Electrolyzers: Evolution, Prospects and Challenges

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Abstract

Amid escalating climate change, transformation to sustainable energy sources has become imperative. Green hydrogen, produced via water electrolysis, emerges as a crucial element in this transition, offering a carbon-free alternative to fossil fuels. This review outlines the various types of electrolyzers that facilitate green hydrogen production. Alkaline electrolyzers (AEs), proton exchange membrane (PEM) electrolyzers, solid oxide electrolyzers (SOEC), and anion exchange membrane (AEM) electrolyzers each bring unique advantages and operational mechanisms. Furthermore, we discuss the emerging concept of decoupled electrolyzers, which promise enhanced efficiency and safety by separating hydrogen and oxygen evolution processes. Despite the promising potential of green hydrogen, several challenges remain, including high production costs, technological hurdles, and the need for robust infrastructure. This review aims to provide an overview of water electrolysis technologies while addressing the challenges facing the green hydrogen economy, paving the way for future research and development in this vital field.

Keywords: *Green hydrogen, Electrolyzers, Hydrogen economy, Decoupled electrolyzer*

1.Introduction

Global energy consumption has significantly increased in recent decades due to population growth and advancements in personal comfort [1]. According to studies by the International Energy Agency (IEA), fossil fuels remain the primary source of energy supply [2]. However, fossil fuels are expected to be depleted in the near future, and the carbon footprint associated with their use is a major contributor to global warming and climate change [3]. One approach to mitigating climate change and its adverse effects caused by fossil fuels is to gradually transition to energy sources such as wind energy, solar energy, biomass energy, and green hydrogen energy [4-7]. Hydrogen produced without emitting any greenhouse gases into the atmosphere is known as green hydrogen [8]. It uses electricity from renewable sources such as windmills, solar etc. to split water by electrolysis [9, 10]. Among these options, green hydrogen offers several benefits, including the ready and uninterrupted availability of water compared to season-dependent solar and wind energy, and a higher calorific value compared to biomass derived fuels[11]. Renewable energy-driven hydrogen production is also regarded as an effective alternative for mitigating greenhouse gas emissions and combating climate change [12].

Hydrogen can be produced from various feedstocks. The main pathways of hydrogen production and their applications are illustrated in Fig. 1. Among the different sources such as natural gas, coal, naphtha, and water, fossil fuel sources currently dominate hydrogen production [13]. Reports suggest that approximately 78% of hydrogen is produced through fossil fuel reforming, around 18% through coal gasification, and less than 4% through water electrolysis [1, 14]. The reliance on fossil fuels for hydrogen production is due to their lower cost compared to green hydrogen. Hydrogen produced through steam methane reforming and coal gasification costs less than $1/kg, whereas green hydrogen generated from nuclear-powered electricity costs around $3/kg [15]. Similarly, when examining hydrogen consumers, oil refineries, bulk chemical producers, and steel plants currently dominate the market [16, 17]. However, the depletion of fossil fuels and global climate change scenarios could drive the adoption of green hydrogen in the power and transportation sectors [18]. Despite the potential of green hydrogen, this transition may take several decades.

Electrolyzer technology has been known since the early 19th century. During the 19th and early 20th centuries, it was primarily used for ammonia production from hydropower sources [19]. At that time, electrolyzers were based on alkaline systems, and a significant breakthrough was the replacement of hazardous asbestos-based separators with composite material membranes [19]. In the mid-20th century, the advent of polymer chemistry led to the invention of PEM electrolyzers. By the late 20th century, PEM electrolyzer designs had become much more compact, and production capacities had reached a few hundred kilowatts. Since 2010, the integration of photovoltaics with electrolyzer technology has opened new possibilities for renewable energy. Currently, the focus is on developing novel materials and achieving a production level of gigawatt scale, with an emphasis on finding stable materials [20].

