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Review

An Overview of Different Water Electrolyzer Types for Hydrogen Production

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Abstract: While fossil fuels continue to be used and to increase air pollution across the world, hydrogen gas has been proposed as an alternative energy source and a carrier for the future by scientists. Water electrolysis is a renewable and sustainable chemical energy production method among other hydrogen production methods. Hydrogen production via water electrolysis is a popular and expensive method that meets the high energy requirements of most industrial electrolyzers. Scientists are investigating how to reduce the price of water electrolytes with different methods and materials. The electrolysis structure, equations and thermodynamics are first explored in this paper. Water electrolysis systems are mainly classified as high- and low-temperature electrolysis systems. Alkaline, PEM-type and solid oxide electrolyzers are well known today. These electrolyzer materials for electrode types, electrolyte solutions and membrane systems are investigated in this research. This research aims to shed light on the water electrolysis process and materials developments.

Keywords: hydrogen production; water electrolysis; electrolyzer types; electrolyzer materials; electrolyte; membrane technologies

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1. Introduction

Fossil foils are currently being overly used to provide for most of the world's energy needs, resulting in the depletion of natural resources [1]. Hydrogen energy is becoming more important for renewable energy sources, and hydrogen can be used as an energy storage material [2]. Different energy storage scenarios have been proposed by scientists, including photovoltaic houses and cars with a hydrogen cycle and storage for hydrogen gases [3]. Most of the essential solar and wind electricity for future sustainable energy policy will eventually be used for water electrolysis for hydrogen production [4].

Hydrogen gases can be generated via several methods, such as natural and biomass systems, fossil fuels electrolysis with renewable nuclear fission and fusion reactions, which include chemical, electrochemical, catalytic, thermal and biological processes [5,6]. The advantage of producing hydrogen via water electrolysis is that it yields more than 99.9% purity compared to other methods [7]. The technology for water electrolysis can be divided into four groups: alkaline water electrolysis (AWE), polymer electrolyte membrane electrolysis (PEM)/solid polymer electrolysis (SPE), anion exchange membrane electrolysis (AEM) and steam electrolysis (HTEL or SOEL) [8,9]. PEM water electrolysis uses KOH in water electrolytes with palladium, titanium or alternative electrodes [10]. Solid oxide fuel cells can operate reversibly in electrolysis mode and at temperatures between 750 and 1000 °C [11]. Electrolysis at high temperatures supplies high efficiencies in the solid oxide electrolyzer. The typical HTEL can reach a maximum efficiency of 92%, while electrolyzers at low temperatures reach an electrical efficiency of 85% [12].

Some material studies have tried to enhance the performance of the water electrolysis process. These studies are related to the electrode, electrolyte and separator materials used in an electrolysis cell. A review has presented materials for high-, medium- and low-temperature inorganic membrane electrolyzers [10]. Another review has summarized hydrogen production in microbial electrolysis for different efficiencies. Stainless steel, Ni alloys and Pd nanoparticle cathodes show high efficiency compared to other used materials [1]. In another study, a zirconium-based metal oxide electrode was studied for water electrolysis [13]. Ion exchange membranes and ionic activators have been proposed to reduce energy consumption and were tested in acidic and alkaline solutions for the electrolysis process of hydrogen production [2,14]. Some works have aimed to analyze the performances of high-pressure PEM water electrolyzer prototypes [15,16]. The effects of subcritical water conditions on the electrolysis anode effect were investigated in another study using an aluminum anode [17]. Glow discharge plasma electrolysis (GDPE) of methanol solutions was examined in another study for hydrogen generation [18]. Another study reviewed the mechanisms of gas diffusion, corrosion and electro catalysis and ion conduction; the study discussed the influence of these mechanisms on the optimum design of all cell components [19]. A novel approach was proposed in another study to increase the energy consumption of the electrolytic hydrogen production process inside an acidic solution [20].

A new method called green hydrogen is used today for hydrogen generation [21]. Heat energy, electrical energy, photon energy and biochemical energy are used for the generation of hydrogen in an environmentally friendly manner [22]. It is possible to find related studies on this matter, and some of the low-temperature electrolyses have been modelled [23].

Firstly, this paper describes electrolyte structures, equations and thermodynamics, as these are fundamental to the electrolysis process. It then classifies and compares water electrolyzers based on the main electrolysis types. The materials used in electrode, electrolyte and separator are also investigated in light of new trends and applications. Also, current technology is studied and checked for the required revisions and developments in terms of industrial applications. Bibliometric analysis of WOS with VOSviever software for electrolysis types is also provided.

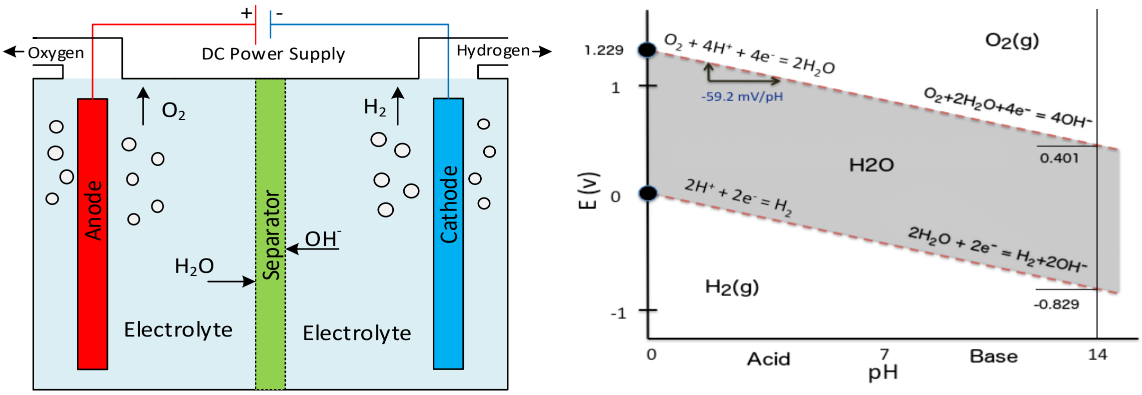
2. The Fundamentals of Electrolysis Processes

Hydrogen was first discovered in the 1493–1521 period by Theophrastus von Hohenheim; Robert Boyle (in 1771), Henry Cavendish (in 1766) and Antoine Lavoisier (in 1783), respectively, defined it in different forms and called it hydrogen gas [12]. The electric current and the amount of evolved hydrogen and oxygen relation at the electrodes were described by Micheal Faraday in the late 18th century. AWE was already used commercially at the beginning of the 20th century, consisting of nickel electrodes and porous separators between them. The General Electric Corporation first presented water electrolyzers with acidic SPEs in late 1960 [19].

Water electrolysis uses electric voltage to separate water into oxygen and hydrogen gas by electrolysis reaction. Electrolysis reaction requires a minimum 1.23 V potential difference between electrodes [24]. Two metal electrodes such as platinum or iridium placed in the water are connected to an electrical DC power source. While two moles of hydrogen gas appear at the cathode, one mole of oxygen gas appears at the anode [25].

The required low voltage is applied to electrodes (called electrolysis) to start a chemical reaction and to analyze the behavior of the electrolysis load. Two moles of H2 gas are obtained at the cathode and one mole of O_2 gas is obtained at the anode where 1.23 V electrical voltage is required, as shown in Equation (1), and a chemical reaction occurs, as seen in Figure 1a [26]. The increasing current from anode electrodes to cathode electrodes simultaneously increases the electron flow and hydrogen gas production [27]. The potential/pH diagram, also known as the Pourbaix diagram, for water at standard pressure and temperature is seen in Figure 1b, and the electrode potential and the pH of the electrolyte are provided by [28].

$$\begin{array}{ll}\text{Anode (oxidation): } 2\ H_2O(L) \rightarrow O_2(g) + 4H + (aq) + 4e- & Eo = +1.23\ V \\ \text{Cathode (reduction): } 2\ H + (aq) + 2e- \rightarrow H_2(g) & Eo = 0.00\ V \\ \text{Overall reaction: } 2\ H_2O(L) \rightarrow 2\ H_2(g) + O_2(g) & Eocell = -1.23\ V\end{array} \quad (1)$$



(**a**) (**b**)

Figure 1. (**a**) Electrolysis process for hydrogen production, (**b**) Pourbaix diagram for water [28].

