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We start this pioneering work, which do not seek perfection as much as aiming to provide a scientific window that opens a wide area for all the distinctive pens, both in the University of Sabratha or in other universities and research centers. This emerging scientific journal seeks to be a strong link to publish and disseminate the contributions of researchers and specialists in the fields of applied science from the results of their scientific research, to find their way to every interested reader, to share ideas, and to refine the hidden scientific talent, which is rich in educational institutions. No wonder that science is found only to be disseminated, to be heard, to be understood clearly in every time and place, and to extend the benefits of its applications to all, which is the main role of the University and its scholars and specialists. In this regard, the idea of issuing this scientific journal was the publication of the results of scientific research in the fields of applied science from medicine, engineering and basic sciences, and to be another building block of Sabratha University, which is distinguished among its peers from the old universities.

As the first issue of this journal, which is marked by the Journal of Applied Science, the editorial board considered it to be distinguished in content, format, text and appearance, in a manner worthy of all the level of its distinguished authors and readers.

In conclusion, we would like to thank all those who contributed to bring out this effort to the public. Those who lit a candle in the way of science which is paved by humans since the dawn of creation with their ambitions, sacrifices and struggle in order to reach the truth transmitted by God in the universe. Hence, no other means for the humankind to reach any goals except through research, inquiry, reasoning and comparison.

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- Keywords, max. 5 words.
- Introduction.
- Methodology.
- Results and Discussion.
- Conclusion.
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ELECTROCHEMICAL TECHNOLOGIES FOR HYDROGEN PRODUCTION: A REVIEW

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Abstract

Hydrogen has become a key player in energy generation due to its potential to decarbonize the energy sector by offering carbon-free fuel flexibility and high energy content. Various electrochemical technologies exist for hydrogen production, including alkaline electrolysis, anion exchange membrane electrolysis, proton exchange membrane electrolysis, solid oxide electrolysis, and bipolar membrane electrolysis. This review paper provides an overview of these technologies, addressing their different aspects, challenges, and potential advancements, albeit not exhaustively. The findings indicate that each electrochemical production process has its own set of advantages and disadvantages concerning greenhouse gas emissions, operational complexity, and performance characteristics. Generally, the benefits outweigh the drawbacks for each method. However, it is evident that relying on diminishing non-renewable fossil fuels for hydrogen production poses significant operational and environmental challenges.

Keywords: Electrolysis; alkaline electrolysis; anion exchange membrane; proton exchange membrane; solid oxide electrolysis.

Introduction

In a 2021 review by the International Energy Agency (IEA) on global energy and CO₂ emissions, it was reported that greenhouse gas emissions, which significantly contribute to global warming, have reached unprecedented levels (IEA, 2021). The primary factor driving this increase is the burning of fossil fuels for energy generation, which releases harmful pollutants such as CO₂, CO, SO₂, NO_x, and ozone, along with lead, soot, and ash.

Compounding the issue further is the projected 50% rise in global energy demand by 2040, driven largely by population growth and industrialization in developing regions, particularly in Asia and South America (IEA, 2014).

This trend poses a serious threat to the environment, as these emissions trap heat from the sun, leading to global warming and its associated effects, including heatwaves, droughts, floods, wildfires, and rising sea levels. Efforts are being made globally to address climate change and limit temperature rise, with a consensus on the need to reduce CO₂ emissions.

One promising solution is the transition to renewable and clean energy sources to replace traditional fossil fuels. The shift away from fossil fuels is illustrated in Figure (1), which shows the transition from solid and liquid fuels to gaseous fuels such as methane and, eventually, to environmentally friendly hydrogen. This transition is crucial for achieving a sustainable energy future and mitigating the harmful effects of traditional fossil fuels on the environment.

