

CHAPTER 9

Electrochemical hydrogen generation

Ali Keçebaş^a, Muhammet Kayfeci^b, Mutlucan Bayat^c

^aDepartment of Energy Systems Engineering, Muğla Sıtkı Koçman University, Muğla, Turkey

^bDepartment of Energy Systems Engineering, Karabük University, Karabük, Turkey

^cDepartment of Mechanical Engineering, Karabük University, Karabük, Turkey

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9.1 Introduction

The electrochemical hydrogen production has been widely investigated for decades, largely driven by the potential to reduce environmental effect, satisfy distributed demand, reduce hydrogen cost, and enhance public perception. As an alternative to steam methane reforming for hydrogen production, these approaches have enjoyed renewed vigor over the last several years. Renewable sources contribute about 5% of the total hydrogen production. Various ways of producing hydrogen from electrochemical technologies include: proton exchange membrane electrolysis, alkaline electrolysis (AEL), and high-temperature electrolysis process. These technologies are still in the developmental phase. In this chapter, electrochemical hydrogen producing methods are given in detail.

AEL is the oldest and only commercially available technology. For each electrolyzer cell, there are two electrodes, one positive and one negative, and an electrolyte sandwiched in between. In the case of alkaline electrolyzer with electrodes made of metals, most commonly Ni, Co, Fe, or Pt/C, the electrolyte would be liquid KOH and the two electrolyzer chambers are divided by a diaphragm (e.g., NiTiO₃/NiO). This technology is the most energy intensive one and produces hydrogen of the lowest purity [1].

Polymer exchange membrane (PEM) electrolyzers, or as they are often called solid polymer electrolyzers (SPE) are based on reversed PEM fuel cell technology. They can operate at the same temperature as alkaline electrolyzers or higher (in the case of high-temperature PEM) and generally achieve better efficiency. They are about to become commercially available in the near future. PEM electrolyzers can be viewed as an incremental development of alkaline electrolyzers. The main difference is that they use a more advanced diaphragm (i.e., polymer membrane) [2].

Solid-oxide electrolyzers are the least commercially developed technology. They operate at much higher temperatures than the other technologies, and consume much less electricity due to superior energy conversion efficiency. However, due to high-temperature operation, special materials are required to withstand the conditions of the process. As regards the plant, there are no promising products available that provide long-term hassle-free operation of the accessories. The technology, besides offering the highest faradic efficiency, also offers a possibility of direct electrolyzing of CO_2 . Apart from that, the technology can extend to co-electrolyzing H_2O and CO_2 simultaneously. The product of such co-electrolysis is syngas, which can then be reprocessed to yield synthetic fuel. For this reason, solid oxide electrolyzers offer the possibility of chemical energy storage/carrier when converting renewable energy or excess energy from fossil power plants to hydrogen or syngas [3–6].

9.2 Hydrogen production from water electrolysis

The simplest method for hydrogen production is electrolysis method, which is the separation process of water into hydrogen and oxygen, by being used of direct current. In principle, in an electrolysis cell, there are two electrodes, which are usually planar metal or carbon plates, and a conductive liquid called electrolyte into which they are immersed. The current will flow from the positive electrode (anode) to the negative electrode (cathode) in the conductive liquid when the direct current source is connected to these electrodes. As a result, the water in the electrolyte will decompose into the hydrogen released from the cathode, and the oxygen released from the anode. In response to the decomposition of the water here, a substance such as potassium hydroxide is usually added to the electrolyte as conductivity enhancer since the water is not a good conductor. Electrochemical reactions are given as follows:

The efficiency of the electrolysis can be increased by reducing the dissociation voltage for a given current value. The voltage drop process should be also adjusted so that the surface of the electrode accelerates the electrolysis process. One of the methods developed is the coating of fine powdered platinum pieces onto any metal base. However, other electrode surfaces can also be used due to the fact that platinum is a very expensive metal. Nickel-plated steel electrodes are used in the electrolysis cells used in practice. The effective areas of the electrodes, and therefore the electrolysis process rate are increased by placing porous nickel strips on a wire mesh. The investigations continue on the electrode structures and placement arrangements to obtain higher efficiency from the electrolysis process. In industrial electrolysis cells, two types of electrode arrangement are usually made as the tank type. The economics of hydrogen production depends on the efficiency of the method used and can be expressed as the ratio of the output energy in the hydrogen to the input. The efficiency of the hydrogen production via the electrolysis is only 80% when the electricity is considered. However, the heat efficiency of this electricity generation varies from about 34% in light water reactors to 50% in advanced systems

and is on the average about 25%–40%. Despite their low efficiency, these systems are extremely vital because of the fact that they have no negative impact on the environment and use solar energy.

The water is composed of 11.2% of hydrogen. The purest hydrogen is obtained by this method constituting a significant part of world hydrogen production. This method of the hydrogen production widely used in the 1950s is now very rarely applied. In the water electrolysis, reactions occur in the opposite direction of the reactions in a fuel cell. Electrolysis is usually classified according to the electrolyte used.