The pressure variation with volume when heated by electrolysis is given in Figure 2. The constant of gas (k) is 8.3145 J/(mol K) and is defined with the P × V = k equation where the pressure (P) unit is Pascal and volume (V) is m^3. When the volume is increased, the pressure will be decreased automatically. For this reason, the storage of hydrogen has become a very important topic, and storage technologies are progressing every day depending on the storage materials technology advances [13].

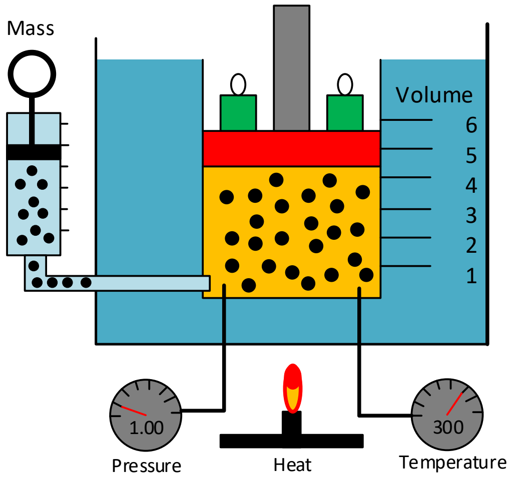


Figure 2. Electrolysis variation with pressure and temperature.

3. Main Electrolysis Types

Water-splitting electrolytes can be separated into alkaline, PEM, AEM, solid oxide, acidic–alkaline amphoteric, photo–electrochemical and microbial electrolysis technologies, as shown in Figure 3 [5].

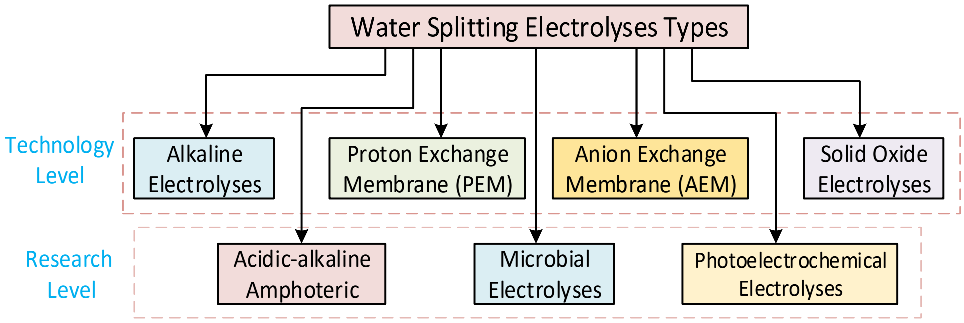
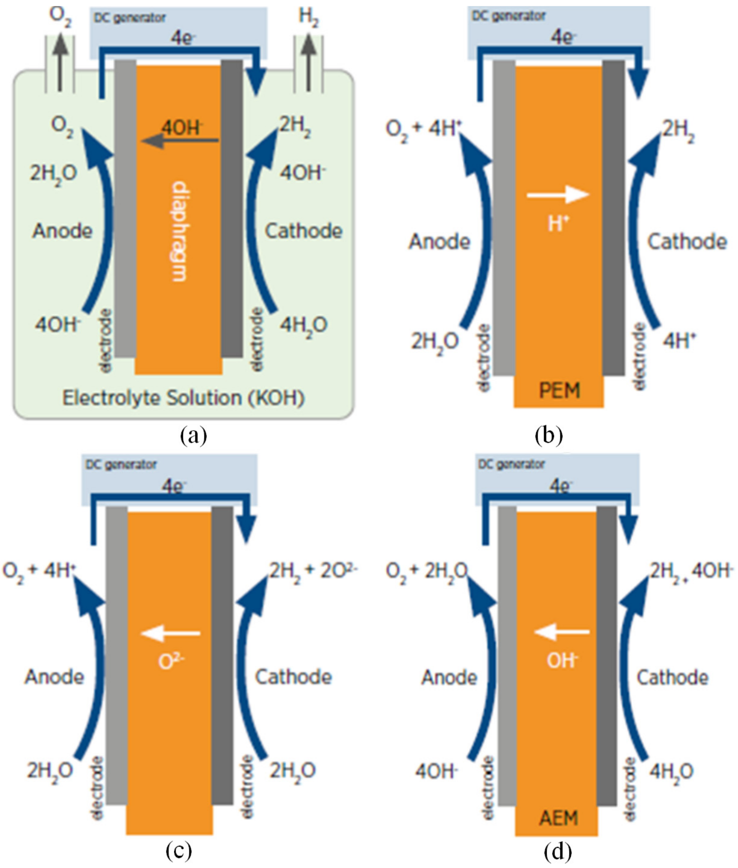


Figure 3. Water-splitting electrolysis technologies for hydrogen production.

Two main low-temperature electrolyzers on the market are alkaline and PEM-type electrolyzers. Although alkaline electrolyzers are cheaper, they are less efficient. The alkaline electrolysis basic setup is shown in Figure 4a [24]. Conversely, PEM-type electrolyzers are more expensive because of the use of platinum-group metal catalysts. Therefore, if the hydrogen production is large enough, it can be possibly cheaper. The principle experimental setup for the PEM-type electrolysis system is shown in Figure 4b [23]. With today's technology, average working efficiencies for PEM electrolysis are around 80%, although conventional alkaline electrolysis has about 70% efficiency. Moreover, the PEM electrolyzer's theoretical efficiency is predicted to be up to 94%, which will be possible with future advanced technologies [27,29].

Solid oxide electrolyzers (SOEs) operate between 500 to 850 °C and are more efficient than alkaline and PEM-type electrolyzers. The process is also called stem electrolysis or high-temperature electrolysis (HTE) and uses a ceramic electrolyte material. The oxygen passes through the membrane and reacts at the anode and generates electrons [30]. The HTE process and the symbolic scheme are given in Figure 4c [31].

An AEM and catalyst-layer ionomer was used without the addition of a liquid electrolyte for hydroxide ion conduction. The AEM electrolysis cell indicates a current density of 399 mA/cm^2 at 1.80 V and 50 °C. Optimizing the water feed configuration and ionomer in the catalyst layer could improve the durability of the AEM-based electrolysis cell [32,33]. This technology is commercialized only by a few companies, with limited deployment. Moreover, the performance of the electrolyzer is not yet as good as expected [34,35]. The SOE electrolyzer efficiency is between 45% to 55%, and the AEM electrolyzer efficiency is between 57% to 69% with today's technology, according to an IRENA report [34]. The AEM process and the symbolic scheme of the electrolyzers are given in Figure 4d.



(a) (b) (c) (d)

Figure 4. Different types of electrolyzer technologies: (**a**) Alkaline type, (**b**) PEM type, (**c**) Solid oxide type, (**d**) AEM type [24,30,34].

The electrolyte that separates the two electrodes is the environment for transporting the cations (+) or anions (−) in the alkaline-type electrolysis from one electrode to the other. In PEM, AEM and solid oxide electrolyzers, the electrodes are separated by an electron-insulating solid electrolyte. This solid electrolyte physically separates the produced gases, and it is liable for transporting ions. It is not required to add a liquid electrolyte solution for this reason. The different types of water electrolysis chemical reactions and typical temperature ranges are given in Table 1 [8,33]. This table explains the symbolic schemes of electrolyzers given in Figure 4.

Table 1. Different types of water electrolysis chemical reaction comparison [8,34].

Electrolysis Type	Anode Reaction	Cathode Reaction	Charge Carrier	Temperature Range
Alkaline	$2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$	$H_2O + 2e^- \rightarrow H_2 + 2OH^-$	OH^-	40–90 °C
Proton-exchange membranes	$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$	$2H^+ + 2e^- \rightarrow H_2$	H^+	20–100 °C
High-temperature (solid oxide)	$O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-$	$H_2O + 2e^- \rightarrow H_2 + O^{2-}$	O^{2-}	700–1000 °C
Anion-exchange membranes	$4OH^- \rightarrow 2H_2O{+}O_2 + 4e^-$	$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$	OH^-	40–60 °C

The comparison of the alkaline water electrolysis type with other electrolysis types is shown in Table 2. The process is more reasonable, efficient, and relatively cost-effective than the other types of water electrolysis currently [8,36].

