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Review Article

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Advances in electrocatalyst development for hydrogen production by water electrolysis

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Abstract: Hydrogen is increasingly recognized as a clean, sustainable energy carrier with the potential to play a pivotal role in future energy systems. Among the various methods for hydrogen production, water electrolysis stands out for its ability to generate highly pure hydrogen in an environmentally sustainable manner. The development of efficient electrocatalysts is critical for enhancing the performance of water electrolysis, particularly in the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). While precious metals like Ag, Au, Ru, and Pt have been traditionally used due to their high catalytic activity, their high cost and scarcity limit their widespread use. Recent research has focused on non-precious metal-based electrocatalysts, which offer comparable catalytic efficiency, lower cost, and greater environmental friendliness. These alternatives have the potential to replace expensive noble metals in water electrolysis, but further research and innovation are required to improve their performance and long-term stability. This work examines the advancements in electrocatalyst development for three major electrolysis techniques – alkaline water electrolysis (AWE), proton exchange membrane electrolysis (PEME), and solid oxide electrolysis (SOE) – and discusses the challenges and future directions for optimizing these technologies for large-scale hydrogen production.

Keywords: electrolysis; electrocatalysts; hydrogen production; hydrogen evolution reaction (HER); oxygen evolution reaction (OER)

Abbreviations

AWE	Alkaline Water Electrolysis
COE	Cobalt Oxide Electrocatalyst
CPE	Cobalt Phospide Electrocatalyst
CSE	Cobalt Sulfide Electrocatalyst
CSEE	Cobalt Selenide Electrocatalyst
FeS2/CNTs	Cobalt doped iron disulphide CNTs
HER	Hydrogen Evolution Reaction
MoS2/CNTs	Molybdenum disulphide-maintained carbon nanotubes
Ni2P/CNTs	Nickel Phosphide Supported Carbon Nanotubes
NI-YSZ	Nickel-yttria Stabilized Zirconia
OER	Oxygen Evolution Reaction
OH	Hydroxyl Ion
PEME	Proton Exchange Membrane Electrolysis
SOE	Solid-Oxide Electrolysis
WO2/C	Tungsten dioxide-maintained carbon nanowires

1 Introduction

Industrial innovation and population increases have significantly boosted the world's energy consumption of late. Economic growth and modernisation of society depend on energy, and resources that are not renewable, such as fossil fuels, currently provide around 65 % of worldwide energy needs.[1] Non-renewable energies have the potential to release dangerous emissions of greenhouse gases such carbon monoxide (CO), Carbon dioxide (CO_2)¸ CO, Oxides of Nitrogen (Nox), and Sulfur oxide (SO_X), which can have a negative influence on the economy and society by generating climate change, pollution in the atmosphere, and product and equipment failure.[2,3] The increasing need to produce renewable energy is estimated to be 10 TW by 2050

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due to the declining availability of petroleum and coal with the increase in carbon dioxide emissions.[4] Green energy comes mainly from the sun, wind, power generations, nuclear power, biomass, oceanic thermal, and other sources. It has become accepted that electrochemical reactions are the most efficient way to store and convert power from renewable sources in a number of practical energy-generation strategies.[5] Among the most important sources of clean electricity is hydrogen, which produces no carbon emissions apart from water as a side effect. Because of its great energy conservation, sustainability, and lack of contaminating things can also be used as a substitute for carbon-based fuels.[6] A key characteristic of hydrogen as an energy carrier is its high energy density of 140 MJ/kg, which is double that of traditional solid fuels.[7] Currently, global hydrogen production reaches approximately 500 billion cubic meters annually. The natural gas and metals processing business, petrochemical companies, the substance being burned cell industry, fertiliser manufacturing, and the oil and gas sector are the primary industries that use hydrogen gas.[8] Various nonrenewable and renewable sources, including fossil fuels, are used to make hydrogen gas. These include the reforming and composting process, the biomass, solar, water electrolysis (WE), nuclear, & hydro sources of energies. Figure 1 illustrates several hydrogen-generating techniques.[9,10] Environmentally friendly power regulations that might be placed by renewable energy sources to generate hydrogen power are receiving a lot of focus at the moment. It is emerging as a promising technique for producing energy from hydrogen. Transforming electrical energy through wind, solar, and marine sources into substances such as hydrogen and petrochemical fuel.[11]