In PEM water electrolysis, gold, platinum, platinum-palladium, and iridium are used as a base material on the anode and cathode electrode, respectively, which are very expensive. Hence, the manufacturing cost of the PEM electrolyzer is higher than other electrolysis device. Furthermore, the electrolysis efficiency of the PEM electrolyzer is quite low when compared with the other electrolysis processes. Hence alkaline electrolyzer is well-known and widely used electrolysis system is since it is capable of overcoming all these problems. This electrolyzer works on low temperature (average 80°C). If solution increases in electrolyzer, it can work more on high temperatures. Despite being a very new technology compared to alkaline electrolytes, it has the lower efficiency. A third type of electrolyzer device has high temperature in which a ceramic ion-conducting electrolyte is used, and its efficiency is very high. High-temperature electrolyzer is the newly developed technology. This kind of electrolyzers are not widely commercialized but have been developed in laboratory scale. Potential advantages are higher temperature, high efficiency, low material cost because temperature, options to working reverse as fuel cell or electrolyzer mode [7–10]. PEM devices have begun to be used in small factories where particularly variable productions are done, but PEM electrolyzer scaled-up in the recent years and are available up to 2 MW, with alkaline being available for a size of 6 MW [11]. Large businesses prefer alkaline systems. Although hydrogen is obtained by reversing the operation of PEM fuel cells, the conditions of electricity generation and the hydrogen production are greatly different.

9.2.1 PEM electrolyzers

The basic structure and operating principle of a PEM-based electrolyzer is shown in Fig. 9.1. The system consists of polymer membrane allowing only protons to pass, anode catalyst layer in which the water is decomposed by an electrochemical reaction and the oxygen is formed, cathode catalyst layer in which hydrogen is formed, and electrode layers that take on task of the transmission and removal of liquids and gases to the catalyst surfaces at the same time in which the electricity is applied. The water taken into the cell through the anode inlet dissociates into hydrogen ion (H^+ , Proton) and oxygen gas in the anode catalyst layer. While the oxygen gas is given from the anode outlet to outside, the hydrogen ion receives electrons in the cathode catalyst layer by crossing

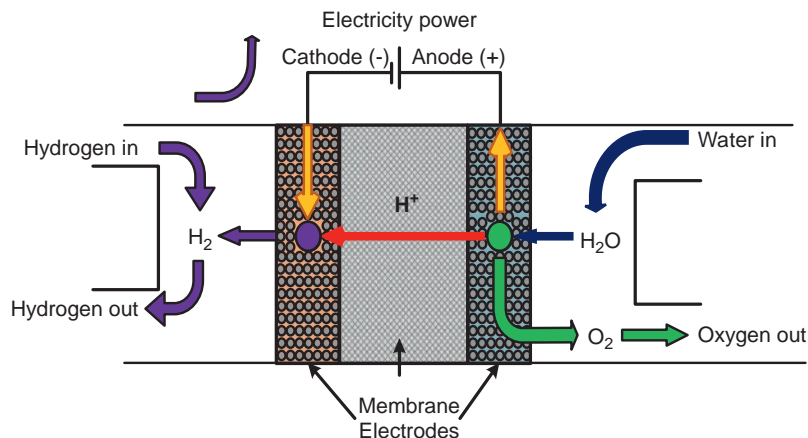
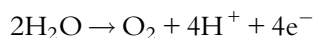


Fig. 9.1 The working principle of PEM electrolyzer.

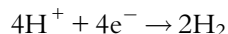
through the Nafion membrane, and converts into the hydrogen gas. The reactions occurring in this process are given in the following:

Anode reaction:



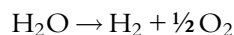
The oxygen is obtained as a result of the above reaction with the effect of the ruthenium, iridium catalyst layer on the membrane surface in the anode region. Hydrogen migrates to the cathode region by giving electrons (H^+), too. Due to the structure of the Nafion membrane, some water migration takes place in this transition.

Cathode reaction:



By the electricity supplied to the cell, the hydrogen ions in the cathode region by taking electrons, hydrogen gas is obtained as the product.

Total reaction:



As a total reaction product in the cell, the oxygen is obtained in the anode region, and hydrogen in the cathode region. Some of the electricity given for the electrolysis is converted into the heat energy due to the ohmic, concentration, and activation losses in the cell, thus the cell temperature rises. As the water circulation occurs in the cell in the PEM electrolyzer, the problem of overheating disappears. However, depending on the water flow used for cooling, and the heat transfer conditions, the temperature in the cell increases at a certain level. This increase in the temperature improves reaction kinetics and positively affects the performance. However, as the temperature increases, the corrosion of metallic particles in the cell also accelerates.

For this reason, keeping the cell temperature in the range of 40–60°C is suitable for both the performance and life.

9.2.1.1 The reaction mechanism in PEM electrolyzers

Electrochemical reactions in PEM electrolyzers occur on anode and cathode catalyst layers. Under normal conditions, 1.229 V is sufficient to theoretically separate the water into oxygen and hydrogen molecules. However, extra voltage (overvoltage) is required because of the realization of anode and cathode reactions and losses. In a typical PEM electrolyzer, most of the overvoltage voltage losses are due to the anode in which the oxygen-induced reaction occurs [12]. For a high-performance PEM electrolyzer, the catalysts that keep the overvoltage losses to a minimum are needed to be selected.

9.2.1.2 The I–V characterization of PEM electrolyzers

In Fig. 9.2, the polarization curve of a PEM electrolyzer is given. As it is seen in the figure, no current is drawn when the theoretical voltage (1.48 V) is applied to the system. In order to be able to be drawn of current from the electrolyzer (reaction speed), the operating voltage is needed to be greater than the theoretical voltage (voltage loss). The voltage loss is due to the activation, ohmic, and concentration losses depending on the drawn current. The details of these losses are given below. The reaction speed at the electrode surface in the PEM electrolyzer is related to the speed of the current. The electrolysis does not perform at the theoretical voltage, but it is necessary to apply a voltage above the theoretical voltage to the system in order to perform anode and cathode reactions. The applied extra voltage is called the loss of activation.

