



Review of Alternative Energy Production Methods by Oxidation of Electrolysed Hydrogen in a Hydrogen Fuel Cell

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Abstract

Hydrogen fuel could be utilized in a hydrogen fuel cell, and could be produced sustainably from the electrolysis of water in an electrolyzer. The various types of electrolyzers: alkaline electrolyzers, PEM electrolyzers, and solid oxide electrolyzers, have been studied in this paper. This paper focuses on the reviews of several studies that have been carried out on the use of alkaline electrolyzers and PEM electrolyzers, and the utilization of the hydrogen product in hydrogen fuel cells. Studies show the use of alkaline electrolyzers to be cost effective, of less gas purity, and offer long-term stability against PEM electrolyzers which are more expensive, of high gas purity, and offer near-term stability. Acid solutions used as electrolytes in PEM electrolyzers show high ionic conductivity and are free from carbonate formation, as compared to alkaline electrolytes. However, the acid requires the use of noble metals as electrocatalysts for OER. Furthermore, KOH is used in alkaline water electrolyzers because of its high ionic conductivity over NaOH. It was concluded that adopting a zero-gap cell configuration for the electrolyzer cell electrodes increased operating current density, while decreasing parasitic ohmic resistance.

Keywords

Alkaline water, electrolyzer, fuel cell, hydrogen, PEM.

Introduction

Hydrogen is the most abundant chemical element in the universe, making up more than ninety percent of all known matter. The hydrogen atom is composed of one proton and one electron, making it the lightest element in existence. The abundance of hydrogen on Earth, minimal environmental consequences of its use, and the need to replace fossil fuel, make it suitable and an attractive fuel for the future. Since the weight of hydrogen is less than that of air, its low density causes it to rise in the atmosphere, as a result of this, it is rarely found in its pure form, H₂ [1].

The several methods of hydrogen extraction include steam reforming, a high-temperature process in which steam reacts with a hydrocarbon fuel to produce hydrogen. Many hydrocarbon fuels can be reformed to produce hydrogen, including natural gas, diesel, renewable liquid fuels, gasified coal, or gasified biomass. Today, about ninety-five percent of all hydrogen is produced from steam reforming of natural gas [2]. According to Kalamaras and Efstathiou [3], this method of

hydrogen production occurs at temperatures between 700-1100°C and a resultant efficiency of between 60-75%.

Hydrogen can also be produced from water through electrolysis; a process in which water is separated into oxygen and hydrogen in an electrolyzer. An electrolyzer function more like a fuel cell in reverse – instead of using the energy of hydrogen molecules like a fuel cell does, it creates hydrogen from water molecules [2]. This process is less carbon-intensive, if the electricity used in the reaction process does not come from fossil-fuel power plants, rather, could be got from renewable energy sources of nuclear energy instead. The efficiency of this process is between 70-80% [4].

The electrolysis of water is a simple electrochemical process of producing hydrogen. A low voltage current is run through the water, and gaseous oxygen forms at the anode while gaseous hydrogen forms at the cathode. Typically, the cathode is made from platinum or another inert metal when producing hydrogen for storage. If however, the gas is to be burnt on site, oxygen is desirable to assist the combustion, and so both electrodes would be made from inert metals.

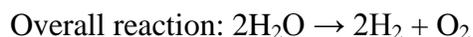
Hydrogen has high energy content per weight (nearly three times as much as gasoline); however, the energy density per volume is quite low at standard temperature and pressure. Volumetric energy density can be increased by storing the hydrogen under increased pressure or storing it at extremely low temperatures as a liquid. Hydrogen is highly flammable; it only takes a small amount of energy to ignite it. It also has a wide flammability range, meaning it can burn when it makes up 4 to 74 percent of the air by volume. Hydrogen burns with a pale-blue, almost invisible flame, making hydrogen fire difficult to see [5].

Electrolysis of water is an electrochemical process of splitting water into gaseous hydrogen and oxygen. In recent years, water electrolysis has attracted great interest due to the progress that fuel cells have made in different applications, hence, the anticipated higher demand for clean hydrogen. Electrolytic reaction takes place in a unit called an electrolyzer. Electrolyzers consist of an anode and a cathode separated by an electrolyte. The challenge of electrolyzers is the requirement of electrical energy to complete the reaction. Ideally, the electrical energy needed for the electrolysis reaction should come from renewable energy sources such as wind, solar or hydroelectric sources. Some of the advantages of using electrolyzers include guaranteed purity of the hydrogen produced; hydrogen production can be done directly at the location, and at the time at which it will be used and does not necessarily have to be stored; it is also a much cheaper method than gas supplied in high-pressure cylinders [6]. Different electrolyzers function in slightly different ways; this is mainly due to the different types of electrolyte materials involved.

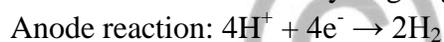
According to Fuel Cell Store [6], electrolyzers can be categorized into two main designs: unipolar and bipolar. The unipolar design typically uses a liquid electrolyte (alkaline liquids), and the bipolar design uses a solid polymer electrolyte membranes. Potassium hydroxide was a

commonly used electrolyte in the past, but recently polymer electrolyte membranes are more typical.

a) **Alkaline Electrolyzers:** Alkaline electrolyzers often use aqueous potassium hydroxide (KOH) solution as the electrolyte. Other frequently used electrolytes include sulfuric acid (H₂SO₄), sodium chloride (NaCl), and sodium hydroxide (NaOH). Alkaline electrolyzers work well at operating temperatures between 25-100°C and pressures of 1-30 bar. Commercial alkaline electrolyzers have current densities in the range of 100-400 mA/cm² [6]. The chemical reactions for the alkaline electrolyzer are:



b) **Proton Exchange Membrane Electrolyzers:** The proton exchange membrane (PEM) electrolyzer is quite popular, and many modern electrolyzers are built with this technology. The electrolyte is a thin, solid ion-conducting membrane, which is used instead of the aqueous solution. It uses a bipolar design and can be made to operate at high differential pressures across the membrane. Water reacts at the anode to form oxygen and positively charged hydrogen ions (protons). The electrons flow through an external circuit and the hydrogen ions selectively move across the PEM to the cathode. At the cathode, hydrogen ions combine with electrons from the external circuit to form hydrogen gas. The reactions are as follows:



c) **Solid Oxide Electrolyzers:** Solid oxide electrolyzers, which use a solid ceramic material as the electrolyte that selectively conducts negatively charged oxygen ions (O²⁻) at elevated temperatures, generate hydrogen in a slightly different way. Water at the cathode combines with electrons from the external circuit to form hydrogen gas and negatively charged oxygen ions. Then, the oxygen ions pass through the solid ceramic membrane and react at the anode to form oxygen gas and generate electrons for the external circuit.