Table 2. The comparison of electrolysis technologies [8,34–39].

Electrolysis Types	Advantages and Technologies	Disadvantages and Technologies
Alkaline Electrolysis	• Oldest and well-established technology • Cheapest and effective cost • Noble-type catalyst • Long-term durability • MW range stacks • 70% efficiency • Nickel-coated stainless steel electrodes • Nickel mesh for diffusion layer • Nickel-coated stainless steel bipolar plate • Polysulfone for frame and sealing	• Low current density • Low degree of purity • Corrosive liquid electrolyte • Low dynamic operation • Low load range for partial load • Low operating pressure • Crossover of gas
PEM Electrolysis	• High current density • High voltage efficiency • Good partial load range • Compact system design • The high degree of gas purity • High dynamic operation • Rapid system response • Iridium oxide electrode oxygen side • Platinum nanoparticles electrode hydrogen side • Sintered porous titanıum for diffusion layer • Polysulfone for frame and sealing	• New and partially established technology • High cost of components • Acidic environment corrosion • Comparatively low durability • Below MW range stack • Limited and costly membrane • Commercialization is in the near term • Higher discharge pressure • Mature and small-scale technology • Nobel metal catalyst
High-Temperature Electrolysis	• 100% efficiency • Thermal neutral efficiency > 100% • Non-noble catalyst • High-pressure operation • Perovskite-type electrode • Cobalt-coated stainless steel bipolar plate • Nickel foam for diffusion-layer anode	• Laboratory-phase technology • Low durability due to high heat, ceramics • Bulk system design • No diffusion layer cathode • No bipolar plate anode • Ceramic glass for frame and sealing

Table 2. *Cont.*

Electrolysis Types	Advantages and Technologies	Disadvantages and Technologies
Anion Exchange Membranes	• Zero-gap arrangement possible • Without the addition of liquid electrolytes • High durability • Lifetime of > 535 h • Low cost • Higher charge density • High-surface-area nickel electrodes • Nickel foam for diffusion layer • Nickel-coated stainless steel bipolar plate • Silicon for frame and sealing	• Laboratory-phase technology • Additional progress in synthesis needed • Certain limitations remain • Chemical and mechanical stability problems • Low current density • Low production yield • Excessive catalyst loading • Low current efficiency • Low power rate

4. Electrolysis Materials

Depending on the electrolysis process type, there is required some electrolysis materials. The electrolyte is one of them and affects the electrolysis process efficiency. The electrode is one of the other materials and must be supplied with some of the microscopic properties. A separator prevents the direct mixing of the produced gases inside the electrolysis cell and is placed between the electrodes. Some of the different electrode, electrolyte and separator types and how they affect the electrolysis process are investigated in this section.

4.1. Electrolyte

An electrolyte anion with less standard electrode potential than hydroxide and an electrolyte cation with a greater standard electrode potential than hydrogen will be oxidized instead of the hydroxide, and no oxygen gas and hydrogen gas will be produced. Lithium and sodium have lower electrode potentials than H+ and are commonly used cheap cations which are suitable for electrolytes. Sulfate (SO_{2-4}) is the most widely used anion with the standard +2.01 V potential for oxidation [40,41].

KOH and NaOH, strong bases, and strong acids such as H_2SO_4 are widely used as electrolytes due to their strong conducting abilities. A solid polymer such as a Nafion electrolyte can also be used when applied with a special catalyst on each side of the membrane and can split the water molecule efficiently with about 1.5 V. Several other commercially available solid electrolyte systems have been tried and developed [42]. Using nanogap electrochemical cells, electrolyte-free pure water electrolysis has been achieved in another study [43].

A PEM or polymer-electrolyte membrane generally made from ionomers is semipermeable and is designed to conduct protons [44]. An electrolysis system made of inexpensive and abundant nickel and iron, such as platinum or iridium, was proposed by researchers in 2014 [45]. The nanogap electrochemical cells can be even larger than those from 1 mol/L NaOH solution to achieve high-efficiency water electrolysis, as shown by experiments published by researchers in 2017 [43]. The efficiency of the PEM electrolysis device can be greatly enhanced by increasing the working temperature. Solid-acid materials are present in ducting electrolytes and a temperature above 140 °C makes them attractive for use in a PEM electrolyzer [46].

To reduce the ohmic drop in alkaline water electrolyzers for hydrogen production, the gap between the electrodes and diaphragm reduced to zero is a common strategy, but the ohmic resistance is substantially larger than zero. In a study, an additional ohmic drop was found to arise over an e-folding time. An overpotential was observed for electrolyte concentrations below 0.5 M. A high supersaturation of hydrogen and oxygen was found to increase the equilibrium potential significantly at elevated current densities. A purely empirical equation is used to describe these overpotential losses, which depend on the specific electrode and separator properties strongly and on local flow conditions [47]. So it can be different in different electrolyzer type structures.

4.2. Electrode

The water electrolyzer electrode structure of today is based on in-depth research and experience with water electrolyzers and fuel cells. The solid polymer electrolytes (SPEs), iridium-based catalysts for the anode, and platinum-based catalysts for the cathode, still consist of the same core materials [19].

Based on the structure and degree of electrolyte movement, electrode supports are divided into 3D and flat surface electrode categories and play a critical role in determining the performance of an electrolyte [43,44]. The 3D substrates involve all the material in a catalytic reaction, allowing multiple pathways for electrolyte penetration from all sides of the catalyst [48–50]. Ni-foam, Au (111), and gold-plated Ni-foam electrodes are used to analyze their effect on the electrochemical performance of different catalysts in a study, and due to the higher conductivity, gold-plated Ni foam obtains much better results [51,52]. Sahin et al. used some different electrodes, i.e., copper, stainless steel and aluminum, with dimensions of 10 cm × 10 cm, and investigated equivalent dynamic resistance and volumes of hydrogen gas production depending on different electrode gaps [27,53,54]. Also, this study proposed to use solar sources and calculated nearly 100 W power to be generated at 10 L/h theoretically using this electrolysis process and some converters [26,53,54].

An electrode ideally must show the following properties [19]:

- Minimizes ohmic drops, for high conductivity of electrons and ions.
- The catalyst is in contact with the aqueous phase, known as high wettability.
- The catalyst has a high surface.
- Low amount of bubble-blocked pores and coverage of the catalyst.
- Gases and electrolytes have high permeability to ease mass transport.

The restrictions of the water splitting, which is a comparatively straightforward reaction, are the large thermodynamic barrier and sluggish kinetics of the OER associated with the HER. Designing very reactive noble-metal-based catalysts has been possible over the last few decades of efforts to enhance the rate of water oxidation and diminish the working potential. The copper-based materials have been used successfully in a study, although they have not been explored for electrode materials previously [55]. In a natural photosystem (NPS), electrons released and stored in adenosine triphosphate (ATP) and nicotinamide adenine dinucleotide phosphate (NADPH), which are the key reductants used in CO_2 reduction, are shown in Figure 5, modified from [56]. Water splitting inspired by a natural photosystem consists of water oxidation attended by the use of electrons for the building of NADPH and ATP.

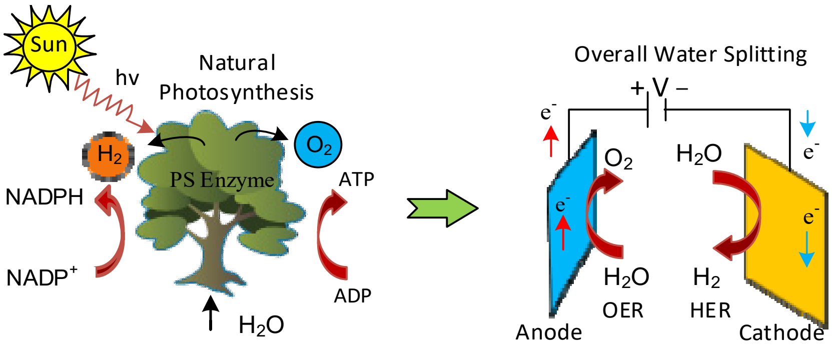


Figure 5. Development of overall water splitting.