Electrolyzer electrical model:

A very high-voltage drop is observed when the input voltage is applied to the PEM cell. These declines are characterized by reversible decline V_{rev} , activation losses V_{act} ,

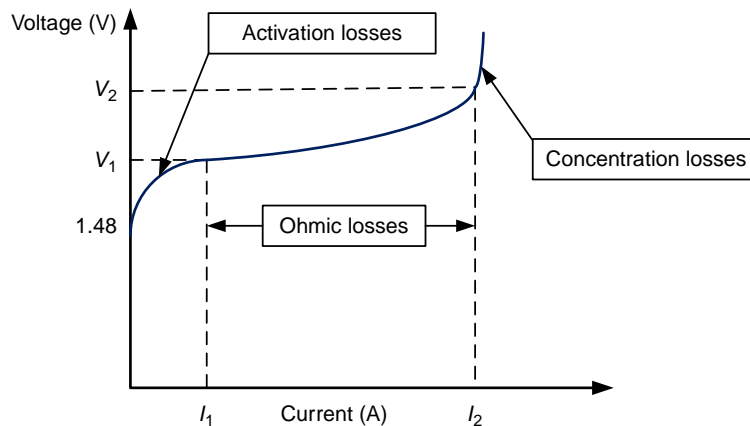


Fig. 9.2 The polarization curve of PEM electrolyzer.

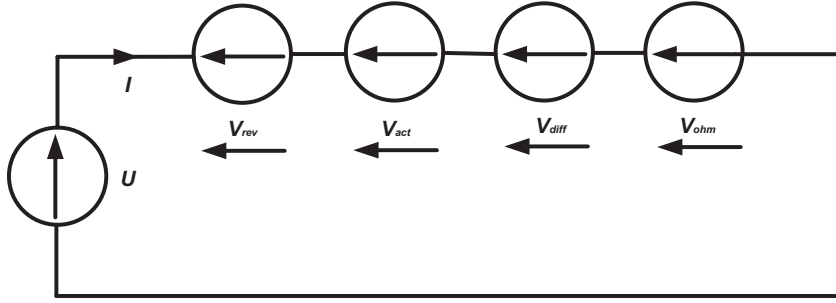


Fig. 9.3 The electric circuit of PEM electrolyzer.

diffusion losses V_{diff} and ohmic losses V_{ohm} . These losses are influenced by the nonlinear changes of the current. The electrical scheme is given in Fig. 9.3.

According to the figure, the following equation can be written by the law of electric circuit:

$$U = V_{rev} + V_{act} + V_{diff} + V_{ohm}$$

In order to be able to create a steady-state electrical model, each voltage drop must be examined individually.

Reversible voltage:

This voltage drop occurring from chemical redox reactions is called also as open-circuit voltage. If the current is not drawn ($I = 0$), the reversible voltage indicates the cell potential. The reversible voltage, V_{rev} is calculated from Gibbs energy and can be determined by the NERST equation as follows:

$$V_{rev} = V_0 + \frac{RT}{2F} \ln \left(\frac{P_{H_2} P_{O_2}^{1/2}}{a_{H_2O}} \right)$$

where universal gas constant, $R = 8.314 \text{ J/mol K}$, Faraday constant, $F = 96487 \text{ C/mol}$, $V_0 = 1.23 \text{ V}$ the reversible voltage, the water activity, $a_{H_2O} = 1$ (liquid), P_{H_2} is hydrogen partial pressure, and P_{O_2} is oxygen partial pressure.

Loss of activation voltage:

Activation voltage losses shown with electrochemical kinetic behaviors are due to proton transfer and chemical reaction rate. Activation voltage losses, V_{act} can be determined by Butler-Volmer and Tafel's laws [4]. As a function of the current, V_{act} can be written for the electrolyzer as follows:

$$V_{act} = \frac{RT}{\alpha nF} \ln \left(\frac{I}{I_0} \right)$$

where α is the transfer coefficient and I_0 is the variation current.

Diffusion voltage losses:

Fluid (gas and water) concentration near the electrodes and the diffusion affects the existing current values. It affects the present values of close diffusion of electrodes. The diffusion behavior changes depending on the partial pressure and the chemical reaction rates. This change causes to the diffusion losses, V_{dif} . The diffusion equation, V_{dif} proposed by Fontes [13] for the PEM fuel cells can be given as

$$V_{dif} = \frac{R T}{\beta n F} \ln \left(1 + \frac{I}{I_{lim}} \right)$$

where β and I_{lim} are the constant coefficient and the limit of the diffusion current, respectively.

Ohmic voltage losses:

The main reason for ohmic losses is the selective polymer membrane, R_{mem} . The resistance value is usually given by empirical equations proposed by Springer et al. As it is given in the equation, the selective membrane, R_{mem} is a function of area A_m (cm²), membrane thickness, l_m (cm), hydration rate l_m (if $l_m = 7$ dry, if $l_m = 14$ good hydration, if $l_m = 22$ wet), and the temperature T given below is

$$R_{mem} = \frac{I_m}{A_m \cdot (0.005139 \lambda_m + 0.00326) \exp \left(1267 \left(\frac{1}{303} - \frac{1}{T} \right) \right)}$$

Ohmic losses can be given as follows:

$$V_{ohm} = R_{mem} I = \frac{I_m}{A_m (0.005139 \lambda_m + 0.00326) \exp \left(1267 \left(\frac{1}{303} - \frac{1}{T} \right) \right)} I$$

Electrical model:

The electrical model can be written by putting the voltage losses in its place in the equation, as follows:

$$U = V_0 + \frac{R T}{2 F} \ln \left(\frac{P_{H_2} P_{O_2}^{1/2}}{a_{H_2O}} \right) + \frac{R T}{a 2 F} \ln \left(\frac{I}{I_0} \right) + \frac{R T}{\beta n F} \ln \left(1 + \frac{I}{I_{lim}} \right) + R_{mem} I$$

If the hydrogen flow is given as (mol/s):

$$F_{H_2} = \frac{I}{2 F}$$

Thermal model:

The electrolyzer cell temperature is affected by the relationship between U and I . In order to form the temperature behavior and thermal model, all heat sources are defined.