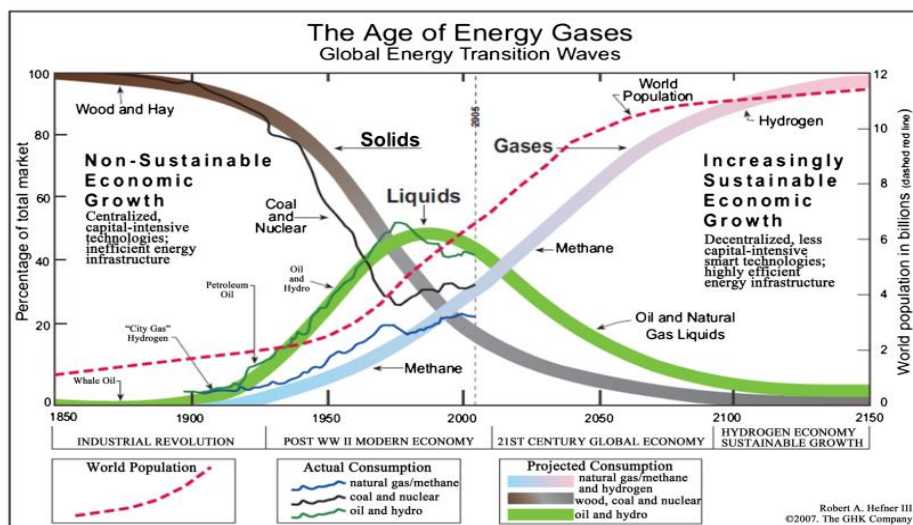


Figure (1): Global Energy Transition Waves Since 1850 to 2150 (Hefner, R.A., 2007).

Among the renewable energy sources that are sustainable, abundant, and naturally replenished are solar, wind, biomass, and geothermal energy. These resources, combined with energy conservation and enhanced efficiency, support the sustainability of renewable energy, help protect the environment, and mitigate climate change. This review paper centers on the production of hydrogen, another renewable energy source. Hydrogen is widely present in hydrocarbons, which are ubiquitously found in the universe, as well as in water and plants. Due to its lightweight nature, hydrogen easily escapes the Earth's atmosphere when exposed to solar radiation. It is a simple element that can bond with other elements to form water and is non-toxic, renewable, and plentiful. Additionally, hydrogen can be utilized as a clean energy source (fuel) after being extracted from water, natural gas, or biomass. Like other

renewable sources, hydrogen is environmentally friendly, socially advantageous, and economically feasible. As a fuel, hydrogen holds significant potential to play a crucial role in the future of energy systems.

Furthermore, hydrogen has found applications in a variety of fields, including wind turbines, solar photovoltaics, electric vehicles, and batteries. When employed as a fuel for energy generation in wind turbines or solar panels, hydrogen enhances their efficiency. It is also utilized in industries such as chemical manufacturing, iron and steel production, metal treatment, petroleum refining, fertilizer production, and food processing, all while producing minimal to no CO₂ emissions compared to fossil fuels. One key advantage of using hydrogen for energy generation is its potential to decarbonize the energy sector by offering carbon-free fuel options and energy storage solutions for the global grid. Moreover, with a high energy content of 142 MJ/kg (Zainal et al., 2024), hydrogen ranks among the most energy-dense fuels available. It has even been used as a fuel for vehicles in outer space, utilizing liquid hydrogen. Furthermore, blending hydrogen with other gases such as ammonia and methane has been explored to enhance energy efficiency and lower greenhouse gas emissions (Dinesh et al., 2022; Xin et al., 2022; Bayramoglu et al., 2023; Habib et al., 2024; Zhang et al., 2024). Notably, green hydrogen is employed in fuel cells for electric vehicles, the production of green ammonia, refrigeration processes, power generation, and as a fuel for heavy transportation in sectors such as shipping and manufacturing, including the cement and steel industries.