Electrolysis of Water

Electrolysis of water is the decomposition of water into oxygen and hydrogen at the electrodes when an electric field is applied through it. In this process, oxidation takes place near the anode generating hydrogen ions (H⁺) and oxygen (O₂), and reduction takes place near the cathode generating hydroxyl ions (OH⁻) and hydrogen (H₂) [7].

Water electrolysis is currently the simplest method of producing hydrogen, but accounts for only about 4% of all the hydrogen production methods. This is because the technology is limited due to high cost associated with a higher power consumption relative to production, high installation cost, equipment maintenance cost, and low equipment durability and safety [8]. Recently, various studies have been conducted to overcome the limitations in hydrogen production and to

increase its efficiency through water electrolysis. In line with this concern, Choi and Lee [8] conducted an experimental study on water electrolysis using cellulose nanofluid (CNF, $C_6H_{10}O_5$) as an electrolyte. The variables of the experiment were CNF concentration, anode material, voltage applied to the electrode, and initial temperature of the electrolyte. De Souza et al. [9] used imidazolium ionic liquid as an electrolyte for hydrogen production through water electrolysis, and found that the electrolyte improved efficiencies of hydrogen production. Mandal et al. [10] on the other hand, experimented and analyzed the changes in the amount of hydrogen produced according to the concentration during electrolysis.

The three basic types of water electrolysis cell configurations according to Grigoriev et al. [11] are: (i) the gap-cell configuration – there is a gap distance between the electrodes and the cell separator; (ii) the zero-gap cell configuration – porous electrodes are pressed against the cell separator; (iii) the PEM cell – the electrolyte is confined in a thin layer that acts as electrolyte and cell separator at the same time. For comparison, whereas modern PEM water electrolyzers are commonly operated at 1 A/cm^2 , with a cell voltage of approximately 1.8 V and an enthalpy efficiency of approximately 80%, large-scale commercial alkaline electrolyzers are usually operated in the $0.2 - 0.5 \text{ A/cm}^2$ range, with a cell voltage of approximately 2 V corresponding to a cell efficiency of approximately 75% [12].

An electrolyzer, or an electrolytic hydrogen production plant in general, requires several sub-systems to guarantee the success of the process. Hydrogen and oxygen are generated in the electrolysis module as a result of the direct current (DC) delivered by the power supply. The gases produced are cooled, purified, compressed, and stored. Many facilities do not store the oxygen but discharge it into the atmosphere. Some electrolyzers operate at high pressure to eliminate the compression stage and thereby reduce the production and energy costs of the process. The excess heat generated in the electrolytic process is removed through an air-cooling system, in the case of very small units, or a water-cooled system for larger units. Finally, a supply stage is responsible for replenishing the water consumed during the process. The water is treated to ensure that it complies with the minimum purity requirements, thereby avoiding mineral deposits on the cells, the accelerated deterioration of the cell components, and potential undesirable collateral electrochemical reactions [13].

Studies on alkaline electrolyzers

In alkaline electrolyzers, concentrated aqueous potassium hydroxide (KOH) solution is used as the electrolyte as KOH is relatively cheap and is more conducting than aqueous sodium hydroxide solution [14]. Mutlu et al. [15] studied the effect of subcritical water condition, and the use of aluminium anode while generating hydrogen through an alkaline water electrolysis system. The research is based on recent studies showing that heating under sufficient pressure to maintain water at the boiling point (called subcritical water) is beneficial in improving the rate of chemical reaction in water electrolysis.

Amores et al. [16] proposed that the process efficiency of an alkaline water electrolyzer system was sensitive to operating parameters such as electrode/diaphragm distance and electrolyte concentration. Their study observed that an optimum distance exists between electrodes when sheet electrodes are used instead of porous ones. Amores et al. [16] reported that the distance between electrode and diaphragm had a decisive influence on the ohmic overpotentials in the electrolyzer cells. It was observed that when the width of the electrolyte chamber decreased, overall conductivity increased due to the lower amount of electrolyte which separated the anode and cathode.

Rearden et al. [17] designed an optimized alkaline water splitting device test cell for renewable energy storage as hydrogen. The research focused mainly on the design optimization of a small-scale water splitting device, aimed at a bench test cell, but scalable to the domestic and small-scale production market. Design parameters such as energy efficiency, rate of hydrogen production, product gas purity, physical footprint, and cost factors were considered in the optimization process. This optimization was achieved by iteratively modifying and improving upon the geometry of the existing cell designs. The cell design was initially modified to allow for compression bolts to run through the centre of the cell edges, this modification provided a more uniform compression distribution across the cell eliminating the bowing of the cell electrodes previously observed. Zhang et al. [18] also designed an optimized alkaline water electrolyzer system for hydrogen production. The optimization was targeted to utilizing the surplus heat developed in the electrolyzer during the hydrogen production process. Based on semi-empirical equations and thermodynamic electrochemical analyses of an alkaline water electrolyzer system, it was found that when electrolyte concentration was increased, the input voltage of the electrolyzer first decreased, and then increased for other given parameters.

In the same way, Chakik et al. [19] studied the effect of operating parameters on the production of hydrogen by alkaline water electrolysis using Zinc alloys as materials for the cathode. The main aim of their study was to select the best alloy for producing hydrogen while investigating the effects of some operating parameters such as electrode composition, electrolyte concentration, operating voltage and current. Different concentrations of sodium hydroxide (NaOH) solution was used as the electrolyte throughout the experiment, and binary alloys of Zinc with Iron, Copper, Chromium and Cobalt were prepared as electrodes for the cathode. From the experiment conducted, Chakik et al. [19] obtained that the amount of hydrogen production increased on the increase of both current and voltage. Also, Kovac et al. [20] in their study of solar hydrogen production via alkaline water electrolysis, constructed a laboratory alkaline electrolyzer for the production of hydrogen. The electrolyzer novelty is related to the bipolar design using porous nickel (Ni) metal foam as the electrode material. It also consisted of three cells connected into a stack with the applied bipolar design. The electrolyzer design improved hydrogen production to 1.138 grams of hydrogen per hour, compared to the single-cell alkaline electrolyzers which produce less.