Copper sulfides have been tried as an anode material for OER, and metal sulfides are seen as future materials for their bifunctional behavior. A copper foam was used as a substrate to design a copper sulfide nanostructure chemical approach in a recent study [57]. One-dimensional $Cu(OH)_2$ nanorods were synthesized using NaOH and $(NH_4)2S_2O_8$ via chemical oxidation in an aqueous form at first. The addition of Na_2S to the solution at

90 °C led to the production of a Cu_2S nanostructure, as seen in Figure 6, modified from reference [55].

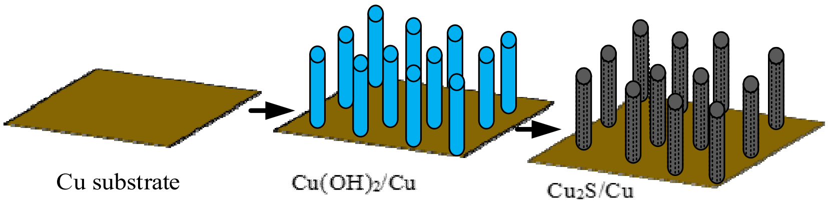


Figure 6. Preparation of Cu_2S/Cu nanorods on copper substrate.

4.3. Separator

A separator is placed between two electrodes inside the electrolysis cell to hinder the mixing of the produced gases directly. Various improvements in the porous separator and the electrode design in the case of industrial alkaline water electrolysis were presented in the late 20th century [58,59]. However, nickel still represents the advanced active component for the anodic and cathodic catalyst [60].

Nafion membranes were investigated as a separator in an alkaline electrolyzer in one research paper. The cell voltage with 30% KOH electrolytes was more than twice that with 30% NaOH for the same current densities. Nafion membranes can be used at temperatures of up to 250 °C and have perfect mechanical and physical properties in alkaline electrolytes [61]. Figure 7 shows a PEM electrolyzer stack included as a separator of the Nafion membrane with other components modified from [60,62].

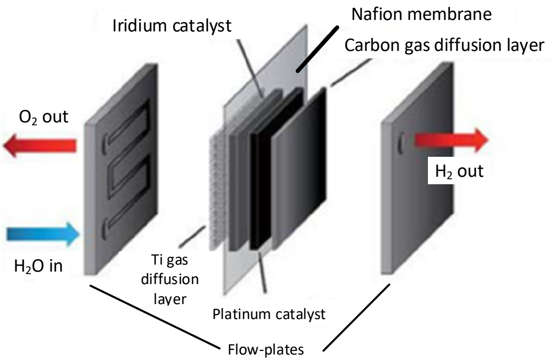
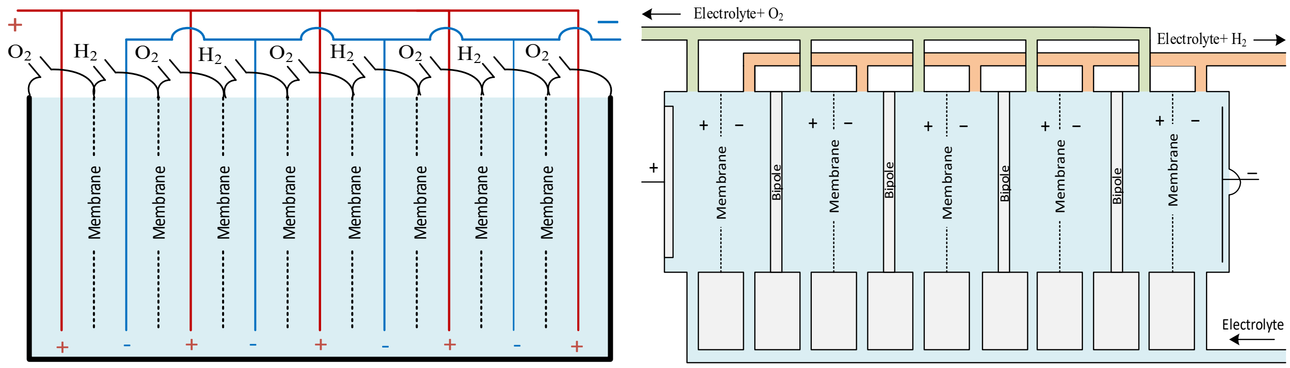


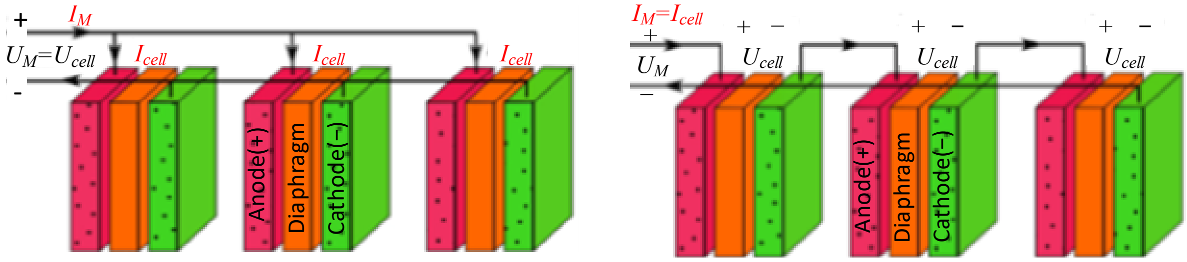
Figure 7. A PEM-type electrolyzer stack with all components.

The preparation and characterization of TiO_2 polysulfone composite membranes were discussed in an article, and the membrane was found to be stable in an alkaline environment [63]. The cheaper and more effective Nafion membranes are favoured today; however, it was the expensive solution for PEM electrolyzers previously. Hydrogen production by water splitting is presented in research with CuCl–HCl electrolysis and its operating parameters. Also, critical suggestions were made and addressed the challenges and future trends in this field [64].

A comparison of different water electrolysis systems required a discussion of several practical parameters, including operating conditions and electrolysis cell configurations. Electrolyzer cell configurations may be built in either bipolar or unipolar forms, as seen in Figure 8. A tank-type unipolar electrolyzer consists of alternately positive and negative electrodes, as in Figure 8a. Positive and negative electrodes are all coupled together in parallel with the same voltage, and to form a unit cell the whole assembly is immersed in a single electrolyte bath. On the other hand, in a bipolar electrolyzer, as seen in Figure 8b, a metal sheet connects electrically adjacent cells in series. These modules are connected in parallel to increase the current and to meet the requirements of a large electrolysis plant [65].



(**a**) unipolar (**b**) bipolar



(**c**) unipolar (**d**) bipolar

Figure 8. Electrolyzer modules gas flow configurations with (**a**) unipolar and (**b**) bipolar cells, (**c**) unipolar and (**d**) bipolar cell current flow configurations.

Two different HER and OER reactions take place simultaneously on the opposite sides of each electrode in the bipolar configuration. The unipolar configuration presents a cell voltage of about 2.2 V for typical industrial processes [66,67]. While a unipolar connection total current is the sum of every cell, bipolar connection voltage is the sum of every cell, as shown in Figure 8c,d [68].

The hydrogen diffusivity and electrolyte permeability of the Zirfon PERL separator were characterized as a function of the temperature and molarity of the KOH filling in a study, and the diffusivity of hydrogen in the separator was found to be approximately 16% [69].

A novel composite membrane separator was synthesized in another work using a composition of polysulfone (PSF), polyvinylpyrrolidone (PVP) and zirconium oxide (ZrO_2)O by the phase-inversion precipitation process. Electrolysis process parameters considered were the effects of temperature, membrane thickness, and KOH concentration on the prepared polymer-coated asbestos in a cell assembly of 10 cm^2 separators in this study. When operating the cell voltage of 2 volts with a 30 wt% KOH solution at 80 °C temperature, a current density of 0.21 A/cm^2 was achieved. The H_2 production rate was 20 mL/min, and the purity of H_2 was 99.9%; as well, pure O_2 was obtained [70].