Hydrogen gas can be produced through a variety of methods and processes, collectively referred to as hydrogen production technologies (Yu et al., 2021). These technologies encompass electrochemical, thermochemical, biological, and photocatalytic production methods. Electrochemical production involves using electricity to facilitate chemical reactions that yield hydrogen (Dotan et al., 2019), with water electrolysis being the most common technique employed in this category (Anwar et al., 2021). Key electrochemical processes include alkaline electrolysis, anion exchange membrane electrolysis, proton exchange membrane electrolysis, solid oxide electrolysis, and bipolar membrane electrolysis. This method is recognized as an environmentally friendly and sustainable approach for large-scale hydrogen production (Zhang et al., 2024).

In contrast, thermochemical production generates hydrogen through high-temperature chemical reactions utilizing various feedstocks (Guban et al., 2020). Prominent thermochemical processes include steam methane reforming, partial oxidation, auto-thermal reforming, dry reforming, and the gasification of coal and biomass. Among these, steam methane reforming is particularly prevalent for large-scale hydrogen production (Zhang et al., 2024). Biological production, on the other hand, employs microorganisms or their enzymes to generate hydrogen from diverse organic substrates through processes such as dark fermentation and photo-fermentation (Pal et al., 2022).

Generally, biological methods are considered more environmentally friendly and sustainable compared to electrochemical and thermochemical approaches (Zhang et al., 2024). Photo-catalytic production utilizes semiconductor photo-catalysts (Ishaq et al., 2021) to decompose water or other substrates into hydrogen, a clean energy carrier (Hassan et al., 2023), and oxygen under the influence of sunlight (Luo et al., 2021). While photo-catalytic processes are also environmentally friendly and sustainable, they can still produce some greenhouse gas emissions (Hassan et al., 2023; Zhang et al., 2024). Figure (2) illustrates these various hydrogen production technologies, highlighting the different colors associated with hydrogen based on the production method used. This review paper focuses specifically on electrochemical hydrogen production technologies, exploring their various aspects, challenges, and potential advancements.

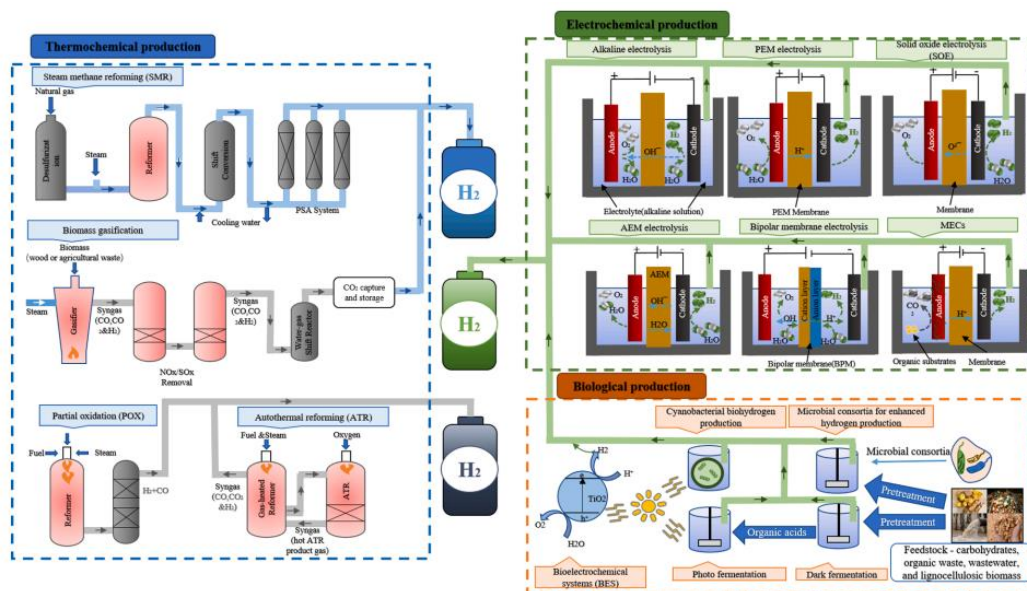


Figure (2): Overview of Different Hydrogen Production Technologies (Chen P-Y, et al, 2021).