Palhares et al. [21] designed a cylindrical alkaline water electrolytic cell made of acrylic, with a working volume of approximately 675 cm³, and 304 stainless steel electrodes to produce hydrogen. Sodium hydroxide was used as the electrolyte (NaOH 2-5 mol L⁻¹), and the direct current voltages applied were 2.0, 2.7, and 3.4V. The maximum hydrogen production was achieved with 5.0 mol L⁻¹ NaOH and 3.4V electric voltage. Abe et al. [22] produced hydrogen from an alkaline water electrolyzer test plant. The test plant was operated under various operating conditions, with different combinations of electrodes. Expanded sheet porous polytetrafluoroethylene (PTFE) impregnated with potassium titanate was used for the diaphragms. The several electrodes tested in the plant include raney nickel electrode, sintered alloy nickel electrode, and high surface area nickel electrode. The high surface area nickel electrode showed the best results with a cell voltage of 1.64 V (90% efficiency) at 120°C and 400 mA cm⁻¹. The purity of the hydrogen and oxygen gases was measured under various operating conditions. The purity of hydrogen was sufficiently 99.95 vol %, however, some amount of hydrogen was observed in the product of oxygen gas, up to about 1 vol %.

Haug et al. [23] developed a model for the prediction of the product gas purity in alkaline water electrolyzer as a function of the current density, electrolyte flow rate, temperature and concentration as well as electrolyte cycling strategies. The developed model was validated through an experiment carried out on the electrolyzer. Potassium hydroxide solution with a concentration of 31 wt% was used as the electrolyte and was continuously pumped through the electrolysis cell to avoid gas accumulation and to check the rate of temperature rise. Experimental results suggested an improvement of the gas purity through a reduction of the electrolyte flow rate, an increase in the electrolyte temperature, and an increase in the electrolyte concentration. Shen et al. [24] on the other hand, studied the overall energy conversion efficiency and the power regulation performance of the alkaline water electrolyzer system for hydrogen production. In their study, a design of a new alkaline water electrolyzer was developed, aimed to improve the dynamic power regulation performance and increase the overall energy efficiency. This aim was achieved through the development of a new modular structure of the alkaline water electrolyzer based on heat energy exchange. It was obtained that the overall energy efficiency could be improved under all working conditions up to about 16%, and the average energy loss per unit time be reduced.

Schalenbach et al. [25] presented a highly efficient alkaline water electrolyzer which consisted of a thin diaphragm and thin high surface area Ni electrodes that were prepared by hot-dip galvanizing (HDG) of Ni meshes in zinc, and subsequent dealloying. The increase in the surface area led to a significantly improved performance in an alkaline electrolysis cell assembly, reaching current densities as high as 2 A/cm² at reasonable overpotentials, which is well comparable to state-of-the-art noble-metal based acidic water electrolyzers. Pierozynski et al. [26] also developed an innovative, laboratory size alkaline water electrolyzer (AWE) system, capable of efficiently producing ultra-pure hydrogen and oxygen gases. The system is composed of a zero-gap, bipolar-electrode stack, equipped with a polymer-based membrane, along with two

drying columns which offers effective purification of hydrogen and oxygen gaseous products. Results of the experiments carried out on the developed system showed that the use of high-quality commercial membrane just with single-stage gas drying columns aided the achievement of pure hydrogen and oxygen products of about 99.90% and 99.60% respectively.

Studies on proton exchange membrane (PEM) electrolyzers

A PEM electrolyzer is an acid-based electrolyzer in which a highly acidic polymer membrane serves as the electrolyte that conducts protons to the cathode, and also as the separator between the anode and cathode compartments [27]. No ionic compounds are added to a PEM electrolyzer to increase the water ion conductivity. Only pure water is added to the electrolyzer where it is converted into pure streams of hydrogen and oxygen [28]. Furthermore, according to the study carried out by Kelly [28], electrolyzers using acidic solutions need noble metal electrodes, especially at the anode where the process is usually corrosive. A common electrolyte in acid-based electrolyzers is sulfuric acid; this is because it is a strong acid that dissociates to produce hydrogen ions in water solution. The bisulfate and sulfate anions are very difficult to oxidize, so they remain in solution and are not oxidized at the anode.

Koponen et al. [29] investigated the effect of power quality on the specific energy consumption of PEM water electrolyzers, with a semi-empirical cell model. The model allowed the simulation of the electrolyzer specific energy consumption as a function of time. To get a concrete example, the method was applied on a single cell with Nafion 117 membrane. Results obtained showed that the effective electrolyzer cell area should be up to five times as high as an ideal DC power supply when powered by the 12-pulse thyristor rectifier supply to match the specific energy consumption between the two power supply configurations. It is worthy to note that Koponen et al. [29] achieved their study analysis on the design of PEM water electrolysis system using simulation tools, and afterwards verified the outcomes experimentally. It was concluded that a higher power quality offers lower specific energy consumption. Also, Selamet et al. [30] designed a 100 cm² single cell and a 10-cell stack PEM electrolyzers, and investigated the effects of some operating parameters such as temperature, pressure, and feed water flow rate of the system. The single-cell reached an efficiency of 87%, whereas 85% efficiency was obtained with the 10-cell stack system at 1 A/cm². The performance of the operating parameters was found to be enhanced at higher operating temperatures because of lower activation barrier, enhanced reaction kinetics, better conductivity of the membrane, and improved mass transport. However, it was reported that as the pressure increased, the performance of the PEM electrolyzer stack decreased. On the other hand, the feedwater flow rate was found to have an insignificant effect on the performance, aside from it also being used as a coolant.