A double-layer diaphragm with an internal KOH supply, which is called an "E-by-pass separator", and an adapted cell concept with a compartment electrolyzer was achieved by Denmark Technical University and three corporations with a project called "RESelyser". The progress achieved for double-side-coated PPS spacer-fabric and 2.4 mm to 2.9 mm thicknesses realized is shown in Figure 9, modified from [67]. Dual-layer Zirfon is used, each layer is 0.5 mm thick, and the intervene-free electrolyte channel is 1.5 mm. The variation of permeability is changed from 120 L/(h m^2 bar) to 900 L/(h m^2 bar) [71].

Aqueous solutions which are used in water electrolyzers with proton or hydroxide concentrations between 4 to 8 mol display the highest conductivities typically. These concentrations correspond to below −0.5 or above 14.5 pHs, respectively [19].

The saturation of hydrogen and oxygen increased the overpotential at elevated current densities. Most of these voltage losses can be decreased by a small 0.2 mm gap, improving the performance compared to zero gap. There are some additional advantages of a small gap, including decreased separator damage and reduced gas cross-over. These advantages can be applied to this method for all electrolyzer types to overcome the overpotential. To model the cell voltage, depend on overpotential is given in Equation (2), where E_{eq} is equilibrium cell voltage after switching of current density (j), l is effective-length scale, K is electrolyte conductivity using areal resistance (AR), and the activation overpotential is $n = n_c + n_a + n_i$ with $i = c$ and a [47].

$$E_{cell} = E_{eq} + \frac{jl}{K} + ARj + n \tag{2}$$

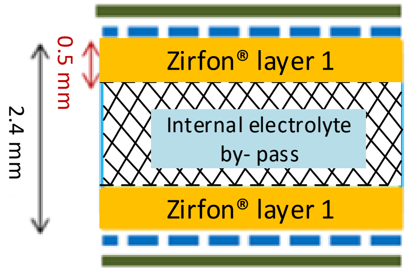


Figure 9. Proposed "E-by-pass separator" structure and dimensions.

5. Industrial Applications for Electrolyzers

The technology of hydrogen production became industrialized, such as petroleum refining, between the 1920s to 1970s during the historical development. The development of PEM water electrolysis was led by the advancement in space exploration and military needs between the 1970s and the present. Renewable energy technologies are integrated with the rapidly evolving conceptual development of water electrolysis for distributed energy production, and storage, especially today. The emergence of PV electrolyzers is a recent development [26,72].

Water electrolysis was still in its infancy in 1900, commercially. Two decades later, 100 MW-rated large-size electrolyzer plants were developed in Canada, for fertilizers primarily [73]. Electrolyzer manufacturers made a great effort all over the world. The Aswan company installed a 162 MW-rated hydrogen generation capacity of 32,400 m^3 with 144 electrolyzers by late 1980. The water electrolysis units of several electrolyzer corporations are given to be compared in Table 3. Some commercial corporations are not mentioned, such as the Stuart Cell Company, which is the only monopolar tank-type cell manufacturer from Canada. Hamilton Sundstrand and the Proton Energy Systems company, also from the USA, the Shinko Pantec corporation from Japan and the Wellman-CJB corporation from the UK are the latest famous manufacturers of PEM electrolyzers [72].

Table 3. Water electrolyzer developer companies and electrolyzer cell operating parameters [74].

	Company Names				
Parameters	**De Nora S.A.P**	**Norsk Hydro**	**Electrolyzer Corp.**	**Teledyne Energy System**	**General Electric**
Type of cell	B-FB	B-FP	M-T	B-FP	B-FB
Anode	Expanded Ni-plated Mild steel	Activated Ni-coated Steel	Ni-coated Steel	Ni screen	PTFE-bonded Noble metal
Cathode	Activated Ni-plated Steel	Activate Ni-coated Steel	Steel	Ni screen	PTFE-bonded Noble metal
Electro. pressure (MPa)	Ambient	Ambient	Ambient	0.2	0.4
Electro. temperature (°C)	80	80	70	82	80
Percentage of electrolyte	29% KOH	25% KOH	28% KOH	35%	Nafion
Density of current (Am^{-2})	1500	1750	1340	2000	5000

Table 3. *Cont.*

	Company Names				
Parameters	**De Nora S.A.P**	**Norsk Hydro**	**Electrolyzer Corp.**	**Teledyne Energy System**	**General Electric**
Voltage of cell (V)	1.85	1.75	1.9	1.9	1.7
Efficiency of current (%)	98.5	98.5	>99.9	NR	NR
Purity of oxygen (%)	99.6	99.3–99.7	99.7	>98.0	>98.0
Purity of hydrogen (%)	99.9	98.9–99.9	99.9	99.99	>99.0

The most important components and operation conditions for the four types of different electrolyzers are seen in Table 4. The significant variation from different manufacturers or research development institutions is represented by the grey-coloured cells [34]. The abbreviations of some chemicals used in Table 4 are given below. PFSA = Perfluoroacidsulfonic; PPS = Polyphenylene sulphide; PSU = Polysulfone; ETFE = Ethylene Tetrafluorethylene; PTFE = Polytetrafluoroethylene; PSF = Poly (bisphenol-A sulfone); YSZ = Yttriastabilized Zirconia; DVB = Divinylbenzene; LSCF = $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ -δ; LSM = $(La_{1x}Sr_x)_{1-y}MnO_3$; § = Crofer22APU with co-containing protective coating. This table is based on the analysis results of the IRENA agency [34].

Table 4. Four types of water electrolyzers: characterization [34].

Condition and Component	**Alkaline**	**PEM**	**AEM**	**Solid Oxide**
Operating temperature	70–90 °C	50–80 °C	40–60 °C	700–850 °C
Operating pressure	1–30 bar	<70 bar	<35 bar	1 bar
Electrolyte type	Potassium hydroxide (KOH) 5–7 $molL^{-1}$	PFSA membranes	DVB polymer support with KOH or $NaHCO_3$ 1 $molL^{-1}$	Yttria-stabilized zirconia (YSZ)
Separator solid electrolyte (above)	ZrO_2 stabilized with PPS mesh	Solid electrolyte (above)	Solid electrolyte (above)	Solid electrolyte (above)
Electrode/catalyst (oxygen side)	Nickel-coated perforated stainless steel	Iridium oxide	High surface area Nickel or NiFeCo alloys	Perovskite-type (e.g., LSCF, LSM)
Electrode/catalyst (hydrogen side)	Nickel-coated perforated stainless steel	Platinum nanoparticles on carbon black	High surface area Nickel or NiFeCo alloys	Ni/YSZ
Porous transport layer (anode)	Nickel mesh (not always present)	Platinum-coated sintered porous titanium	Nickel foam	Coarse nickel-mesh or foam
Porous transport layer (cathode)	Nickel mesh	Sintered porous titanium or carbon cloth	Nickel foam or carbon cloth	None
Bipolar plate anode	Nickel-coated stainless steel	Platinum-coated titanium	Nickel-coated stainless steel	None
Bipolar plate cathode	Nickel-coated stainless steel	Gold-coated titanium	Nickel-coated stainless steel	Cobalt-coated stainless steel
Sealing and frames	PSU, PTFE, EPDM	PTFE, PSU, ETFE	PTFE, silicon	Ceramic glass
Efficiency (%)	62–82	67–82	48–60	50–60
Power unit (kW)	1000	1000	70	05–100
Min. stack cost	270 USD/kWh	400 USD/kWh	Unknown	>2000 USD/kwh
Lifetime stack	50,000–80,000 h	60,000 h	>5000 h	<20,000 h

Through the equivalent electrical model and detailed operation process analysis of alkaline water electrolyzers (AWEs), the mechanisms of inconsistency and inefficiency of low-load AWEs were revealed. To improve the efficiency and consistency of AWEs, a multi-mode self-optimization electrolysis-converting (MMSOEC) strategy is proposed in a work. The provided working current can conduct all bipolar plates on time for the low-load AWEs. The current is zero and AWEs stop working (zero) during off time, but only the electrical double-layer capacitor (EDLC) discharges. As a result, the AWEs always operate under optimal conditions, as seen in Figure 10, which is modified from [75]. The DC power supply method for the high-load AWEs is still adopted, and thanks to the operation ranges of the electrolyzer, the maximum efficiency can be doubled compared to a conventional DC power supply. Hydrogen production from renewable energy sources is suitable for this method.