Hydrogen, while fundamentally a colorless gas, has been categorized using thirteen distinct colors, each representing a different method or source of hydrogen production. The colors include white, brown/black, grey, red, pink, purple, turquoise, blue, and green. In the energy sector, color codes such as green, blue, turquoise, pink, yellow, and brown are employed to differentiate various types of hydrogen. However, the lack of a standardized naming convention means that hydrogen produced through a specific process may be assigned a unique color, leading to potential variations in coding over time and across different countries. White hydrogen refers to naturally occurring hydrogen. In contrast, black/brown and grey hydrogen are generated from non-

renewable energy sources like coal and natural gas, making them significant contributors to greenhouse gas emissions. In the United States, the predominant form of hydrogen produced is brown hydrogen, derived from lignite coal (Arcos and Santos, 2023), while black hydrogen is produced using bituminous coal. Although coal gasification is a widely used method for hydrogen production, it releases substantial amounts of CO₂ and CO. Similarly, steam methane reforming of natural gas to produce brown or grey hydrogen also results in the emission of unwanted CO₂.

Red hydrogen is generated through a high-temperature catalytic water splitting process that utilizes nuclear thermal energy as its power source. Similarly, purple hydrogen is produced via water splitting that combines thermal and nuclear energies through chemical-thermal electrolysis. Pink hydrogen is also created using nuclear power to electrolyze water. Turquoise hydrogen is obtained through the thermal decomposition of methane via pyrolysis. Blue hydrogen is produced through thermochemical methods, such as steam methane reforming of natural gas or biomass gasification, which results in CO₂ emissions. However, these emissions can be captured and stored underground to mitigate their environmental impact. Despite this, the reliance on natural gas for blue hydrogen production raises sustainability concerns. In contrast, green hydrogen is produced through methods that emit little to no greenhouse gases, leading to minimal or zero emissions. Currently, green hydrogen is mainly derived from renewable energy sources like solar and wind power, which produce no emissions. The energy harnessed from these sources is used to electrolyze water, generating hydrogen through solar panels or wind turbines. Additionally, electrochemical and biological processes can also contribute to green hydrogen production. Furthermore, waste heat from industrial processes can be utilized as a source for green hydrogen (Ni, 2009). In this context, water electrolysis is an electrochemical method that leverages renewable energy to produce green hydrogen gas and oxygen without any carbon emissions.

Hydrogen via Electrochemical Technology

In electrochemical technology for hydrogen production, regardless of the method employed, electricity is utilized to decompose water into its primary elements, hydrogen and oxygen (Dotan et al., 2019). This electricity can be supplied by traditional fossil fuels or renewable energy sources. When renewable energy is used, these electrochemical processes can facilitate large-scale, clean, and sustainable green hydrogen production (Amin et al., 2022a). The water electrolysis method is commonly employed in electrochemical hydrogen production technologies (Anwar et al., 2021). These processes primarily depend on various electrolysis technologies, including alkaline electrolysis cells, proton exchange membrane cells, solid oxide electrolysis cells, anion exchange membrane cells, bipolar membrane electrolysis cells, and microbial electrolysis cells.

In a typical electrochemical process, hydrogen is generated through the breakdown of water into hydrogen and oxygen when an electrical current is passed through an electrolyzer filled with water. An electrolyzer consists of two electrodes, an anode and a cathode, immersed in an electrolyte, across which the electrical current flows.