Four basic heat sources are assumed. These are the chemical reaction (entropy), chemical component thermodynamics (gas and water), the outside ambient temperature T_a , and Joule effect caused by the current. The heat energy conservation principle has been used to form a thermal model. The thermoneutral cell voltage $V_{th} = 1.48$ V has been used to be able to be calculated the chemical reaction heat energy. This voltage remains constant or varies slightly with the temperature effect. Furthermore, the Joule effect is neglected and the temperature, T_a is assumed to be constant. The thermal model can be written as a continuous dynamic equation:

$$V_{th} = \frac{\Delta H}{2F}$$

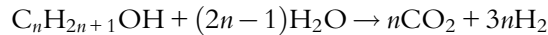
$$C_p \frac{d(T - T_a)}{dt} = (U - V_{th})I - h(T - T_a)$$

where C_p (J/K) stands for the total heat capacity of the electrolyzer, h (W/K) for the total heat input of the electrolyzer, u ($U - V_{th}$) for the heat transfer rate generated by the chemical reaction (from entropy energy), I for the ambient temperature, and $h(T - T_a)$ for the heat transfer rate caused by the flow.

With assumptions u , $x = (T - T_a)$, and $y = x$ is the dynamic thermal model input, and the state and output values, respectively. In the continuous case, the state and output equations are given by the first-order linear dynamic model:

$$\begin{cases} \frac{dx}{dt} = -\frac{h}{C_p}x + \frac{1}{C_p}u \\ y = x \end{cases}$$

In the general case of a saturated monoalcohol, the corresponding overall electrolysis reaction in a direct alcohol PEMEC, considering the complete oxidation of alcohol into CO_2 , is as follows:



From this cell reaction, the following calculation can be made to determine the standard proton exchange membrane cell voltage, U_{cell}^0

$$\Delta G_r^0 = n\Delta G_f^{\text{CO}_2} + 3n\Delta G_f^{\text{H}_2} - (2n - 1)\Delta G_f^{\text{H}_2\text{O}} - \Delta G_f^{\text{C}_n\text{H}_{2n+1}\text{OH}}$$

Here ΔG_r^0 is the standard Gibbs free energy of the electrolysis reaction, ΔG_f^i is the free energy of the alcohol formation under standard conditions. The determination of the standard free energy changes for the electrolysis reaction. We can calculate the standard cell voltage for different alcohol formation. The voltage is a cell:

$$U_{cell, alcohol}^0 = \Delta G_r^0 / nF$$

Here n is the electron number of reactions, and F is the Faraday constant (96485.33 sA/mol). The thermodynamic data related to different fluent, including some polyols, lead to relative standard cell voltages for the electrolysis reaction (Table 9.1) much lower

Table 9.1 Electrical properties of fluids of the PEM electrolyzer [18]

Fluid	ΔG_r^0 (kJ/mol)	ΔH_r^0 (kJ/mol)	U_{cell}^0	U_{cell}^{th}	N_{H_2} (mol)
Water (H ₂ O)	237.2	285.8	1.229	1.481	1
Methanol (CH ₃ OH)	9.0	131.3	0.016	0.227	3
Ethanol (CH ₃ -CH ₂ OH)	97.6	348.0	0.084	0.301	6
Ethylene Glycol (CH ₂ OH-CH ₂ OH)	25.5	460.0	0.026	0.477	5
Glycerol (CH ₂ OH-CHOH-CH ₂ OH)	4.0	342.9	0.0029	0.254	7

than that obtained for the water electrolysis (i.e., c.0.1 V for alcohols vs. 1.229 V for water). It could be expected that hydrogen can be produced at an acceptable cost.

9.2.1.3 Materials of PEM electrolyzers

The, by far, most commonly used membranes for PEM water electrolysis are perfluor-sulfonic acid membranes. These consist of a perfluorinated polymeric backbone (polytetrafluoroethylene) having ether bonded perfluorinated side branches. These side branches are terminated with sulfonic acid groups. The most well-known membrane in the PFSA family is the Nafion[®] membrane from DuPont.

The anode electrocatalyst is in PEM electrolyzers most often an oxide of a noble metal like iridium or ruthenium or mixtures thereof. It is clear that RuO₂ has the highest activity toward oxygen evolution since it has the lowest overpotential. However, RuO₂ is not stable in the oxygen evolution reaction, it is further oxidized to its highest oxidation number, Ru(VIII), RuO₄ is a liquid at room temperature. IrO₂ on the other hand is less active toward the oxygen evolution reaction but it is far more stable [14], so it has been used extensively on its own [15–17] or in order to stabilize the RuO₂ [14] as a mixed oxide with ruthenium Ir_xRu_{1-x}O₂ [15, 19, 20]. Other mixed oxides have also been used such as Ir_xSn_{1-x}O₂, Ir_xTa_yO₂, Ir_xRu_yTa_zO₂, and Ir_xRu_{1-x}MO_yO_z [16, 17]. The addition of Ta₂O₅ to mixed oxides of Ir_xRu_yTa_zO₂ or Ir_xTa_yO₂ does not seem to have a significant negative influence on the performance. Cheng et al. [20] found that adding molybdenum oxide to Ir_{0.4}Ru_{0.6}O₂ improved the performance in real PEM electrolysis testing. An Ir_{0.4}Ru_{0.6}Mo_xO_y with a Mo content of 40 mol% of the total metal content had a cell voltage of 40 mV lower than Ir_{0.4}Ru_{0.6}O₂ at 1 A cm⁻² [20], at higher current densities the difference was even more pronounced with approximately 150 mV at 2 A cm⁻², Cheng et al. explained the improvement in performance with the similar particle size of the Ir_{0.4}Ru_{0.6}Mo_xO_y compared to Ir_{0.4}Ru_{0.6}O₂, hence increasing the effective catalytic active area of the anode. Table 9.2 summarizes the MEA characteristics, MEA performance and electrolysis testing temperatures for the different anode catalysts described above.