Despite all the techniques for producing hydrogen, the electrolytic breakdown of water can yield pure oxygen and hydrogen, resulting in highly dense and environmentally friendly hydrogen. However, because of its small hydrogen emission and significant power consumption, the water electrolysis method's hydrogen productivity is quite limited.[12] Only 4 % of the hydrogen gas has been generated worldwide using the electrochemical water electrolysis method since there was a shortage and elevated price of the precious electrode. Platinum (Pt) and ruthenium (Ru)-based combinations are now among the greatest efficient electrocatalysts for HER & OER, respectively. Certain valuable metals are in short supply and highly costly.[13,14] These considerations impact their widespread commercial use. Identifying affordable and highly efficient non-precious metal electrocatalysts for HER & OER is essential.[15] Metal-organic framework (MOF) composites and transition-metal-based compounds, such as metal hydroxides, sulfides, phosphides, nitrides, and selenides, have consistently exhibited superior electrocatalytic performance in these processes.[16]

Finding a non-precious electrocatalyst that is cost-effective, accessible, and incredibly effective for HER & OER is fascinating. To improve efficiency and lower hydrogen energy consumption, emphasis should be placed on developing alternative, cost-effective electrocatalysts that enhance hydrogen production while reducing energy demand. A summary and discussion of the various hydrogen production techniques have also been included, as well as recent developments in effectiveness and affordability utilising electrocatalysts for OER and HER.[17] Enhancing energy efficiency, catalytic activity, and stability to meet projected energy needs requires a thorough examination of nanoparticle structures and an electrochemical study of recently developed electromagnetic catalysts. The structural composition of an electrocatalyst plays a crucial role in determining its electrocatalytic performance for HER and OER. Recent studies have demonstrated significant progress in the development of advanced electrocatalysts for HER and OER. For example, Wang et al. (2023) reported a bimetallic Ni–Fe phosphide with enhanced electrochemical surface area and long-term stability under alkaline conditions, showing an overpotential of only 112 mV at 10 mA cm^{-2} for HER.[18] Similarly, Zhao et al. (2022) developed Co–Mo sulfide nanostructures that exhibited excellent bifunctional performance for both HER and OER, supported by high intrinsic activity and strong structural integrity. These studies highlight the trend of employing synergistic effects between transition metals and heteroatom doping to optimize electron transfer and catalytic durability. Such advancements underscore the evolving landscape of cost-effective and scalable electrocatalyst design.[19] Additionally, emerging approaches involving metal–organic framework-

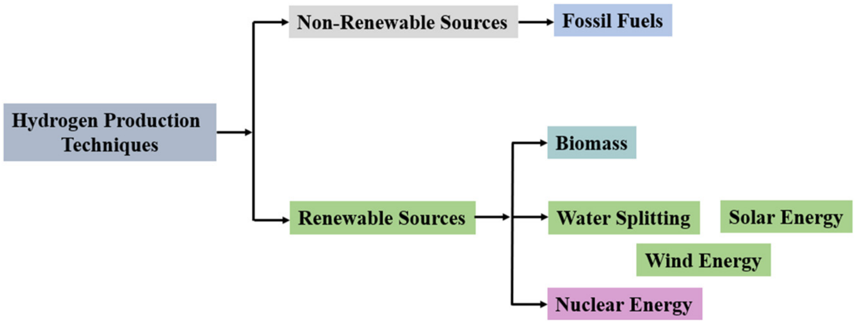

Figure 1: Various hydrogen generation techniques.

derived structures and high-entropy alloys have gained attention due to their tunable active sites and enhanced conductivity, offering promising directions for future electrocatalyst engineering.[20,21]