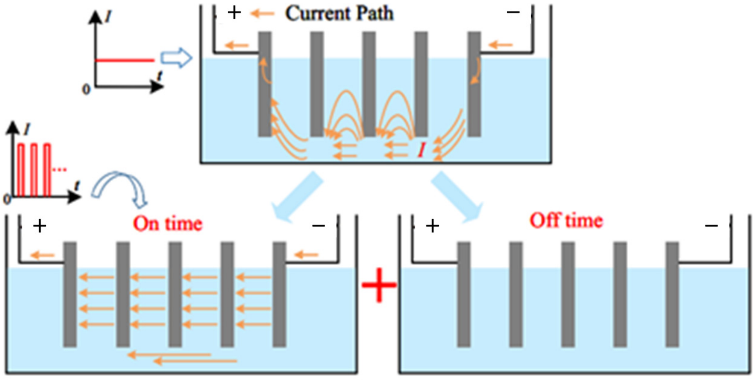


Figure 10. Mechanism to enhance efficiency and consistency.

A prototype has been designed for the AWE type used in hydrogen energy storage-based renewable energy sourced power plants. A printed two-dimensional sketch is proposed for the technology of the nickel–cobalt electrode and electrochemical formation. For the synthesis of diaphragms, a new technique with a zirconium hydroxide hydrogel as a hydrophilic filler is considered. The current–voltage characteristics of electrolytic cells designed for pressures up to 160 atm, as seen in modified Figure 11a–d, are investigated from [76].

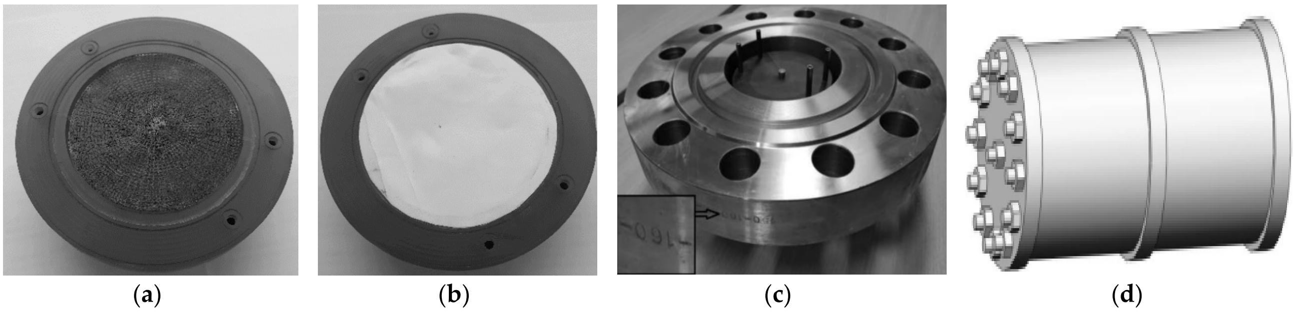

(**a**) (**b**) (**c**) (**d**)

Figure 11. (**a**) Modified $NiCo_2O_4$ catalyst and porous coated anode. (**b**) Polymer-based diaphragm. (**c**) Electrolysis cell installed inside of the outer containment shell. (**d**) Single high-performance planar module.

The most cost-effective applications of public support would support their development with a comprehensive technology improvement and target market development effort for the introduction of hydrogen and other clean energy technologies. These development programs combination have proved to be effective, particularly in solar PV development and deployment in Japan [77].

For renewable hydrogen production, recent research activities in the USA are reviewed and pioneering methods that are still in the R&D stages are discussed in this section. Hydrogen production through biomass gasification of agricultural products is being worked on by researchers at Iowa State University. A research team at the Hydrogen Energy Center at Penn State University has several projects on biomass-based hydrogen to produce hydrogen from wastewater. Research on hydrogen production from algae is being conducted by leading researchers at the University of California at Berkeley with Oak Ridge National Laboratory collaboration. Karen Brewer's laboratory at Virginia Polytechnic University is focused on the electrochemical properties of photo-electrochemical water-splitting devices. Photo-electrochemical water splitting is also being studied by NREL researchers [77–79]. A detailed report of summary tables "Plant-Gate" and delivered hydrogen costs was published by the Clean Energy Group [78,79].

The Nel Hydrogen Corporation is the well-known industry leader in PEM water electrolysis, with 3500 reliable electrolyzers installed around the globe. Sustained R&D efforts have contributed to the improvement of electrolyzer technology since its founding in 1927. This company has produced different types of electrolyzers, such as the Containerized PEM electrolyzers (M series); the Atmospheric Alkaline Electrolyzer, which is the world's most efficient electrolyzer (A series), shown in Figure 12; PEM Electrolyzers, which are ideal for hydrogen generation using renewable energy sources (M Series), or ideal for a diversity of industrial applications (C Series); the H Series and S series, for different purposes [80].

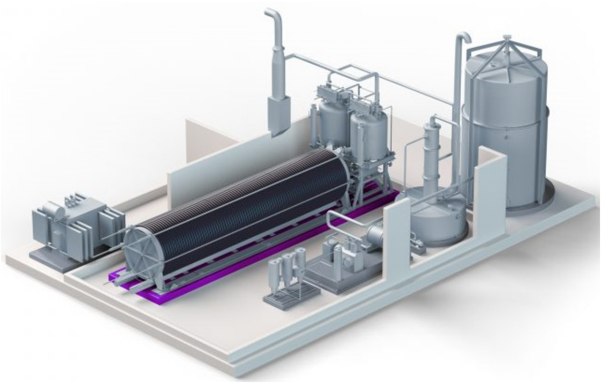


Figure 12. A series of atmospheric alkaline electrolyzers was produced by Nel Corporation [80].

ASPILSAN Energy, as a stakeholder of the South Marmara Hydrogen Shore Platform Guided Project, will take part in the development of a domestic PEM electrolyzer system, with a capacity of 30 kW, with TUBITAK MAM. This electrolyzer will produce hydrogen, which will be used in the cooling system of the generators located at the plant. They also aim to realize an investment of more than EUR 3 million for hydrogen in five years. A prototype PEM electrolyzer model of a corporation is given in Figure 13a [81]. Electric-Hydrogen Corp.'s first EH2 electrolysis cell data were recorded in June 2021, as given in Figure 13b [82]. Angstrom Advanced Inc. produced a hydrogen-generating plant by water electrolysis with 1~10,000 Nm^3/h capacity in recent years; the electrolyzer model is seen in Figure 13c [83]. Some commercial products for R&D studies are produced by HFK China company, which can produce 3000 mL/s with 2000 W/h capacity, starting at a price of USD 100, as seen in Figure 13d [84].

The PEM-type and solid oxide electrolyzers are given in this section because their process is more simple than the others. PEM systems are much simpler than alkaline, as seen in Figure 14. They typically need the use of pressure control, heat exchangers, circulation pumps, and monitoring at the anode side. A gas separator, a gas dryer, a de-oxygenation component to remove residue oxygen, and a final compressor step are required at the cathode side [34].

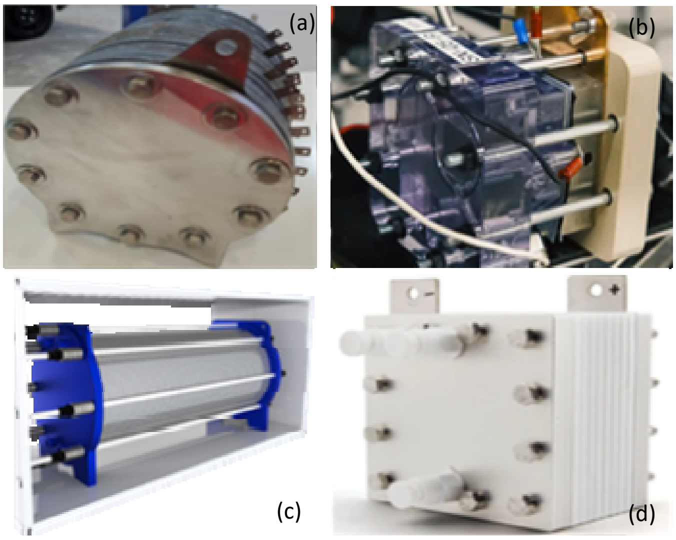


Figure 13. Some prototype and commercial PEM electrolyzer models. (**a**) PEM electrolyzer model. (**b**) EH2 electrolysis cell. (**c**) Electrolyzer model plant. (**d**) Commercial electrolyzer product [81–84].

