the grid. In doing so, the hydrogen systems can contribute to the implementation in wind farms and photovoltaic plants of grid operation services such as the primary and secondary regulations. Electrolysis systems can also give support to the management of renewable plants to meet their power forecast. Fuel cells can improve this configuration and even make the system completely manageable and predictable. In this configuration, the capacity factor of the electrolysis system depends on the grid operation service for which the system is designed.

Apart from the traditional classification between autonomous and grid-connected applications, there is a third interesting application, which is the distributed generation of electric energy by means of microgrids [134]-[138]. These microgrids can operate either independently from the grid or supporting weak grids which are connected to the main grid. Depending on the microgrid characteristics, hydrogen energy systems, including also storage tanks and fuel cells, can be highly useful in this scenario, in which additional elements such as batteries, ultracapacitors and diesel generators can also be used.

### B. Demonstration projects

There are relatively few demonstration projects worldwide on the integration of electrolytic hydrogen production systems with renewable energies. However, in recent years a number of them have been started in the USA, Canada, Germany, Italy, Norway, Finland, UK, Japan, and Spain [139], [140]. Most of the projects involve either autonomous systems isolated from the electric grid or systems consisting of microgrids. The renewable source is mainly photovoltaic although in some of them, wind energy or both are considered. The electrolyzers are most frequently of the alkaline type working at atmospheric pressure, intermediate pressures (4-30 bar), and even very high pressure (448 bar). A variety of electric powers (0.8-111 kW) and hydrogen storage procedures (compressed gas, liquid, and as metal hydrides) are considered. Fuel cells of the PEM, alkaline, and phosphoric acid type are included in the projects. Regarding the use of hydrogen, some cases employ it for transport and also to feed fuel cells to produce electricity that returns to the system. Electric conversion stages and their management vary remarkably among studies. The simplest cases disregard the conversion structures because the renewable sources are directly connected to the electrolyzers. The facilities and results obtained in these projects are

reported in [141]-[159].

As concerns the demonstration projects involving grid-connected systems, there are two relevant examples that merit special attention. The first one named Wind2H2 is being developed by the US National Renewable Energy Laboratory (NREL) and Xcel Energy [160]. One of its aims is to analyze several configurations for grid integration of hydrogen, photovoltaic, and wind systems. The project includes a 10 kW photovoltaic solar array, two wind turbines of 10 and 100 kW, two PEM electrolyzers of 1.05 Nm<sup>3</sup>/h each, an alkaline electrolyzer of 5.6 Nm<sup>3</sup>/h, a hydrogen storage system in pressurized tanks (around of 1300 Nm<sup>3</sup> at 241 bar), and a 50 kW hydrogen-fueled internal combustion generator. With the aim of improving costs and efficiency, the performance of a complete renewable electrolysis system is evaluated, and particularly the operation of hydrogen technologies under variable power feeding regimes. The second one is being carried out in the Sotavento's wind farm (Galicia, Spain) [161]. The main objective is the use of hydrogen as a means of renewable energy storage in order to optimize the coupling of a wind farm to the electric grid. In this case, the alkaline electrolyzer, with a 60 Nm<sup>3</sup>/h rated production, is partly fed by the wind farm, which has a rated power of 17.56 MW. The hydrogen produced is later combusted in a 55 kW generator to inject electricity into the grid. The hydrogen storage consists of pressurized bottles, achieving a maximum capacity of 1725 Nm<sup>3</sup> at 200 bar.

## VII. CONCLUSION

Water electrolysis has the potential to play a key role in a future energy model based on two energy carriers: electricity and hydrogen. This is because the renewable energy sources, mainly hydropower, wind, and photovoltaic, can be easily coupled with water electrolysis processes producing clean and sustainable hydrogen.

Presently, alkaline and polymer electrolyte membrane (PEM) electrolyzers are commercially available. Both are safe and reliable but only alkaline electrolyzers have a sufficiently large capacity to produce energy at significant rates. Nevertheless, their production capacity has to considerably increase in the long-term to satisfy the massive demand of hydrogen that will occur in a hydrogen economy. Sensible reductions of the investment and operating costs are also necessary for both alkaline, and specially PEM electrolyzers. In this regard, an advanced concept such as solid oxide electrolyzers (SOEs) is attracting great attention in recent years. These devices allow producing hydrogen through electrolysis of high temperature steam. In this case, a significant part of the energy required by the electrolysis can be supplied in the form of high-temperature heat instead of electricity, which is more expensive. SOEs are currently at the R&D stage and much effort is still required to improve the performance and lifetime of these electrolysis units.

Sustainable hydrogen production from water has also a great potential as a tool to facilitate the integration of renewable

energies in both autonomous and grid-connected systems. Several configurations are possible, resulting in different balances between the cost and the renewable character of the produced hydrogen. The interesting results obtained in a number of demonstration projects give evidence of the suitability of water electrolysis to become the main route for producing renewable hydrogen in the future.

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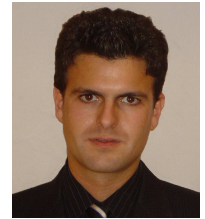
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