Balaji et al. [31] designed a PEM water electrolyzer system that can produce 80 l/h hydrogen (purity > 99.99%) with a moderate pressure range up to 500 kPa (73 psi), at an operating current of 100 A with an energy efficiency of 77.48%. The PEM electrolyzer stack was designed to operate on two cells with an electrode area of 100 cm² and a stack voltage of 3.88 V. Platinum

black (0.4 mg/cm^2), Iridium (IV) oxide (1.2 mg/cm^2), and Nafion 117 were used as the cathode, anode, and electrolyte respectively. The PEM electrolyzer system designed by Balaji et al. [31] comprised an electrolyzer stack, water reservoir, water level and purity indicator, switched-mode power supply for running the electrolyzer stack at desired current, hydrogen purity level indicator, oxygen gas sensor, pressure transducer, and many more. From the experiments carried out on the system, a stack efficiency of 77.48% was achieved at a current density of 1 A/cm^2 at 500 kPa pressure. It was also concluded that it is possible to store hydrogen directly in pressurized vessels from PEM electrolyzers. Briguglio et al. [32] equally designed a 10-cell stack compact prototype system for hydrogen production based on proton exchange membrane. The 1 kW PEM electrolyzer system was designed to operate in automated mode to enable the check and control of some important operating parameters such as pressure, temperature, single-cell voltage, etc. Experimental data on the system showed that the flow rate influenced the stack performance. A flow rate too high reduced the stack outlet temperature because of the relevant extraction of heat produced. Consequently, a lower stack performance was recorded at a very high water flow rate. Thermal energy produced by the 10-cell stack (irreversible process) was not enough to sustain a temperature level of $75 \text{ }^\circ\text{C}$ since part of the heat was absorbed by the thermodynamic endothermic process. Consequently, the electric heat source consumption increased with operating temperature and the maximum system efficiency was obtained at $40 \text{ }^\circ\text{C}$. However, the stack voltage was more stable at $75 \text{ }^\circ\text{C}$ than at $40 \text{ }^\circ\text{C}$ because at high temperatures the reaction kinetics were faster, allowing the operation to reach a stable condition in a short time. The investigation on the system component's energy consumption showed that the efficiency could be increased with better insulation of stack and using an AC/DC converter with higher efficiency. Besides, system efficiency would reach a level higher than 68% using waste heat or heat produced by solar panels.

Corrosion properties and interfacial contact resistance (ICR) development of a selection of non-coated bipolar plate materials have been tested by Lædre et al. [33], at conditions relevant for PEM water electrolysis. In both the potentiostatic and potentiodynamic polarization tests, tantalum, niobium, and titanium produced low current densities compared to the other materials. Neither of these materials experienced any weight loss during polarization, which indicates that they did not corrode. On the other hand, both niobium and tantalum showed a significant increase in ICR, as compared to the negligible increase for titanium during the one-hour potentiostatic test. However, prolonged polarizations at 2.0 V showed that the ICR increased also for titanium with time. Auger electron spectroscopy (AES) analysis confirmed that the increase in ICR for titanium, tantalum and niobium could be attributed to the oxide layer growth on the material surface. Out of the tested materials, titanium gr. 2 was the best performing material with excellent corrosion resistivity.

Lu et al. [34] claimed that water electrolysis application is limited by the high overpotential of oxygen evolution reaction (OER). In their study, however, hydrogen fuel was obtained from wastewater by replacing OER with aniline electrochemical polymerization. The potential of

aniline electro-polymerization is 0.32 V and 0.90 V at a current density of 10 and 30 mA cm⁻² respectively. Compared to the OER on the carbon paper, the potential of aniline polymerization decreases 1240 mV at the current density of 30 mA cm⁻². Producing the same amount of hydrogen, it could be found that up to 56% of the energy input could be saved.

Studies on electrodes and diaphragm technology

An electrode is an electric conductor, usually metal, used as either of the two terminals of an electrically conducting medium. It conducts current into and out of the medium, which may be an electrolytic solution as in a storage battery, or a solid, gas, or vacuum. The electrode from which electrons emerge is called the cathode and is designated as negative; the electrode that receives electrons is called the anode and is designated as positive [35]. Electrode materials according to Coutanceau et al. [36] have to be corrosion-resistant whereas keeping high catalytic properties versus time. The most used materials for alkaline electrolyzer cell anodes are based on nickel, cobalt, and iron. However, electrodes based on nickel, and particularly nickel electrodes recovered by a nickel oxide layer, show very good stability in alkaline media and are currently used in commercial systems. Platinum nanoparticles deposited on a carbon black support can be used for the hydrogen evolution reaction (HER) at the cathode of an alkaline electrolyzer cell. In such media, cheaper materials also display relatively good activity for this reaction. Scott [14] considered four main factors to be important in developing a commercial electrode for alkaline water electrolysis: electrochemical efficiency; stability; scalability; and cost. The choice of electrode materials is initially governed by requirements of good electrical conductivity, minimum overvoltage (high electrocatalytic activity), and good corrosion resistance in the alkaline electrolyte at the proposed operating temperature. In conventional water electrolysis, the cathode material is either steel or nickel, which may be activated. The anode, which is subject to greater corrosion than the cathode is based on nickel (an example is Ni plated steel or an activated Ni plate or coating).

Zayat et al. [37] reported the performance of an “all-iron” alkaline water electrolyzer cell that uses inexpensive steel-based electrodes. The electrolyzer uses a steel mesh coated with a thin catalytic coating of alpha-nickel hydroxide for the oxygen evolution electrode, and another steel mesh sputter-coated with nickel and molybdenum for the hydrogen electrode. The electrolyzer system with these steel-based electrodes, a commercial Zirfon separator, and a solution of 30% potassium hydroxide operated continuously for 100 h at 1 A cm⁻² with no noticeable degradation. It further exhibited an electrolysis cell voltage of 1.83 V and 1.71 V at 100 mA cm⁻² when operating at 23 °C and 70 °C, respectively. The study goes to show that the performance of the steel-based electrodes is comparable to commercial electrodes based on nickel substrates.