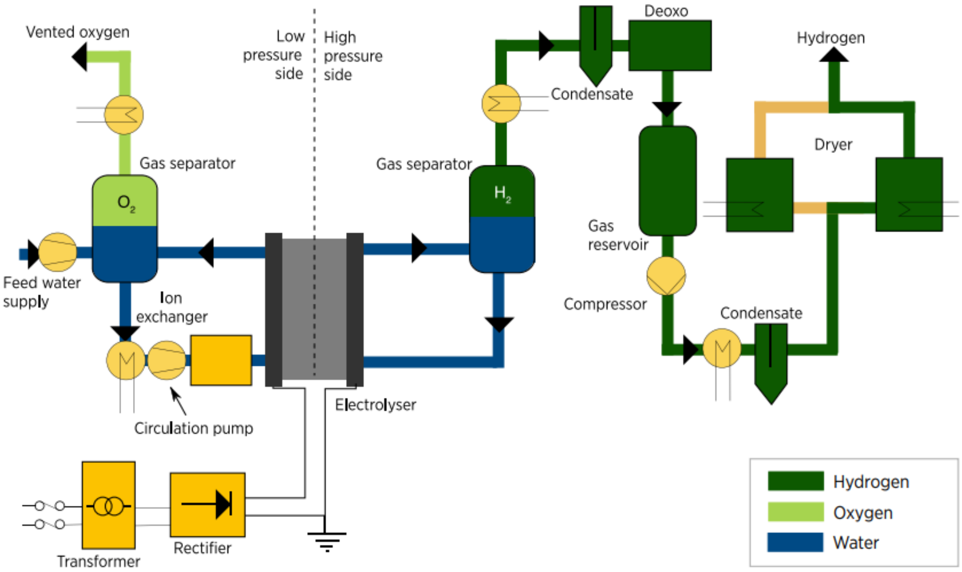


Figure 14. Typical system design for a PEM electrolyzer [34].

The SOEs can be coupled with heat-producing technologies, and a typical system configuration is shown in Figure 15. Energy demand is rapidly reduced and then utilized in the water-splitting reaction at high temperatures. Heat for water vaporization can be supplied from concentrated solar power plants [34].

The same increase in hydrogen production rate, from 10 MW/year to 1 GW/year, leads to a cost reduction of about 40% in the balance of the PEM electrolysis plant. This means the balance of the plant goes from about 55% of the total cost to almost 75% on a 1 GW/year scale, as seen in Figure 16, obtained from [85]. The dominant costs of the power supply and hydrogen processing were only reduced by about 30% [34,85].

Strong technology, field experience and manufacturing capacity examples are given in Figure 17: (a) nameplate capacity of PEM Electrolyzers of ~40 MW/year, (b) nameplate capacity of ~40 MW/year, ~500 MW/year in 2021, ~2 GW/year if fully expanded for alkaline electrolyzers, (c), nameplate capacity of ~300 HRS/year for hydrogen refueling stations [39]. The Electric Hydrogen Company produced a 100 MW hydrogen power plant that produced 1900 kg/hour of hydrogen in California at last and made a new agreement with the AES Corporation to establish a 1 GW large-scale electrolyze plant [86].

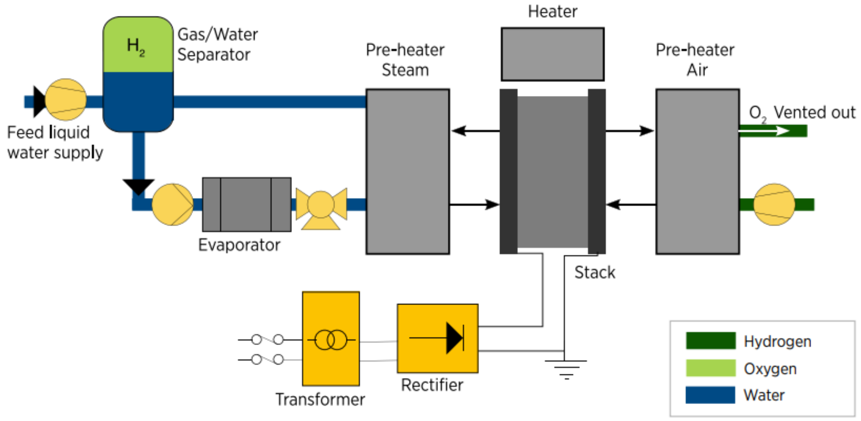


Figure 15. Typical SOE system design [34].

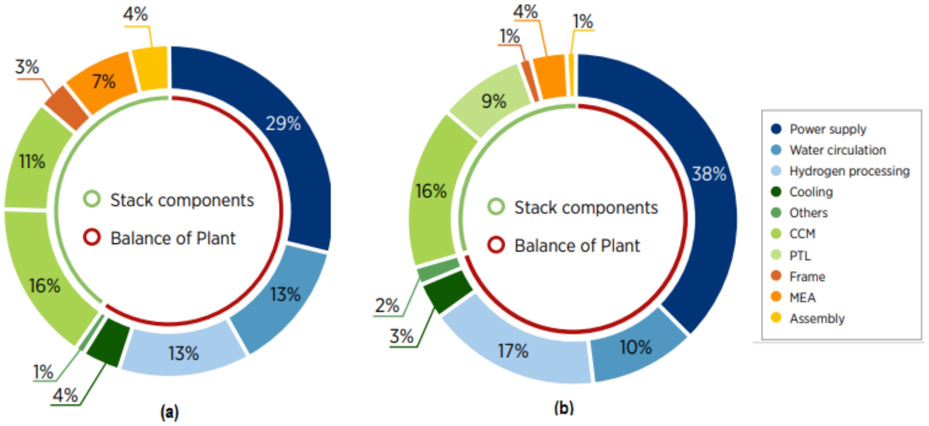


Figure 16. Cost analysis for PEM electrolyzers: (**a**) 10 MW/year; (**b**) 1 GW/year production scale.

(**a**) (**b**) (**c**)

Figure 17. Strong technology, field experience and manufacturing capacity examples. (**a**) PEM electrolysers, Wallingford, USA. (**b**) Alkaline electrolysers, Notodden/Herøya, Norway. (**c**) Hydrogen refuelling stations, Herning, Denmark [39].

Green hydrogen is a new industrial application trend, generally referred to as 'renewable hydrogen', and is a revolutionary energy carrier obtained through the electrolysis of water using electricity generated from renewable energy sources [87,88]. Green hydrogen supply cost that is as low as possible to ensure needs to be applied to system design and operation. To minimize the cost, a variety of factors such as variability of electricity supply, the technology used for electrolysis (e.g., alkaline, PEM, AEM, solid oxide) and the flexibility of hydrogen demand need to be taken into account. Storage of hydrogen in tanks, caverns and pipelines can help to decouple the variable supply from hydrogen demand. The combination with electricity and hydrogen storage can effectively provide the flexibility which is shown in Figure 18 [34]. There are still a variety of challenges, such as cost-effective hydrogen production and its technological challenges, storage, safety, transportation, and cost issues. The challenges regarding production, storage technologies and transportation of hydrogen and green hydrogen are given in another, more detailed study [89].