On the cathode the electrocatalyst is very often Pt, either as Pt-black or as supported Pt on carbon (Pt/C). A commonly used catalyst support is Vulcan XC-72R carbon,

Table 9.2 MEA performance and electrolysis temperature for different anode catalysts

References	Anode (mg cm ⁻²)	Cathode (mg cm ⁻²)	Electrolyte	U (V) 1 A cm ⁻²	Temp. (°C)
Marshall et al. [21]	IrO ₂ (2)	Pt (0.4)	Nafion [®] 115	1.61	80
Marshall et al. [21]	Ir _{0.8} Sn _{0.2} O ₂ (2)	Pt (0.4)	Nafion [®] 115	1.65	80
Marshall et al. [21]	Ir _{0.2} Sn _{0.8} O ₂ (2)	Pt (0.4)	Nafion [®] 115	1.78	80
Mayousse et al. [19]	IrO ₂ (2.5)	Pt (0.4)	Nafion [®] 115	2.3	RT
Mayousse et al. [19]	Ir _{0.7} Sn _{0.3} O ₂ (2.5)	Pt (0.4)	Nafion [®] 115	2.39	RT
Mayousse et al. [19]	Ir _{0.5} Sn _{0.5} O ₂ [2.5]	Pt (0.4)	Nafion [®] 115	2.43	RT
Cheng et al. [20]	Ir _{0.4} Ru _{0.6} Mo _x O _y (1.5)	Pt (0.4)	Nafion [®] 1035	1.61	80
Cheng et al. [20]	Ir _{0.4} Ru _{0.6} O ₂ (1.5)	Pt (0.4)	Nafion [®] 1035	1.65	80
Marshall et al. [21]	Ir _{0.6} Ru _{0.2} Ta _{0.2} O ₂ (2)	Pt (0.4)	Nafion [®] 115	−1.60	80
Marshall et al. [21]	Ir _{0.8} Ru _{0.2} O ₂ (2)	Pt (0.4)	Nafion [®] 115	−1.60	80

Table 9.3 MEA performance and electrolysis temperature for different cathode catalysts

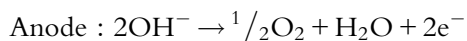
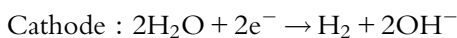
References	Cathode (mg cm ⁻²)	Anode (mg cm ⁻²)	Electrolyte	U [V] 1 A cm ⁻²	Temp. (°C)
Millet et al. [23]	Co(dmg) (1)	Ir black [2.5]	Nafion [®] 115	—	90
Millet et al. [23]	Co(dmg)/C (1)	Ir black [2.5]	Nafion [®] 115	~2.1	90
Millet et al. [23]	Pt(1)	Ir black [2.5]	Nafion [®] 115	~1.8	90
Millet et al. [23]	α-H ₄ SiW ₁₂ O ₄₀ (0.8)	Ir black [2.5]	Nafion [®] 115	~1.84	90
Millet et al. [23]	Pd/C 40 wt% (0.7)	Ir black [2.0]	Nafion [®] 115	~1.7	90
Millet et al. [23]	Pt/C 40 wt% (0.7)	Ir black [2.0]	Nafion [®] 115	~1.68	90
Grigoriev et al. [22]	Pd/C 40 wt% (0.7)	Ir black [2.4]	Nafion [®] 115	~1.7	90
Grigoriev et al. [22]	Pt/C 40 wt% (0.7)	Ir black [2.4]	Nafion [®] 115	~1.68	90
Grigoriev et al. [24]	Pt/GNF 40 wt% (0.8)	Ir black [2.0]	Nafion [®] 115	1.67	90
Grigoriev et al. [24]	Pt/C 40 wt% (0.8)	Ir black [2.0]	Nafion [®] 115	1.72	90

which is carbon black with a very high surface area. The high surface area combined with the high electronic conductivity of carbon gives it excellent properties for a catalyst supporting material. The content of Pt in Pt/C varies from 20 wt% [21] to 70 wt%. Other support materials tested for the electrocatalyst of the electrolyzer cathode are graphitic nanofibers (GNFs) [22] and multiwalled carbon nanotubes (MWCNT) [18]. Other tested cathode electrocatalysts are: Pd/C, RuO₂, Pt-Ir, Pt/TiO₂-MWCNT, Co-Ru/TiO₂-MWCNT, Co-Ru-Pt/TiO₂-MWCNT, Co-Pt/TiO₂-MWCNT, Pt/GNF, and Pt-Pd/GNF [22–25]. Also carbon black supported palladium Pd/C has shown reasonable activity. In Table 9.3 the MEA data, MEA performance and electrolysis testing temperatures are summarized for the different cathode materials compared above [25].