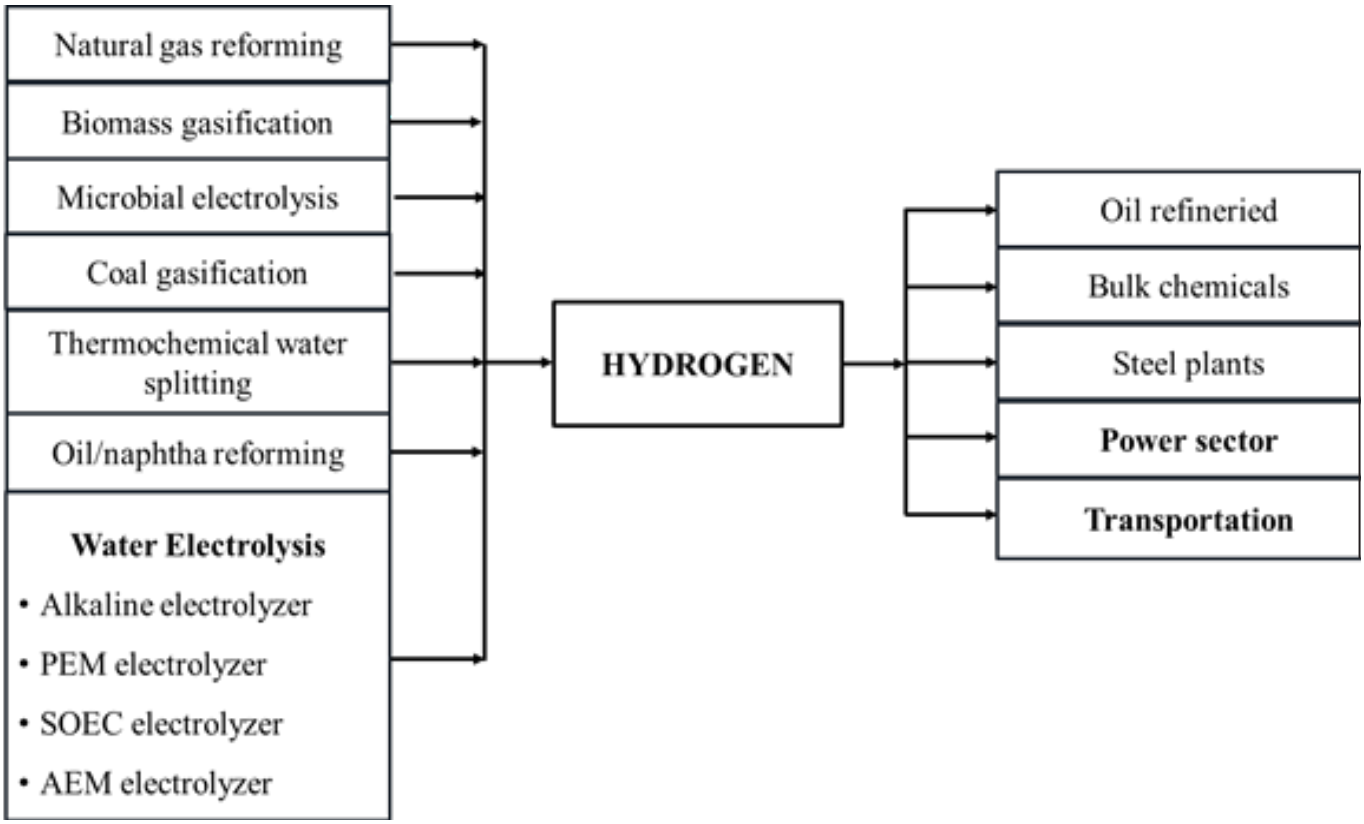


Fig. 1. Various pathways for hydrogen production and its applications (Our focus in this paper and future aspects of hydrogen are highlighted in bold letters)

In this mini review, a brief introduction to water electrolysis is presented. The main types of electrolyzers, viz. alkaline electrolyzers (AE), proton exchange membrane (PEM) electrolyzers, solid oxide (SOEC) electrolyzers, and anion exchange membrane (AEM) electrolyzers are described along with their operating mechanisms. In conventional water electrolysis, the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) are coupled, which can lead to crossover and, in the worst case, the formation of an explosive H_2/O_2 mixture [21, 22]. A decoupled water electrolyzer can separate the HER and OER reactions. This review also discusses the working mechanism of decoupled water electrolyzers. Despite the significant surge in the field of green hydrogen, many challenges remain. This review highlights the current and expected obstacles to establishing a green hydrogen-based economy.