Coutanceau et al. [36] described a diaphragm as a microporous material with average pore sizes less than 1µm, allowing the transport of water and hydroxyl ions between the anode and the cathode compartments, and the separation of gases. The characteristics required for the diaphragm are high permeation to water, high corrosion resistance in strongly alkaline media,

and high ionic conductivity to obtain high cell efficiency. An electrolyzer diaphragm should isolate oxygen and hydrogen gases and prevent intermixing of catholyte and anolyte two-phase electrolytes to enable the formation of high gas purities and current efficiencies. Hence it should provide a sufficiently high hydrodynamic resistance to the flow of oxygen saturated anolyte and hydrogen saturated catholyte and also provide a good diffusion barrier for the gases [14]. Several kinds of diaphragms have been studied such as composite materials based on ceramic materials or microporous materials: reinforced microporous poly (ether sulfones) (PES) membranes, glass-reinforced polyphenylene sulfide compounds, nickel oxide layers on a mesh with titanium oxide and potassium titanate. The diaphragm should display high performance, low cost, and nonhazardous characteristics. Nickel (II) oxide (NiO) has shown to be a good material and some fabrication methods have been developed for controlling its thickness or porous structure [36].

The separator in an alkaline water electrolysis cell has the function to prevent short circuits between the electrodes and to avoid the mixing of evolved hydrogen and oxygen. For this purpose, the separator needs to be stable under highly alkaline conditions and very conductive for the transport of OH⁻ ions. The conductivity of a separator mainly depends on its porosity and tortuosity as the current passes through the liquid electrolyte in the pores. Furthermore, these properties influence the transport of dissolved gas through the separator. In PEM electrolysis modelling, gas crossover is typically described through a combination of differential pressure-driven convection and diffusional species transport across the membrane. Alkaline water electrolyzers are usually operated with equal anodic and cathodic pressures so that only diffusional crossover occurs [23]. Separators for industrial alkaline water electrolyzers can be made from inorganic, organic or composite materials. For low-temperature electrolyzers, the separator can be nickel oxide, asbestos or polymer. However, many polymers and asbestos become unstable at temperatures above 120 °C. The asbestos diaphragm, widely used in alkaline water electrolyzers has relatively high electrical resistance and is not suitable for use above 100 °C, although stabilization by silicate may be used. It is also carcinogenic and effectively banned from use in new build electrolyzers [14].

Liu et al. [38] investigated the performances of different membranes in an alkaline water electrolyzer at 60°C with 1 M KOH and nickel/iron/cobalt (NiFeCo) catalysts. The membranes investigated were: Sustainion 37-50, Fumasep FAS-50, Fumasep FAPQ, Neosepta ACM, AMI 7001, Nafion 115, and Celazole PBI. Results from the investigation showed that many of the commercially available membranes are not suitable for use in alkaline water electrolyzers. Either they have too high of an area-specific resistance or degrade too quickly under some operating conditions. Sustainion 37-50 membrane was an exception. It was able to operate in an alkaline water electrolyzer at 60 °C in 1 M KOH using NiFeCo catalysts, at 1 A/cm² at about 1.9 V for 2000 h. While the initial voltage was higher than a typical PEM electrolyzer with platinum/iridium catalysts, the stability was better, after about 1000 h, the performance was quite similar. This goes to show the possibility of replacing rare materials such as platinum/iridium with iron or nickel, and still maintaining high currents. PEM electrolyzers represent a zero-gap

concept where a solid electrolyte, typically a humidified perfluorosulfonated polymer (Nafion) is combined directly with two electrodes. The membrane in the PEM electrolyzer provides high proton conductivity, low gas crossover and compact design. No liquid caustic electrolyte is circulated in the cell stack, which makes the PEM electrolyzer both safer and more reliable compared to the alkaline electrolyzer [33]. Furthermore, Santos et al. [39] classified electrolyzer separators into three types:

- i. Porous spaces – They are open structures such as plastic meshes, which provide a physical barrier between electrodes. They can offer dimensional support for fragile electrodes, a membrane, or a microporous separator. These spacers present little or no resistance to the mixing of anolyte and catholyte and have pore sizes in the range of 0.5-12 mm.
- ii. Microporous separators – These diaphragms allow transport of solvent and solute, as well as ions, due to hydraulic permeability. However, these diaphragms act as both convection and diffusion barriers because of their relatively small pore sizes (0.1-50 μm). Examples include porous ceramics (asbestos, glass frits, and porous pot) and porous polymers (porous polyvinylchloride (PVC), polyolefins, and PTFE).
- iii. Ion exchange membranes – These separators divide the cell into two hydraulically separated compartments; they function as barriers to convection and diffusion while permitting selective migration of ions. These materials have chemically designed pores of molecular size, typically in the range of 10^{-9} - 10^{-8} m. Ion exchange membranes include fluorocarbon and hydrocarbon materials that have ion-exchange groups distributed throughout their structure.

Brauns et al. [40] suggested that two variants of electrolyzer cell designs exist. Earlier alkaline water electrolyzers used a conventional assembly with a defined distance between both electrodes. Recently, this concept was replaced by the zero-gap assembly, where the electrodes are directly pressed onto the separator to minimize ohmic losses due to the electrolyte. According to Brauns et al. [40], porous materials like Zirfon Perl UTP 500 (AGFA) or dense anion exchange membranes can be used as separators. The zero-gap design tries to eliminate the electrolyte losses by minimizing the electrode distance. However, there is still a minimal gap between both electrodes which can increase the cell voltage. The activation overvoltages are defined by the electrode materials. Whereas nickel is the most used electrode material, it provides very high overvoltages for the oxygen and hydrogen evolution reaction; hence, electrocatalytic materials are added to the electrodes. Iron is a cost-efficient catalyst for the oxygen evolution reaction. Molybdenum, on the other hand, decreases the overvoltage for the evolution of hydrogen at the cathode.

According to Brauns et al. [40], the most used electrolyte for alkaline water electrolysis is an aqueous solution of potassium hydroxide (KOH) with 20 to 30 wt% KOH, as the specific conductivity is optimal at the typical temperature range from 50 to 80 °C. Sodium hydroxide solution (NaOH) is a cheaper alternative that has a lower conductivity [41]. Calculated specific

electrolyte conductivities for both electrolyte solutions at different temperatures has it that while KOH provides a specific conductivity around 95 Sm^{-1} at 50°C , NaOH reaches a value around 65 Sm^{-1} . At a temperature of 25°C , a similar effect would occur. The conductivity of KOH is around 40 to 50% higher than the conductivity of NaOH solution at the optimal weight percentage. Again, another aspect is the solubility of the product gases inside the electrolyte, as this influences the resulting product gas purity. In general, the gas solubility decreases with an increasing electrolyte concentration due to the salting-out behaviour. NaOH solution also shows a slightly higher salting-out effect than KOH solution. Hence, the product gas solubility is higher in a KOH solution [40]. Water has a very high electrical resistance and cannot be directly split into hydrogen and oxygen. This can only occur when extremely high electrical currents are applied to the system, which is impractical. Therefore, the addition of an electrolyte lowers the electrical energy required to initiate the reaction [42]. Marangio et al. [27] noted that saltwater would not be an appropriate source of conducting water solution for electrolysis because chloride would be oxidized at the anode to chlorine gas. Hydrogen would still be produced at the cathode. Meanwhile, saltwater electrolysis is used commercially in the manufacture of sodium hydroxide and chlorine where those products are desired. However, it is not useful for making hydrogen unless sodium hydroxide and chlorine can also be used.