9.2.2 Alkaline electrolyzer

Alkaline water electrolysis has a long history in the chemical industry. Its application for energy conversion in the hydrogen energy system is attracting attention, and advanced electrolyzers have been developed. The direction of development is toward higher efficiency by applying high-temperature and high-pressure operation. Although some successful results have been reported so far, whether this system can be actually used or not depends on the development of its competitors, SPE water electrolysis, or high-temperature steam electrolysis (HTE).

The principle of the alkaline water electrolysis is quite simple. Oxygen and hydrogen are separated from the water when the direct current is applied to the water, as shown in the equations.



Two water molecules dissociate and hydrogen arises at the cathode by this reaction. At the anode, oxygen arises and a water molecule is generated at the same time (Fig. 9.4). As a result, when a water molecule dissociates, another water molecule moves to the anode. Alkaline electrolyzers contain caustic water solution and 25%–30% of potassium hydroxide (KOH). Sodium hydroxide (NaOH) and sodium chloride (NaCl) are used as the catalyst. The liquid electrolyte allows ions to be transported between the electrodes and is not consumed in the chemical reaction, but is periodically replenished depending on the losses in the system. AEL devices are the most commonly used hydrogen generators in the industry. The hydrogen production becomes pure with 99%. After certain purification processes, it is possible to reach the high purity rates required for hydrogen fuel cells. The efficiency of the hydrogen production is approximately 80%. Potassium hydroxide is used in the rate of 25%–30% as electrolyte for the electrolysis. They become more effective when operated at low current densities (0.3 A/cm^2). In commercial alkaline electrolyzers, the current density range is $100\text{--}400 \text{ mA/cm}^2$. The disadvantages are also high corrosive effect of liquid electrolyte used in high-temperature values. For this reason, they have a very short lifetime.

As mentioned above, the electrolyte should separate the produced gases from each electrode, but with a liquid electrolyte as KOH, it is necessary to use a separator or diaphragm. This should fulfill the same requirements as a solid electrolyte. The most common diaphragm in alkaline electrolysis cells (AECs) has historically been made of porous white asbestos ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$), but there are several drawbacks by using a white asbestos diaphragm, the obvious being its toxicity leading to asbestosis and lung cancer. In a basic solution, the corrosion rate of white asbestos is dependent on temperature—higher temperatures leading to faster corrosion—which means that increasing the efficiencies of

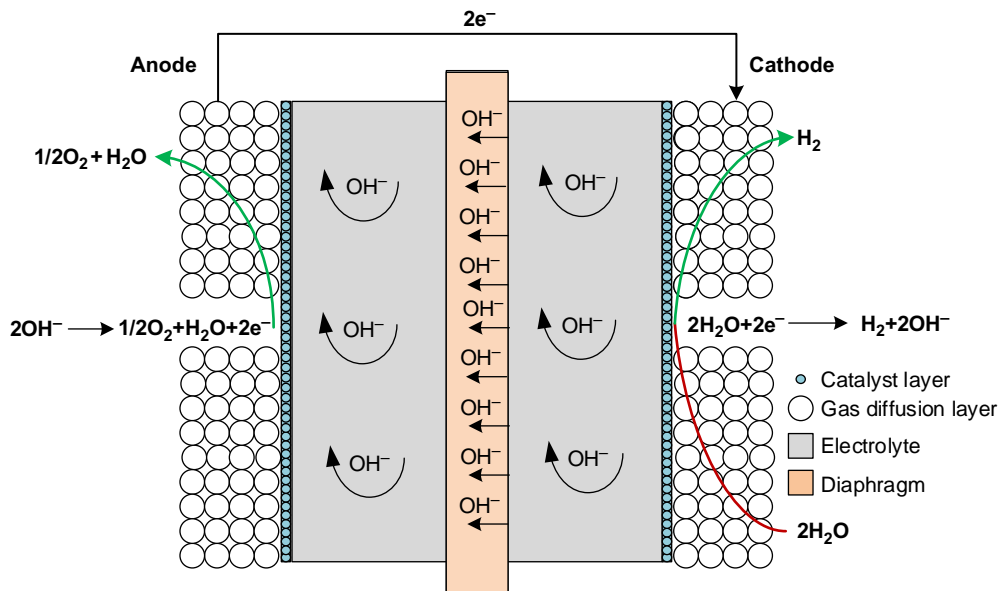


Fig. 9.4 The alkaline electrolyzer.

the electrolyzer by elevating the temperature is a problem when using this kind of diaphragm [26].

Due to these issues other materials have been tested for use as diaphragms, for example, composite of potassium titanate (K_2TiO_3) fibers and polytetrafluoroethylene (PTFE), polyphenylene sulfide, PTFE (as felt and as woven), polysulfone, and asbestos coated with polysulfone [26]. During the last decade or so considerable amount of research has been put into developing hydroxide conducting polymers suitable for alkaline water electrolysis [27]. Recently Li et al. reported very promising results with a hydrocarbon-based polymeric membrane in a zero gap (i.e., zero distance between electrodes and electrolyte) AEC with 4-M NaOH feed to both electrodes. They reached 1 A cm^{-2} at 2.12 V with no decline in performance observed during a 10-day durability test. For electrodes the most common materials used are steel plates with some kind of Ni treatment. It could, for instance, be Ni-plating, since nickel is corrosion resistant in alkaline media and because it is a fairly low-cost metal. Different metals like cobalt, iron, and vanadium are used as additives to the electrodes. Cobalt is added to the anode, while iron and vanadium are used at the cathode. It was found that iron and vanadium can reactivate the cathode. The reactivation of the cathode is promoted by ions of iron or vanadium in solution rather than metal incorporated in an alloy. The deactivation of the cathode is ascribed as a formation of nickel hydride, which iron and vanadium can reverse [25, 27–32].