2. Electrolyzer Technologies and Mechanism

The operational mechanism of hydrogen production differs among various types of electrolyzers, but the fundamental principle remains the same. Electrolysis involves the process of breaking down complex compounds into ions or atoms through the application of electric current. Generally, industrial water electrolyzers can be classified into four categories.

- Alkaline electrolyzers (AE),
- Proton exchange membrane electrolyzers (PEM),
- Solid oxide electrolyzers (SOEC), and
- Anion exchange membrane electrolyzers (AEM).

This categorization is based on the differences in the electrolytes used and the operating conditions. The anodic and cathodic reactions in different electrolyzers are presented in Table 1 and the reactions and separator/membrane details are illustrated in Fig. 2(a)-(d).

Table 1. Half-cell reactions in different types of electrolyzers.

S. No	Type of electrolyzers	Anodic reaction	Cathodic reaction
1	Alkaline electrolyzer	$4OH^- \leftrightarrow 2H_2O + O_2 + 4e^-$	$4H_2O + 4e^- \leftrightarrow 2H_2 + 4OH^-$
2	Proton exchange membrane electrolyzer	$2H_2O \leftrightarrow O_2 + 4H^+ + 4e^-$	$4H^+ + 4e^- \leftrightarrow 2H_2$
3	Solid oxide electrolyzer	$2O^{2-} \leftrightarrow O_2 + 4e^-$	$2H_2O + 4e^- \leftrightarrow 2H_2 + 2O^{2-}$
4	Anion exchange membrane electrolyzer	$4OH^- \leftrightarrow 2H_2O + O_2 + 4e^-$	$4H_2O + 4e^- \leftrightarrow 2H_2 + 4OH^-$

2.1 Alkaline Electrolyzers (AE)

Alkaline water electrolyzers are much more advanced than the other three types of electrolyzers and are considered a commercially matured method for producing cost-effective hydrogen [23]. They utilize readily available and accessible electrolytes, such as sodium hydroxide or potassium hydroxide, which enhances their lifespan and cost-effectiveness [24, 25]. The concentration of alkaline electrolytes may vary from 20% to 30% by weight [26]. Conventional AEs use nickel-based electrodes and porous diaphragm separators [27, 28]. Despite significant advancements in commercial-scale alkaline electrolyzers, there is still a need for improvements in operating current density, compact design, startup time, and safety aspects, such as preventing product crossover [29, 30].