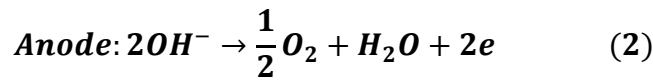
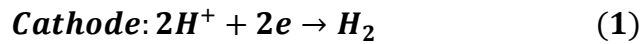
In alkaline electrolysis, the electrolyte is an aqueous solution of potassium hydroxide or sodium hydroxide (de Groot et al., 2022). In contrast, proton exchange membrane cells utilize a solid, proton-conducting polymeric membrane (Sanchez-Molina et al., 2021), which may include catalysts like porous carbon-platinum (Zhang et al., 2024). Solid oxide electrolysis cells, meanwhile, use a solid oxide or ceramic electrolyte, such as yttria-stabilized zirconia (Dey et al., 2020). The anode serves as an oxidizer for water molecules, producing hydroxide ions (OH^-), protons (H^+), or oxygen ions (O^{2-}), depending on the type of electrolysis employed—alkaline, proton exchange membrane, or solid oxide electrolysis, respectively. These ions migrate through the electrolyte towards the cathode, where they are reduced to form oxygen and hydrogen gases (Al-Shara et al., 2021). Once generated, the gaseous hydrogen can be separated from the oxygen and either compressed or liquefied for storage or transportation, as needed.

Alkaline water electrolysis is a straightforward and well-established technology that remains widely utilized (Guo et al., 2019). The electrolysis unit consists of a container holding an electrolyte solution, in which two electrodes are immersed, along with a power supply. The electrolyte typically used is an aqueous solution of sodium hydroxide (NaOH) or potassium hydroxide (KOH) at concentrations ranging from 20% to 30%, maintained at low temperatures between 30°C and 80°C (Seetharaman et al., 2013). The electrodes employed are generally made from nickel materials and asbestos diaphragms. However, this system has limitations due to high operating pressures, low current densities, reduced energy efficiency, and low hydrogen purity (Li and Baek, 2021).

As a more effective and cost-efficient alternative, anion exchange membranes composed of conductive anionic polymers are now being used for alkaline water electrolysis (Hwang et al., 2015). These solid membranes exhibit excellent chemical, mechanical, and thermal properties, addressing issues such as fuel crossover and carbonation associated with the use of aqueous KOH solutions in traditional alkaline water electrolysis (Das et al., 2022). Additionally, anion exchange membranes provide faster response times compared to conventional alkaline water electrolysis, making them a practical choice for applications where speed and high efficiency are critical (Zainal et al., 2024).

When the power supply is activated, electrons begin to flow through the electrolyte solution from the anode to the cathode, where they combine with protons to produce hydrogen. Simultaneously, hydroxide ions migrate to the anode, generating the

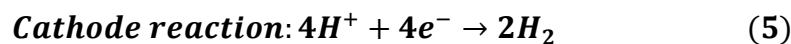
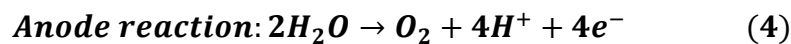
electrons found at the cathode. This process can be described by the following two half-reactions occurring at the cathode and anode, respectively (Falch and Babu, 2021):



Overall, the reaction is as following:

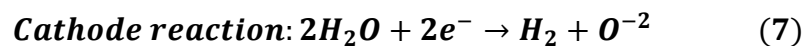
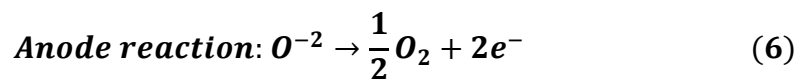


Hydrogen can be efficiently produced through proton exchange membrane electrolysis, which also ensures high purity levels, making it suitable for grid-balancing applications. This method of hydrogen production is advantageous compared to other types of electrolysis due to its compact design. Additionally, proton exchange membrane electrolysis operates at relatively low temperatures, typically between 60 and 80°C. Furthermore, similar to anion exchange membranes, proton exchange membranes provide quicker response times compared to alkaline water electrolysis, making them a viable choice for applications where speed and efficiency are critical (Zainal et al., 2024). However, the performance of this process is significantly influenced by factors such as the electrolyte solution, operating pressure, and the reactions occurring at the electrodes. Hydrogen is generated through the oxidation of water at the anode (oxygen evolution reactions), which releases protons that traverse the membrane and are subsequently reduced to hydrogen at the cathode (hydrogen evolution reactions) (Kumar et al., 2019). The chemical reactions involved in proton exchange membrane electrolysis can be summarized as follows (El-Shafie et al., 2019):