The reversible potential, E_r (equilibrium potential, namely theoretical voltage of electrolysis) is given by following equation:

$$E_r = E_0 - \frac{RT}{2F} \ln \frac{P}{P_0}$$

where E_0 is the standard equilibrium potential, R is the gas constant, T is the absolute temperature, P_0 and P are the vapor pressure of pure water and electrolyte, respectively. E_0 is given by $\Delta G^\circ/2F$, ΔG° is the increment of Gibbs free energy and F is the Faraday constant (96519.4 coulomb), which is 1.226 V under 298 K and 1 atm. This is slightly higher than the decomposition voltage of pure water under the same condition. Electricity required to produce 1 Nm³ of hydrogen is, from Faraday's law, 2393 Ah. As this reaction proceeds almost quantitatively, the minimum energy required is 2.94 kWh for 1 m³ of hydrogen. Since E_r is theoretical equilibrium potential, actual cell voltage needed to continue the reaction is higher with the addition of ohmic loss of electrolyte and diaphragm and overvoltage (overpotential) by electrode reaction. Assuming that the same current flows through every electrolyzer cell, hydrogen production rate can be expressed as

$$f_{H_2} = \eta_f \frac{N_{cell} I_{cell}}{zF} \frac{22.41}{1000} 3600$$

where f_{H_2} is the hydrogen production rate in Nm³/h, N_{cell} is the number of electrolyzer cell, and I_{cell} is the current of cell in ampere. Fig. 9.5 shows the measured reversible and thermoneutral voltage and current characteristics of the alkaline water electrolysis cells in 20 bar pressure. Voltage decreases as temperature increases with current characteristics of the AEL, V_{rev} being more sensitive than V_{tn} . The cell voltage for any current, and consequently the cell power consumption, is lower at 65°C than at 25°C the hydrogen production rate for commercial systems is 0.25–760 Nm³/h and operation temperature is typically between 5°C and 100°C depend on the electrolyzer model and KOH solution in water. In some special system, operating temperature can be high as 400°C. The operating pressure varies between atmospheric pressure and 448 bar. But yet, the maximum operating pressure is typically systems between 25 and 30 bar [33].

The hydrogen production prices for low-temperature AEL were estimated to be 1.6–5 €/kg H₂ (when applying the H2A economic analysis methodology, developed by US Department of Energy-Hydrogen Program, the production price was estimated to be 4.5 €/kg, based on the year 2000 dollars and exchange rates), based on a low electricity price of 1.4–3.7 €/kWh [34, 35].

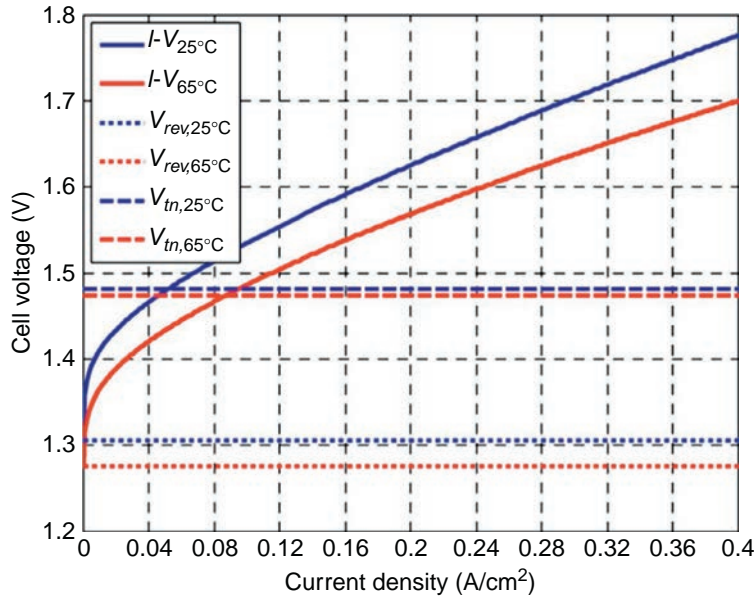


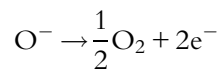
Fig. 9.5 The voltage-current characteristics of the alkaline cell.

9.2.3 High-temperature electrolysis

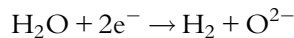
High-temperature electrolysis continues to be an efficient alternative for the hydrogen production as industrial. High temperature can be used for heat recovery systems such as, in this method, solid electrolytes operate at a few hundred degrees centigrade according to the system while oxide or proton conductors are being used. The advantages of the high-temperature electrolysis over the water electrolysis are that it provides a mostly improved reaction kinetics and less loss in reactions called electrode reactions.

High-temperature steam electrolyzers are very similar to high-temperature fuel cells. As it is mentioned earlier, these systems can be considered as a form working in reverse to each other. As it is shown in Fig. 9.6, the cathode (mostly Ni and a single cermet containing a ceramic oxide) consists of electrolyte (SrCeO_3 as protonic conductor) and anode portions (mostly single ceramic oxide).