In alkaline and PEM water electrolysis cells, the cell separators (diaphragm and polymer membrane) are not perfectly gas proof. There are several microscopic phenomena that occur, tending to reduce the faradaic efficiency of the cells. However, this situation can be analyzed by calculating the value of the parasitic current densities associated with these different effects. The first effect is due to the diffusion of hydrogen from the cathodic to the anodic cell compartment. According to the Fick equation, the rate of gas diffusion through a membrane/diaphragm is proportional to the partial pressure of the gas. Therefore, when operating pressure is increased, there is an immediate impact on cross-permeation phenomena and gas purity [11].

Table 1. Comparison of electrolysis cells [43].

| Type | Alkaline | Acid | Acid Polymer Electrolyte | Alkaline Polymer Electrolyte | Solid Oxide |
|----------------|----------------------|--|--------------------------------|------------------------------------|---------------------|
| Charge carrier | OH^- | H^+ | H^+ | OH^- | O^{2-} |
| Reactant | Water | Water | Water | Water | Steam |
| Electrolyte | Na^+ or KOH | H_2SO_4 or H_2PO_4 | Polymer | Polymer | Ceramic |
| Electrodes | Nickel | Ir and Pt | Ir and Pt | Ni and Ag | Nickel cermet |
| Temperature | 80°C | 150°C | 80°C | 60°C | 500°C |

Table 2. Main advantages and drawbacks of electrolysis cell systems [36].

| | PEM Electrolysis | Alkaline Electrolysis | Solid Oxide Electrolysis |
|------------|---|------------------------------|---------------------------------|
| Advantages | Near-term technology | Commercial technology | Efficiency up to 100% |
| | High current densities | Non-noble catalysts | Thermoneutral voltage |
| | High voltage efficiency | Long-term stability | Non-noble catalysts |
| | Good partial load range | Relatively low cost | High-pressure operation |
| | Rapid system response | MW range stacks | |
| Drawbacks | Compact system design, high gas purity, and dynamic operation | Cost-effective | |
| | High cost of components | Low current densities | Mediate-term technology |
| | Acidic corrosive medium | Crossover of gases | Bulky system design |
| | Possibly low duration | Degree of purity | Durability (brittle ceramics) |
| | Stacks below MW range | Low partial load range | no dependable cost information |
| | | Low dynamics | |
| | | Low operational pressures | |
| | | Corrosive liquid electrolyte | |

Table 3. Comparison of water electrolysis methods [44].

| S/N | Parameters | PEM Electrolyzer | Alkaline Electrolyzer |
|-----|---|-------------------------|------------------------------|
| 1. | Cell temperature/(°C) | 50-80 | 60-80 |
| 2. | Cell pressure/(10 ⁵ Pa) (bar) | <30 | <30 |
| 3. | Current density/(mA cm ⁻²) | 0.6-2.0 | 0.2-0.4 |
| 4. | Cell voltage/V | 1.8-2.2 | 1.8-2.4 |
| 5. | Power density/(mW cm ⁻²) | <4.4 | <1 |
| 6. | Efficiency (HHV)/(%) | 67-82 | 62-82 |
| 7. | Specific energy consumption stack/(kW h) (Nm ³) ⁻¹ H ₂ | 4.2-5.6 | 4.2-5.9 |
| 8. | Specific energy consumption system/(kW h) (Nm ³) ⁻¹ H ₂ | 4.5-7.5 | 4.5-7.0 |
| 9. | Partial load range/(%) | 5-10 | 20-40 |
| 10. | Cell area/(m ²) | <0.03 | >4 |
| 11. | H ₂ production rate/(Nm ³ h ⁻¹) | <10 | <760 |
| 12. | Lifetime stack/h | <20,000 | <90,000 |
| 13. | Lifetime system/a (years) | 10-20 | 20-30 |
| 14. | Degradation rate/(μV h ⁻¹) | <14 | <3 |

Studies on Hydrogen Fuel Cell

A fuel cell is an electrochemical cell that converts the chemical energy of a fuel, often hydrogen, and an oxidizing agent, often oxygen, into electricity through a pair of redox reactions. Hydrogen fuel cells combine hydrogen and oxygen to produce electricity, heat, and water. In a hydrogen fuel cell, a catalyst at the anode separates hydrogen molecules into protons and electrons, which take different paths to the cathode. The electrons go through an external circuit, creating a flow of electricity. The protons migrate through the electrolyte to the cathode where they combine with oxygen and the electrons to produce water and heat. Fuel cell electrodes are separated by a membrane whose purpose is to prevent the fuel and oxidant from mixing, as well as providing an ionically conductive pathway for the protons. Thus, its required properties are high ionic conductivity (and zero electronic conductivity) under cell operating conditions, long term chemical and mechanical stability at elevated temperatures in oxidizing and reducing environments, good mechanical strength with resistance to swelling, low oxidant and fuel crossover, pinhole free structure, interfacial capability with catalyst layers and low cost [45].