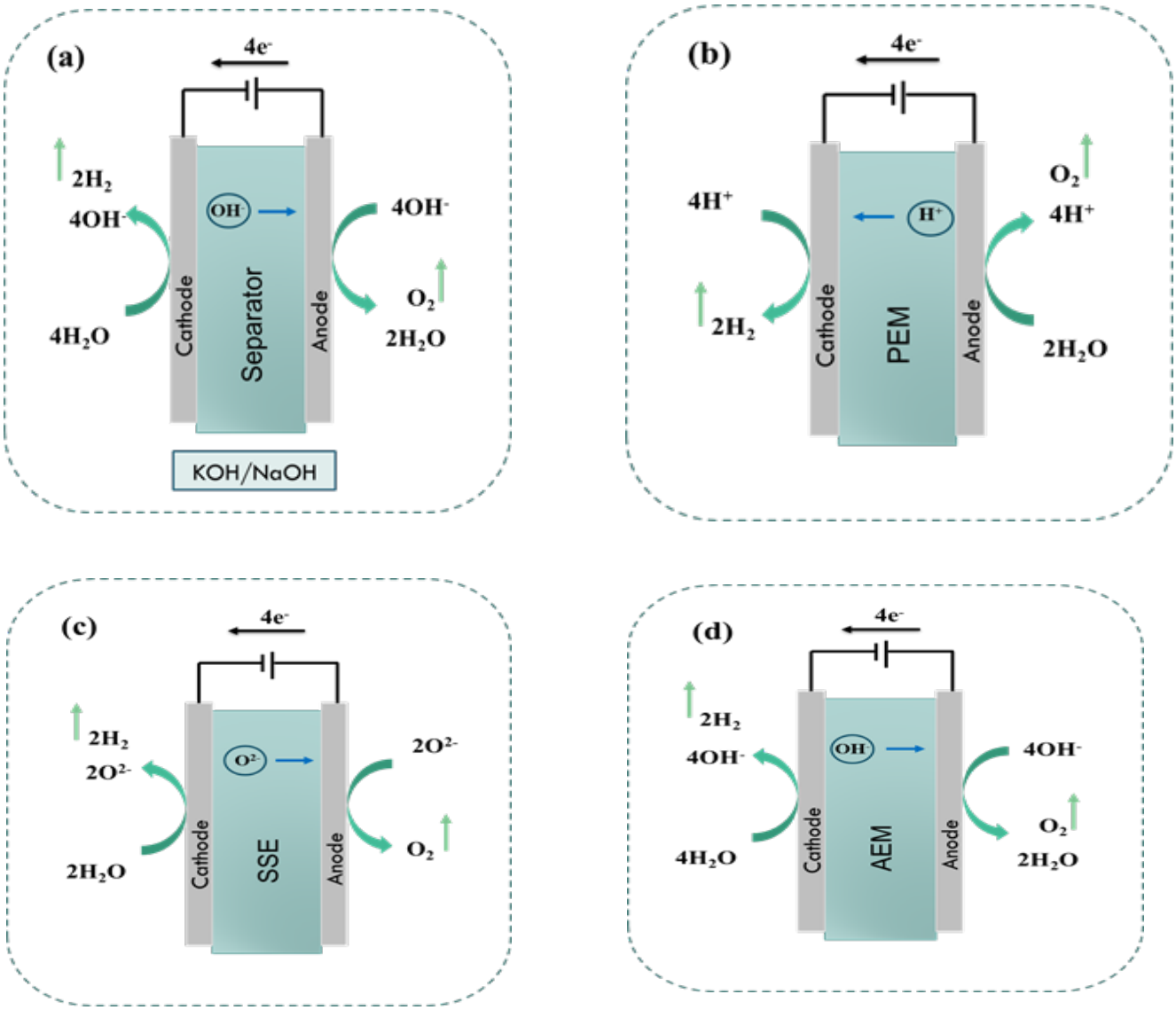
2.2 Proton Exchange Membrane Electrolyzers (PEM)

Proton exchange membrane electrolyzers can operate at lower pH levels, with lower cell voltage

and higher current densities compared to alkaline electrolyzers. Additionally, they have a fast response time and produce high-purity hydrogen. They use a polymer membrane-based electrolyte with platinum and iridium-based cathode and anode respectively. Thus, the high material cost is a drawback of PEM water electrolyzers. Furthermore, cross-permeation at high pressure and the need for dehumidification to remove moisture from the produced hydrogen are also limitations of this technique [31, 32]. With ongoing research on materials and technologies, these challenges can be resolved in the near future.

2.3 Solid Oxide Electrolyzers (SOEC)

Research on solid oxide electrolyzers has gained significant momentum over the past two decades. In solid oxide water electrolyzers, steam is introduced directly to the porous cathode. When sufficient potential is applied, water molecules dissociate at the cathode's active sites, producing hydrogen and oxide ions. These oxide ions then diffuse to the anode, where they oxidize to form oxygen. SOECs operating at high temperatures can generate hydrogen at a faster rate and with lower



energy input compared to alkaline and PEM electrolyzers [33, 34]. However, the system lifetime of SOEC is much lower compared to the alkaline and PEM electrolyzers [35].

2.4 Anion Exchange Membrane Electrolyzers (AEM)

Anion exchange membrane electrolyzers are relatively new compared to the other water electrolyzers described above. They combine the advantages of alkaline and PEM electrolyzers by using a hydrocarbon-based anion exchange membrane and a less caustic bicarbonate or carbonate-based electrolyte [36, 37]. The AEM electrolyzers are still in the developmental stage and require further improvements in electrode and membrane stability, as well as operating parameters [38, 39]. A list of salient features of these four types of electrolyzers is provided in Table 2.

Fig. 2. The working mechanism of (a) Alkaline electrolyzer (b) Proton exchange membrane electrolyzer (c) Solid oxide electrolyzer (d) Anion exchange membrane electrolyzer.