Anode reaction:



Cathode reaction:



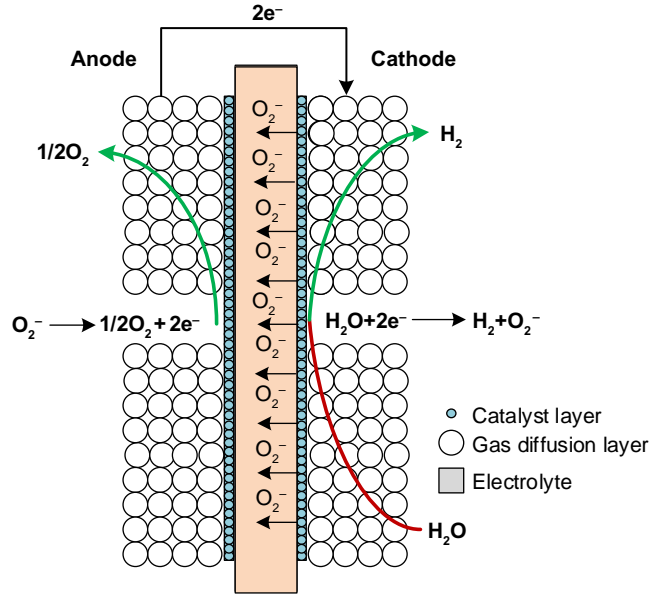


Fig. 9.6 The schematic representation of a solid oxide electrolysis cell.

Fig. 9.7 shows the electrical energy and thermal energy requirement as temperature of electrolysis process increases. The operating temperature range varies between 700°C and 1000°C . In high-temperature electrolyzer cells, gas diffusion is applied for SOEC. The most investigated electrode cells are Ni-YSZ-based cells.

The main parameters of the three type of water electrolyzer technologies are summarized in Table 9.4. AEL represents the most mature technology, having been commercial available for over a century. It has the lowest specific investment and maintenance costs. The low gas crossover rate of the polymer electrolyte membrane (yielding hydrogen with high purity), as described in Table 9.5, allows for the PEM electrolyzer to work under a wide range of power input (economical aspect). This is due to the fact that the proton transport across the membrane responds quickly to the power input, not delayed by inertia as in liquid electrolytes. As discussed above, in alkaline electrolyzers operating at low load the rate of hydrogen and oxygen production reduces while the hydrogen permeability through the diaphragm remains constant, yielding a larger concentration of hydrogen on the anode (oxygen) side thus creating hazardous and less efficient conditions [37].

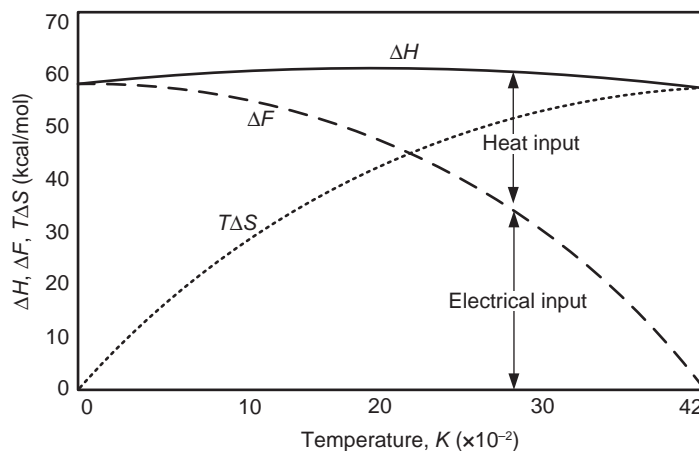


Fig. 9.7 Energy splits for water decomposition as a function of temperature in the high-temperature electrolysis (HIE) process [36].

Table 9.4 Main parameters of three type of electrolyser [38–40]

Parameters	AEL	PEMEL	SOEL
Electrode	Ni/Fe	Noble metals (Pt, Ir)	Ni-doped ceramic
Cell temperature ($^{\circ}\text{C}$)	60–90	50–80	700–1000
Typical pressure (bar)	10–30	20–50	1–15
Current density (A/cm^2)	0.2–0.6	1.0–2.0	0.3–1.0
Load flexibility (% of nominal load)	20–100	0–100	–100/ + 100
Cold start-up time	1–2 h	5–10 min	Hours
Warm start-up time	1–5 min	< 10 s	15 min
Nominal stack efficiency (LHV)	63–71%	60–68%	100%
Specific energy consumption (kWh/Nm^3)	4.2–4.8	4.4–5.0	3
Nominal system efficiency (LHV)	51–60%	46–60%	76–81%
Specific energy consumption (kWh/Nm^3)	5.0–5.9	5.0–6.5	3.7–3.9
Max. nominal power per stack (MW)	6	2	<0.01
H_2 production per stack (Nm^3/h)	1400	400	<10
Cell area (m^2)	< 3.6	< 0.13	<0.06
Life time (kh)	55–120	60–100	(8–20)
Efficiency degradation (%/a)	0.25–1.5	0.5–2.5	3–50
Investment costs ($\$/\text{kW}$)	850–1500	1500–3800	(>2200)
Maintenance costs (% of investment costs per year)	2–3	3–5	n.a.

Table 9.5 Comparison of three type of electrolyzer

Alkaline electrolysis	PEM electrolysis	SOEC electrolysis
Advantages		
Well-established technology Nonnoble catalysts	High current densities High-voltage efficiency	Efficiency up 100% Efficiency >100% w/hot steam
Long-term stability Relative low cost Stacks in the MW range Cost effective	Good partial load range Rapid system response Compact system design High gas purity dynamic operation	Nonnoble catalysts High-pressure operation
Disadvantages		
Low current densities Crossover of gases (degree of purity) Low partial load range Low dynamics	High cost of components Acidic corrosive environment Possibly low durability Commercialization	Laboratory stage Bulky system design
Low operational pressures Corrosive liquid electrolyte	Stacks below MW range	Durability (brittle ceramics) No dependable cost information

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