The fuel cell stack is the heart of a fuel cell power system. It generates electricity in the form of direct current (DC) from electrochemical reactions that take place in the fuel cell. A single fuel cell produces less than 1 V, which is insufficient for most applications. Therefore, individual fuel cells are typically combined in series into a fuel cell stack. A typical fuel cell stack may consist of hundreds of fuel cells. The amount of power produced by a fuel cell depends upon several factors, such as fuel cell type, cell size, the temperature at which it operates, and the pressure of the gases supplied to the cell [2]. U.S. Department of Energy [2] classified fuel cells primarily by the kind of electrolyte they employ. This classification determines the kind of electro-chemical reactions that take place in the cell, the kind of catalysts required, the temperature range in which the cell operates, the fuel required, and other factors. These characteristics, in turn, affect the applications for which these cells are most suitable. The following are the several types of fuel cells currently under development, each with its own advantages, limitations and potential applications.

a) Proton Exchange Membrane Fuel Cells – PEM fuel cells deliver high power density and offer the advantages of low weight and volume compared with other fuel cells. PEM fuel cells use a solid polymer as an electrolyte and porous carbon electrodes containing a platinum or platinum alloy catalyst. They need only hydrogen, oxygen from the air, and water to operate. They are typically fueled with pure hydrogen supplied from storage tanks or reformers.

b) Alkaline Fuel Cells – These fuel cells use a solution of potassium hydroxide in water as the electrolyte, and can use a variety of non-precious metals as a catalyst at the anode and cathode. AFCs that use a polymer membrane as the electrolyte have recently been developed. These developments are similar to the conventional PEM fuel cells, except that they use an alkaline membrane instead of an acid membrane. One of the major challenges of this fuel cell type is that it is susceptible to poisoning by carbon dioxide (CO₂); so much that the smallest

amount of CO₂ in the air can significantly affect cell performance and durability due to carbonate formation. Other challenges of the AMFCs include tolerance to carbon dioxide, membrane conductivity and durability, higher temperature operation, water management, power density, and anode electrolysis.

c) Direct Methanol Fuel Cells – Most fuel cells are powered by hydrogen, which can be fed to the fuel cell system directly or can be generated within the fuel cell system by reforming hydrogen-rich fuels such as methanol, ethanol, and hydrocarbon fuels. Direct methanol fuel cells (DMFCs), however, are powered by pure methanol, which is usually mixed with water and fed directly to the fuel cell anode. DMFCs do not have many of the fuel storage problems typical of some fuel cell systems because methanol has a higher energy density than hydrogen; though less than gasoline or diesel fuel.

d) Phosphoric Acid Fuel Cells – Phosphoric acid fuel cells (PAFCs) use liquid phosphoric acid as an electrolyte; the acid is contained in a Teflon-bonded silicon carbide matrix and porous carbon electrodes containing a platinum catalyst. PAFCs are more tolerant of impurities in fossil fuels that have been reformed into hydrogen than PEM cells which are easily “poisoned” by carbon monoxide (CO); this is because CO binds to the platinum catalyst at the anode, decreasing the fuel cell’s efficiency. Furthermore, the PAFC is considered the “first generation” of modern fuel cells. It is one of the most mature cell types and the first to be used commercially.

e) Molten Carbonate Fuel Cells – Molten carbonate fuel cells (MCFCs) are high-temperature fuel cells that use an electrolyte composed of a molten carbonate salt mixture suspended in a porous, chemically inert ceramic lithium aluminum oxide matrix. MCFCs offer improved efficiencies and have a significant cost reduction over PAFCs. When coupled with a turbine, MCFCs can reach efficiencies of about 65%, considerably higher than the 37% - 42% efficiencies of PAFC plants. Unlike alkaline, phosphoric acid, and PEM fuel cells, MCFCs do not require an external reformer to convert fuels such as natural gas and biogas to hydrogen. At the high temperatures at which MCFCs operate, methane and other light hydrocarbons in these fuels are converted to hydrogen within the fuel cell itself by a process known as internal reforming; this also reduces cost.

f) Solid Oxide Fuel Cells – Solid oxide fuel cells (SOFCs) use a hard, non-porous ceramic compound as the electrolyte. They are about 60% efficient at converting fuel to electricity. SOFCs operate at very high temperatures – as high as 1000 °C (1830 °F). High-temperature operation removes the need for precious-metal catalyst, thereby reducing cost. It also allows SOFCs to reform fuels internally, which enables the use of a variety of fuels and reduce the cost associated with adding a reformer to the system.

g) Reversible Fuel Cells – These fuel cell types produce electricity from hydrogen and oxygen and generate heat and water as byproducts, just like other fuel cells. However, reversible fuel cell systems can also use electricity from solar power, wind power, or other sources to split

water into oxygen and hydrogen fuel through electrolysis. Reversible fuel cells can provide power when needed, but during times of high power production from other technologies (such as when high winds lead to an excess of available wind power), reversible fuel cells can store the excess energy in the form of hydrogen.

Baroutaji et al. [46] developed a PEM fuel cell in which conventional flow plates were replaced with metal foam plates. As an alternative to conventional flow plates, researchers have identified that open pore cellular foam (OPCF) materials can provide several advantages over conventional flow plates such as better gas flow through the fuel cell, lower pressure drop from inlet to outlet [47]. In Baroutaji et al. [46], two different housings were designed to accommodate the foam flow plates on the anode and cathode sides. The OPCF on the cathode side serves as air breathing, allowing air convection from the surrounding atmosphere into the cell. While the OPCF on the anode side is supplied with pressurized hydrogen through appropriate fittings, and gaskets are used to seal the cell. To prove the advantage of using OPCF flow plate, Computational Fluid Dynamic (CFD) analysis was also carried out on the conventional flow plate design. Large pressure drops were recorded and were viewed with serpentine flow plates. Velocity disturbances at the bends could significantly affect flow. In contrast, the OPCF anode housing recorded low pressure drops and velocity disturbances were minimal with an even flow regime visible.

On the other hand, Alhassan et al. [48] designed an alkaline fuel cell that operated between the temperatures of 100 °C and 250 °C, and generated 121 W of power. This design exploited the high conductivity and boiling point of concentrated alkaline (potassium hydroxide) solution, porous nickel electrodes were as well used for the anode and cathode, separated by the electrolyte. The fuel cell was constructed with polyvinyl chloride (PVC). The design parameters of the fuel cell system such as the length, height, and volume of the cell were specified. The enthalpies of hydrogen and oxygen into the cell was 288.98 KJ/hr and 147.06 KJ/hr respectively, while the enthalpies of potassium carbonate and water leaving the cell were -1.11×10^6 KJ/hr and -9.71×10^5 KJ/hr respectively. This showed that the reaction was exothermic, hence the materials for the construction needed to be carefully selected, considering heat production. The fuel cell device generated 121 W of power. Brunton et al. [49] also designed a single cell alkaline fuel cell testbed using the EloFlux electrolyte. The active separator was made from porous plastic film. For improved performance, the cell used gas-diffused electrodes. The electrode at the anode was made of Raney nickel and polytetrafluoroethylene (PTFE), a stable wet proofing agent to bind them together, and the electrode at the cathode was made of silver and PTFE. The electrolyte used was aqueous KOH. The performance of the fuel cell system was affected by small changes in gas supply, pressure variations and temperature, requiring constant monitoring and control.