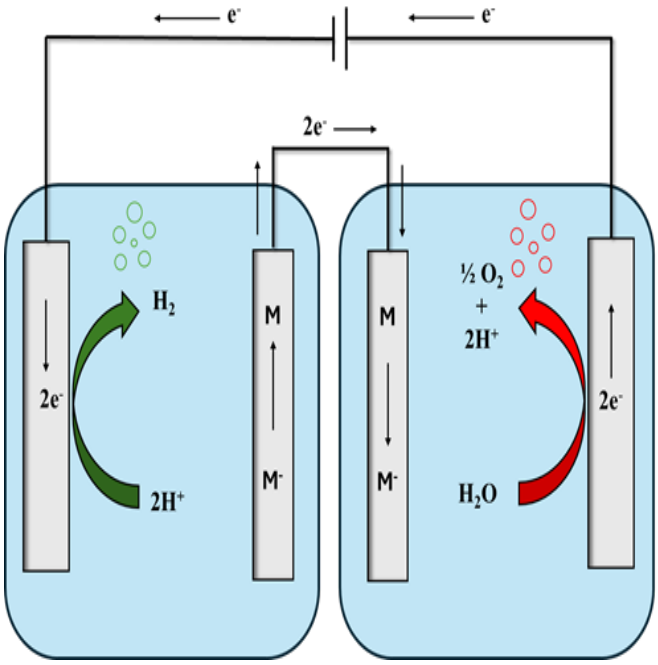
Table 2. Salient features of different types of electrolyzers [1, 20, 40-42].

Components and parameters	AE	PEM	SOEC	AEM
Operating temperature $(^{\circ}C)$	70-90	50-80	700-850	40-60
Operating pressure (bar)	1-30	30-80	1	< 35
Electrolyte	KOH	Polymer membrane	Yttria-stabilized Zirconia	Divinyl benzene supported with KOH/ $NaHCO_3$
Separator	Asbestos/ Zirfon / NiO	Solid electrolyte	Solid electrolyte	Solid electrolyte
Cathode	Nickel-coated stainless steel	Platinum on carbon black	Yttria-stabilized Zirconia	Nickel (High surface area)
Anode	Nickel-coated stainless steel	Iridium oxide	Nickel mesh or foam	Ni/NiFeCo alloys
Transport layer (cathode)	Nickel mesh	Porous titanium or carbon cloth	Nil	Nickel foam or carbon cloth
Transport layer (anode)	Nickel mesh	Platinum-coated porous titanium	Course Nickel mesh or foam	Nickel foam
Cell voltage (V)	1.8-2.4	1.8-2.2	0.95-1.3	1.8-2.2
Current density (A cm^2)	<0.5	1-2	0.3-1	1-2
Cell area (m^2)	3-3.6	<0.13	<0.06	---
Voltage efficiency (%)	62-82	67-82	81-86	---
System lifetime (years)	20-30	10-20	---	---
Hydrogen purity (%)	99.5	99.999	99.9	99.99
System startup time (min)	15	<15	>60	<15
Technology readiness level	Widely commercialized	Commercialized	R&D	R&D

3. Decoupled Water Electrolysis

Research on decoupled water electrolysis has recently become a notable area in hydrogen production, offering a flexible alternative to existing water electrolysis systems.[43-45]. In conventional water electrolysis, hydrogen and oxygen production are explicitly coupled. For one mole of oxygen produced at the anode, two moles of hydrogen are generated at the cathode. The anodic and cathodic compartments are typically separated by an ion exchange membrane or ion-permeable separator to prevent crossover. However, when electrolyzers operate at a low load, gas crossover can occur, reducing hydrogen production efficiency or, in the worst case, forming an explosive H_2/O_2 mixture.

In a decoupled electrolysis system, OER is



paired with the reduction of a redox mediator, which is subsequently re-oxidized to supply the electron needed for HER. Figure 3 illustrates a decoupled water splitting system. The electrochemical reactions in this system are represented by eqn. (1) and (2). The overall reactions for a decoupled water electrolyzers are the same as those of a conventional electrolyzer (Eqn. 3).