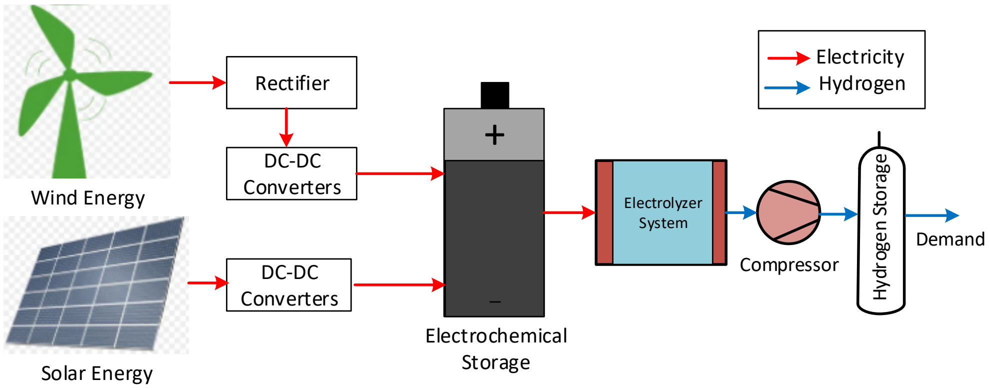


Figure 18. Green hydrogen production plant includes electricity and hydrogen storage on site.

6. Bibliometric WOS Analyses with VOSviewer Software

In this part, the keywords of the manuscript sourced the detailed papers in the Web of Science (WOS); a total of 365 works are categorized in WOS, and this archive file is recorded and used in VOSviewer software version 1.6.19 for bibliometric analyses. Half of these studies are categorized for energy fuels: 48% are chemistry physics, 33% are materials science multidisciplinary, 30% are electrochemistry, and the list continues to relate this topic in decreasing order. An overlay visualization for the WOS category during the last five years is shown in Figure 19. System technology and electrocatalysts to increase current density are the main topics for the last years investigated by scientists. Density visualization for the WOS category is shown in Figure 20 more clearly. The yellow colors are shown as the main density of investigations.

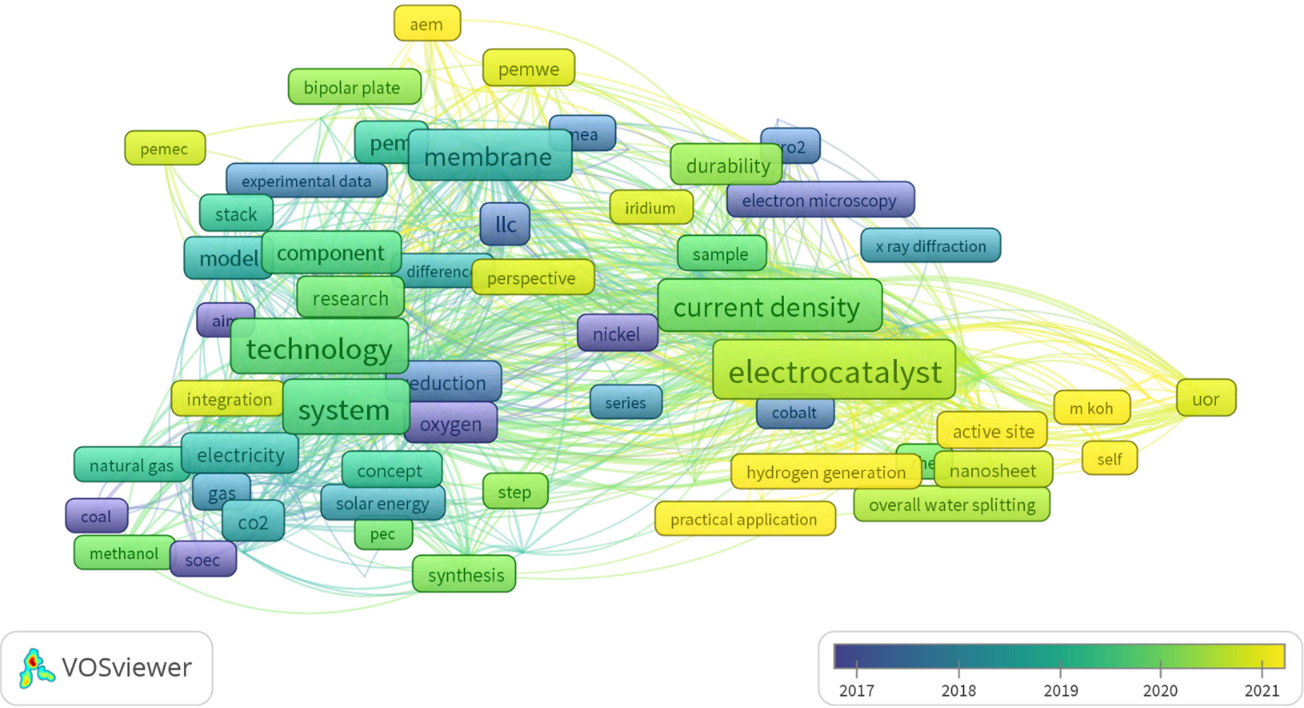


Figure 19. Bibliometric overlay visualization of electrolysis types for the WOS category during the last five years.

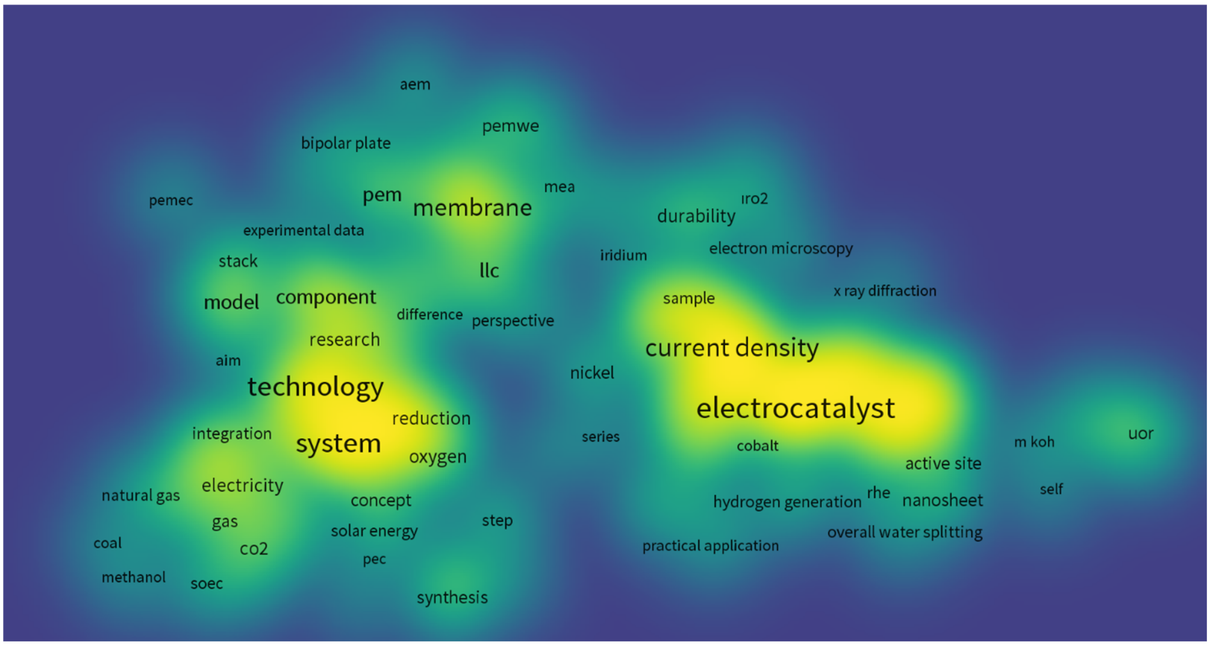


Figure 20. Bibliometric density visualization of electrolyzer types for WOS category.

7. Conclusions

The water electrolysis process is a simple hydrogen production method and requires research. A detailed literature review for different water electrolysis types is given in this paper first. The fundamentals of the electrolysis process and main electrolysis types are presented. The comparable forms of alkaline, PEM-type, anion exchange membranes and high-temperature electrolysis working principle advantages and disadvantages are given in this study. Alkaline electrolytes are seen as popular, but the PEM types will be more popular when commercially produced. High-temperature electrolysis also needs more operations and needs to develop. The components of electrolyzers are investigated in more detail as a study and can be modelled in the future. Also, industrial applications for electrolyzers were investigated to inform us about the future of water electrolysis processes. Finally, bibliometric WOS analyses for electrolysis types with VOSviewer software are presented for the last five years.

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