An alkaline membrane fuel cell (AMFC) dynamic mathematical model with temperature dependence on space and current was developed by Sommer et al. [50]. The developed model was experimentally validated by direct comparison with output voltage and power measurements

performed in a cellulose-based AMFC prototype in the laboratory. The single AMFC voltage power output was obtained numerically with the mathematical model, and the results show good qualitative and quantitative agreement with the measured experimental data. Ariyanfar et al. [51] reported a research on a 100 W alkaline fuel cell with mobile electrolyte, with its peripheral equipment designed in determined steps to achieve a design model. The model was optimized using GAMS codes to determine the optimum values of cost model, electrochemical and heat transfer equations. It was concluded that the electrolyte flow rate, its inlet and outlet temperatures, pressure drop, and heat exchanger area were some of the parameters that significantly affected the performance of the cell, as well as its total cost. Again, the efficiency of the system was found to reduce when the operating temperature was increased.

Table 4. Performance comparison between alkaline fuel cells and PEM fuel cells [52].

| Parameters | Alkaline Fuel Cell | PEM Fuel Cell |
|--------------------------|----------------------------|------------------------|
| Current density | 300-600 mA/cm ² | 600 mA/cm ² |
| Voltage per cell | 0.8-0.85 V | 0.65-0.70 V |
| Power density | 0.17 KW/Kg | 0.25 KW/Kg |
| Lifetime | 4000 hours | ≈ 5000 hours |
| Cost per KW | \$ 100 - 150 | \$ 500 - 1000 |
| Catalyst: | | |
| Anode | Nickel | Platinum |
| Cathode | Nickel/Silver | Platinum |
| Maximum fuel impurities: | | |
| Carbon monoxide | Not critical | < 10 ppm |
| Carbon dioxide | < 100 ppm | Not critical |
| Ammonia | Not critical | Very critical |
| Power density | ≈ 2 KW/L | ≈ 1.75 KW/L |

Table 5. Comparison of fuel cell technologies [53].

| Fuel Cell Type | Common Electrolyte | Operating Temperature | Typical Stack Size | Efficiency | Applications | Advantages | Disadvantages |
|--------------------------------|-------------------------|--|--------------------|--|--|---|---|
| Proton exchange membrane (PEM) | Porfluoro sulfonic acid | 50-100 °C 122-212 °F typically 80 °C | <1-100 kW | 60% Transportation 35% Stationary | <ul style="list-style-type: none"> • Backup power • Portable power • Distributed generation • Transportation • Specialty vehicles | <ul style="list-style-type: none"> • Solid electrolyte reduces corrosion and electrolyte management problem • Low temperature | <ul style="list-style-type: none"> • Expensive catalysts • Sensitive to fuel impurities • Low temperature waste heat |

| | | | | | | | |
|-------------------------|--|--------------------------------|------------------------------|--------|---|--|--|
| Alkaline (AFC) | Aqueous solution of potassium hydroxide soaked in a matrix | 90-100 °C 194-212 °F | 10-100 kW | 60% | <ul style="list-style-type: none"> • Military • Space | <ul style="list-style-type: none"> • Quick start-up • Cathode reaction faster in alkaline electrolyte, leads to high performance • Low cost components | <ul style="list-style-type: none"> • Sensitive to CO₂ in fuel and air • Electrolyte management |
| Phosphoric acid (PAFC) | Phosphoric acid soaked in a matrix | 150-200 °C 302-392 °F | 400 kW 100 kW module | 40% | <ul style="list-style-type: none"> • Distributed generation | <ul style="list-style-type: none"> • Higher temperature enables CHP • Increased tolerance to fuel impurities | <ul style="list-style-type: none"> • Pf catalyst • Long start-up time • Low current and power |
| Molten carbonate (MCFC) | Solution of lithium, sodium, and/or potassium carbonates, soaked in a matrix | 600-700 °C 1,112-1,292 °F | 300 kW-3 MW 300 kW module | 45-50% | <ul style="list-style-type: none"> • Electric utility • Distributed generation | <ul style="list-style-type: none"> • High efficiency • Fuel flexibility • Can use a variety of catalysts • Suitable for CHP | <ul style="list-style-type: none"> • High temperature corrosion and breakdown of cell components • Long start-up time • Low power density |
| Solid oxide (SOFC) | Yttria stabilized zirconia | 700-1,000 °C 1,202-1,832 °F | 1 kW-2 MW | 60% | <ul style="list-style-type: none"> • Auxiliary power • Electric utility • Distributed generation | <ul style="list-style-type: none"> • High efficiency • Fuel flexibility • Can use a variety of catalysts • Solid electrolyte • Suitable for CHP and CHHP • Hybrid/GT cycle | <ul style="list-style-type: none"> • High temperature corrosion and breakdown of cell components • High temperature operation requires long start-up time and limits |

Summary and Conclusion

Acid solutions are good electrolytes in PEM electrolyzers because acidic media show high ionic conductivity and are free from carbonate formation, as compared to alkaline electrolytes. However, the acid needs the use of noble metals as electrocatalysts for OER [28]. On the other hand, potassium hydroxide (KOH), sodium hydroxide (NaOH), as well as sodium chloride (NaCl) are used as electrolytes in alkaline electrolyzers. The use of saltwater as a conducting water solution for electrolysis is discouraged because chloride would be oxidized at the anode to produce chlorine gas [27]. KOH is most commonly used in alkaline water electrolyzers because it has higher ionic conductivity than NaOH. KOH is equally used in water electrolysis, avoiding the huge corrosion loss caused by acid electrolytes, and the use of noble metals as catalysts [28]. Nickel is a popular electrode material due to its high activity and availability as well as low cost. Furthermore, adopting a zero-gap cell configuration for the electrolyzer cell electrodes; this technique was found to increase operating current density, while decreasing parasitic ohmic resistance [12, 16, 23, 40].

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