The hydrogen side electrochemical half-cell reactions can be written as

$$2H^+ + 2e^- \rightarrow H_2$$

$$2M^- \rightarrow 2M + 2e^-$$

$$2H^+ + 2M^- \rightarrow H_2 + 2M \qquad (1)$$

On the oxygen evolution side

The overall reaction is

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \qquad (3)$$

In the above equations 'M' represents the redox mediator, which decouples the HER and OER reactions. M can be solid materials such as NiOOH/$Ni(OH)_2$ or redox species such as $[Fe(CN)_6]^{3+/4+}$ or $V^{2+/}V^{3+}$ [46]. The advancement of decoupled water electrolyzers can offer several benefits, including eliminating the need for costly membrane systems, generating high-pressure hydrogen without membranes, reducing the risk of H_2 and O_2 mixing, and enhancing flexibility in coupling with renewable energy sources. However, the long-term performance and stability of the decoupled water-splitting systems are yet to be understood.

Fig. 3. A schematic of the decoupled water electrolysis system.

4. Green Hydrogen Economy: Challenges and Future Aspect

Green hydrogen is considered a potential fuel source to replace fossil fuels in the industrial and transportation sectors. However, the transformation to a green hydrogen economy faces several challenges, including financial, scientific, social, and political scenarios. Among the challenges associated with green hydrogen, the

primary concern is its cost [47, 48]. According to the International Renewable Energy Agency (IRENA) reports, green hydrogen production is still in its early stages, and to compete with other forms of hydrogen (such as black and blue hydrogen), its cost must be more comparable [49]. Ammonia production is one of the major industrial sectors that utilize hydrogen in large quantities. Currently, hydrogen for the Haber-

Bosch (H-B) process is primarily produced through steam methane reforming [50]. The dependence on fossil fuels for hydrogen production results from the lower cost of grey hydrogen compared to other forms of hydrogen, as discussed in the introduction section. Ammonia production with green hydrogen is significantly more expensive compared to ammonia production using SMR hydrogen [51]. In the short term, imposing carbon taxes is the only viable way to promote the use of green or blue hydrogen for ammonia production [52]. However, recent techno-economic studies suggest that a carbon tax of at least \$62 per ton of CO_2 is necessary to make blue hydrogen a competitive raw material for ammonia production [53]. In addition, the cost of electrolyzers and electricity has a significant impact on the green hydrogen cost. Even though the price of renewable electricity from solar and wind energy has dropped significantly in the past decade, the investment cost in hydrogen electrolyzers remains substantial [54].

Beyond cost considerations, the green hydrogen initiative faces challenges related to the absence of global standards and social support. [55]. Therefore, a global framework and strategy are essential for establishing universal hydrogen terminology and standards [56]. While the research framework demonstrates the technical feasibility of green hydrogen, social acceptance is equally important. The primary concern among the public revolves around the risk of explosions at hydrogen (H_2) refueling stations [57]. Studies indicate that families are more likely to oppose the establishment of such stations near their residences, due to safety concerns [58]. This concern will be more prominent in developing and underdeveloped nations. Effective communication is essential to address safety concerns related to hydrogen (H_2) and to clarify misunderstandings. Alongside all these challenges, the availability of water and land will also impact the global outlook on green hydrogen projects.

Despite these challenges, the future potential of the green hydrogen market remains huge. It promises to reduce emissions across industries, transportation, power systems, and buildings. Green hydrogen can also drive the development of renewable energy sources and enhance the flexibility of the power system. Furthermore, it serves as a long-term energy storage solution to balance seasonal energy variations. A lot of R&D and scaling-up efforts are needed to make a large-scale implementation of green hydrogen a reality.

5. Conclusions

Green hydrogen can play a crucial role in combating climate change as it provides a carbon-free energy source that can significantly reduce greenhouse gas emissions from industries, transportation, power generation, etc. In this review , we described various types of water electrolyzers and their mechanisms. Among the four major technologies, alkaline and PEM electrolyzers are well-established, whereas SOECs and AEM electrolyzers are still in the R&D stage. Safety in water electrolysis remains a concern, and we briefly explore the mechanism of decoupled electrolyzers which can address the safety concerns. Despite the significant interest in hydrogen energy, the hydrogen economy has a long way to go before its widespread adaptation becomes a reality.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

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