In addition to alkaline water electrolysis and proton exchange membrane electrolysis, solid oxide electrolysis has been explored for hydrogen production using hydrocarbon fuels (such as biogas), glucose, or organic materials (including industrial biomass waste and wastewater) as primary feedstocks. In this method, hydrogen is generated through an internal reforming process of the hydrocarbon fuel, which is then efficiently converted into electricity (Mehr et al., 2021). Solid oxide electrolysis boasts the highest hydrogen efficiency, reaching up to 90% (Gaikwad et al., 2023), in contrast to the 50–60% and 60–80% efficiencies achieved by alkaline water electrolysis and proton exchange membrane electrolysis, respectively (David et al., 2019; Nicita et al., 2020; Yu et al., 2021). Additionally, the electrolyte used in solid oxide electrolysis is

a cost-effective ceramic material (Brynnolf et al., 2018). However, these electrolysis processes necessitate high temperatures (Yuksel et al., 2020), which could be advantageous for industrial applications by utilizing otherwise wasted heat to enhance overall process efficiency (Zhang et al., 2024). Despite its advantages, solid oxide electrolysis faces challenges such as the production of CO, catalyst poisoning, and low hydrogen purity and caloric value (Alves et al., 2013). Furthermore, the technology is relatively expensive (Zhang et al., 2024). Another significant drawback is the short lifespan of solid oxide electrolysis systems, typically around two to three years, compared to 10 to 20 years for proton exchange membrane and alkaline water electrolysis systems, respectively, which may hinder their commercialization (Brynnolf et al., 2018). The chemical reactions involved in proton exchange membrane electrolysis are described as follows (El-Shafie et al., 2019):

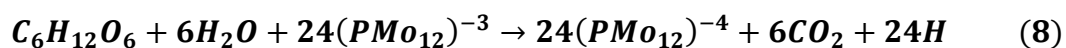


Among these technologies, potassium/sodium hydroxide as an electrolyte is relatively inexpensive, has been utilized for decades, and has demonstrated efficiency across various production scales. Notably, proton exchange membranes, due to their solid polymeric structure, exhibit higher energy efficiency even at elevated electric current densities compared to alkaline electrolysis (Zhang et al., 2024). Additionally, solid oxide electrolysis offers energy efficiencies that surpass those of both alkaline and proton exchange membrane electrolysis, and it can operate at temperatures as high as 1000°C (Dey et al., 2020). Nevertheless, the complexity of the system requirements for solid oxide electrolysis makes it less commercially appealing. As mentioned earlier, other innovative technologies for hydrogen production through electrochemical processes include anion exchange membranes, bipolar membrane electrolysis, and microbial electrolysis cells. Nonetheless, these cutting-edge electrochemical methods for hydrogen production are still in the early phases of research, development, or pilot testing. As these technologies progress, they hold the potential to significantly improve the efficiency, environmental impact, and cost-effectiveness of hydrogen production from water and other raw materials (Zhang et al., 2024).

In anion exchange membrane electrolysis, the electrolyte consists of an anion exchange membrane that conducts OH^{-} ions instead of H^{+} , as is the case with alkaline or proton exchange membranes (Sun et al., 2022). This technology effectively merges the benefits of both alkaline and proton exchange membrane electrolysis (Chen et al., 2021). Additionally, the electrolyte used in anion exchange membranes is composed of cost-effective, non-precious materials like polybenzimidazole (Sugawara et al., 2023), in contrast to proton exchange membranes (Sun et al., 2022). Moreover, bipolar

membrane electrolysis represents an innovative approach that employs a composite membrane featuring both an anion exchange layer and a cation exchange layer, separated by a bipolar junction (Mayerhofer et al., 2020). This configuration further facilitates the separation of water dissociation and hydrogen evolution reactions, potentially improving the overall energy efficiency of the process (Zhang et al., 2024).