This review offers a comprehensive analysis of non-precious metal-based electrocatalysts for hydrogen production, focusing on their application in water electrolysis reactions. It delves into the fundamental principles, catalytic reaction mechanisms, electrocatalyst design, and characterization techniques. Furthermore, the review identifies key challenges and explores emerging opportunities, providing valuable insights into future research directions. It concludes with actionable recommendations aimed at advancing the commercial viability of water electrolysis systems, paving the way for more sustainable hydrogen production. As global energy policies pivot toward carbon neutrality and climate resilience, the advancement of water electrolysis technologies using low-cost, high-performance electrocatalysts is more crucial than ever. Hydrogen, produced sustainably via electrochemical water splitting, represents a cornerstone in the shift to green energy. This review consolidates the current state of electrocatalyst research and explores how recent breakthroughs contribute directly to the realization of global sustainable energy targets. Therefore, the primary objective of this review is to provide a comprehensive assessment of non-precious metal-based electrocatalysts for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in water electrolysis systems. We aim to explore recent advances in material design, reaction mechanisms, structural and electrochemical characteristics, and performance metrics that define catalytic activity. This review also identifies key challenges and research gaps, with the hypothesis that rational design and hybridization of low-cost transition metal compounds can yield electrocatalysts with performance comparable to or better than precious metal-based systems. The insights presented herein are intended to guide future research toward scalable, cost-effective, and sustainable hydrogen production technologies.

2 Alkaline water electrolysis (AWE) and its electrocatalyst development

2.1 Alkaline electrolysis (AWE)

Alkaline water electrolysis, first developed by Troostwijk and Diemann in 1789, is a well-established and advanced method for hydrogen production from water. This process has contributed to the large-scale generation of high-purity hydrogen globally.[22,23] Typically operating within a temperature range of 40–90 °C, it achieves an efficiency of 70–80 %. AWE's most commonly used electrolytic solutions consist of potassium hydroxide (KOH) and sodium hydroxide (NaOH) in concentrations of 20–30 %. A silica membrane separates both ends of the anode loop, while nickel (Ni) electrodes are employed at the anode and cathode to prevent gas mixing.[24,25] During electrolysis, hydroxyl ions (OH^-) migrate toward the anode, following water decomposition at the cathode. Figure 2 illustrates a schematic representation of AWE (Figure 3).

Figure 3 represents the proton exchange membrane technology. At the cathode, the reduction of H_2O molecules results in hydrogen (H_2) gas and hydroxyl (OH^-) ions forming. Meanwhile, at anode, the oxidation of 4 hydroxyl (OH^-) ions leads to the production of oxygen (O_2), along with two water (H_2O) molecules and the transfer of four electrons.[26] The corresponding electrochemical reactions occurring at the anode and cathode in AWE are represented in equations (1) and (2).[27→]

$$4H_2O + 2e^- \rightarrow H_2 + 2OH^- \ (\text{Cathode}) \tag{1}$$

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \ (\text{Anode}) \tag{2}$$

Limited working temperature and pressure and limited electrical current density of about 0.4 A/cm^2 are some drawbacks of alkaline water electrolysis that may result in low energy efficiency. The total volume of water consumed was approximately 11.5 times higher than the hydrogen generated. A novel method for altering the alkaline water electrolysis process is being researched; it uses anion transfer membranes rather than diaphragmatic membranes, which are typically composed of polymers having anionic conductance.[28–30]

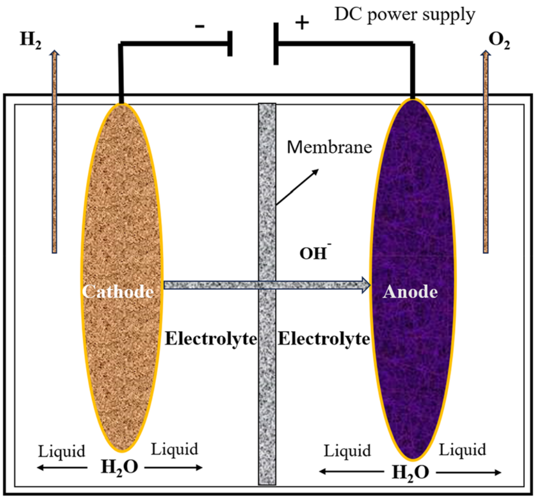

Figure 2: Alkaline water electrolysis (AWE) technology graphical illustration.