In addition, microbial electrolysis cells have demonstrated the ability to generate hydrogen from organic substrates such as glucose, utilizing wastewater or biomass. This process leverages the combined effects of biological and electrochemical technologies by employing electro-active microorganisms that oxidize organic substrates at the anode of the cell, resulting in the production of protons and electrons. The electrons flow through an external circuit, while the protons migrate towards the cathode through an ion exchange membrane, where they are reduced to form hydrogen gas (Li et al., 2019; Amin et al., 2022b). In the microbial electrolysis of organic matter, microorganisms first oxidize the waste substrate at the anode, leading to the generation of electrons, protons, and CO₂. Hydrogen is produced when electrons and protons combine after the protons move to the cathode through the electrolyte, which serves as a proton-conducting membrane, while the electrons travel via the external circuit. However, challenges such as low hydrogen production rates, high internal resistance, complex unit designs, and electrode material issues may hinder the commercialization of this process (Kadier et al., 2016).



Moreover, beyond their effectiveness in hydrogen production, electrochemical methods offer a range of industrial applications and advantages. Excess electricity generated from renewable sources like solar and wind can be transformed into hydrogen through electrochemical electrolysis. This hydrogen can subsequently be stored and converted back into electricity using fuel cells (Mayyas et al., 2020). Additionally, when powered by renewable energy, electrochemical processes for hydrogen production can yield large quantities of clean, sustainable, and green hydrogen (Amin et al., 2022a). Furthermore, electrochemical electrolysis processes can be scaled up to meet varying hydrogen production requirements for different applications (Yue et al., 2021), making them adaptable and suitable for diverse uses. The high-purity hydrogen produced through electrolysis is crucial for specific applications, including fuel cells. However, it is important to note that electrochemical electrolysis processes can be both energy- and capital-intensive, with significant operational costs primarily due to the use of expensive catalysts (Fragiacomo et al., 2022). In addition, their environmental impact varies depending on the electricity source; they can achieve zero carbon emissions when powered by renewable energy but may result in higher emissions if powered by non-renewable sources (Zhang et al., 2024).

Conclusions

This paper has explored various aspects, challenges, and advancements related to electrochemical technologies for hydrogen production, albeit not exhaustively. Electrochemical hydrogen production primarily involves water splitting through various electrolysis techniques, including alkaline electrolysis, anion exchange membrane electrolysis, proton exchange membrane electrolysis, solid oxide electrolysis, and bipolar membrane electrolysis. These processes have demonstrated their capability to generate hydrogen via water electrolysis through diverse methods. Notably, microbial electrolysis cells can produce hydrogen from organic substrates, such as glucose found in wastewater or biomass, by leveraging the combined effects of biological and electrochemical technologies with the help of electro-active microorganisms. When powered by renewable energy sources, electrochemical processes can yield large-scale, clean, sustainable, and green hydrogen. Additionally, these electrolysis methods can be easily scaled up to accommodate varying hydrogen production needs for diverse applications, making them versatile and suitable for a wide range of uses. The high-quality hydrogen produced through electrolysis is essential for specific applications, such as fuel cells. However, it is important to note that electrochemical electrolysis processes can be energy- and capital-intensive, with high operational costs primarily due to the use of expensive catalysts.

Despite the challenges associated with electrochemical technologies for hydrogen production, ongoing research and development have led to significant improvements in efficiency and cost-effectiveness. Anion exchange membranes made from conductive anionic polymers present a viable and economical alternative for alkaline water electrolysis. These solid membranes exhibit excellent chemical, mechanical, and thermal properties, effectively addressing issues like fuel crossover and carbonation that arise from using aqueous KOH solutions in traditional alkaline water electrolysis. Moreover, anion exchange membranes provide quicker response times than conventional methods, making them ideal for applications where efficiency and speed are essential. Furthermore, microbial electrolysis cells have demonstrated the capability to generate hydrogen from organic substrates, such as wastewater or biomass, by employing electro-active microorganisms to oxidize these substrates at the anode. This approach effectively combines biological and electrochemical technologies, offering promising advancements for hydrogen production.

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