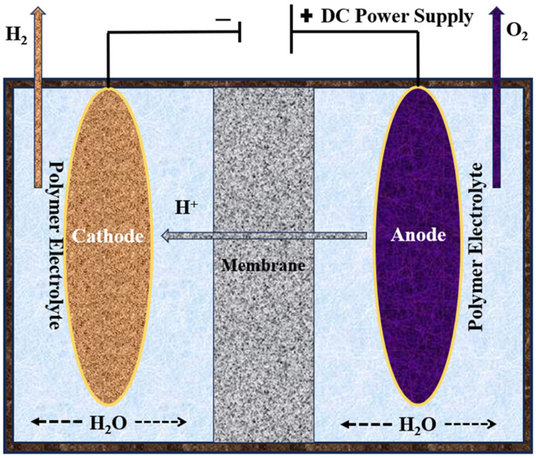

Figure 3: Proton exchange membrane (PEM) technology.

The fundamental process behind hydrogen production in AWE involves oxygen generation at the anode and hydrogen formation at the cathode. A membrane is used to separate these gases while allowing the passage of water and hydroxyl ions (OH^-).[31] Electrolytes, typically liquid solutions like NaOH or KOH, are applied to both electrodes to facilitate the reaction. Common electrode materials include cobalt, iron, and nickel, with nickel being the most widely used due to its superior electrocatalytic performance, cost-effectiveness, and easy availability.[32]

The advantages of employing AWE are its cutting-edge technology and the ability to produce clean hydrogen energy utilising non-precious electromagnetic catalysts. The area can use extremely scalable methods because the AWE cells are removable. The dynamics of gas movements and electrolytes, which nevertheless cause rusting.[33]

2.2 Electrocatalyst development for AWE

2.2.1 Cobalt phosphide electrocatalyst

The cobalt oxides' enzymatic characteristics demonstrated the lowest conductivity level of electricity, making them suitable for application as HER electrocatalysts.[34] To enhance the electrical conductivity of electrocatalysts, research should prioritize the use of highly conductive materials such as carbon cloth, carbon nanotubes (CNTs), metal foam, and graphene. These materials can significantly improve electron mobility, thereby boosting the overall efficiency of catalytic processes.[35] Li et al. Suggested outstanding performance electrocatalysts using a hydrolysis and low-temperature processing technique that linearly expands urchin-like three-dimensional constructed CO_3O_4 configuration nanoscale arrangements on nickel foam. At an electric current average density of 0.010 A/cm^2, this CO_3O_4 nickel foam demonstrated expectational HER function in an alkaline solution, with an excess potential of 0.135 V and a Tafel slope of 0.053 V/dec.[36] Zhang et al.[37] successfully utilised hetero-atom doping to enhance the performance of HER catalysts by encapsulating Co/Co-Ox within a nitrogen (N), oxygen (O), and sulfur (S) tri-doped three-dimensional porous carbon framework, forming the Co/Co-Ox-NOSC composite. This catalyst demonstrated a Tafel slope of 0.078 V/dec and an overpotential of 0.061 V versus RHE at a current density of 0.010 A/cm^2.

2.2.2 Cobalt oxide electrocatalyst

Initial studies on CoP and Co_2P catalysts for HER in acidic conditions revealed that a higher phosphide (P) content in cobalt phosphide exposed more active sites on the catalyst's outer surface, enhancing its overall electrocatalytic performance.[38] Consequently, increasing the rate can significantly increase cobalt phosphide catalytic efficiency. P. Liu and a colleague synthesised cobalt phosphide directly on graphene oxide sheets (Co2P/RGO), and in an acidic solution containing 0.5 mol/1H_2SO_4, they showed excellent HER performance.[39] However, inadequate phosphide doping can significantly restrict the delocalisation of electrons in cobalt atoms, leading to a transition from metallic conductivity to a semiconductive or insulating state in cobalt-based phosphides. This change ultimately reduces the efficiency of the HER process.[40] Therefore, to improve the catalytic capabilities of HER, more research must be conducted regarding the impact of the phosphide concentration in cobalt phosphide. Sophie Carencro et al.[41] discovered that certain thermodynamic properties prevent the complete solubility of metal alloys with phosphide. The formation of a low-solubility phosphate layer on the catalyst surface acts as a protective barrier against corrosion, thereby enhancing the durability of the catalyst. Li et al.[42] documented a simple method for creating hazardous chemical surfactants and tiny CoP nanomaterials injected into carbon matrices in a hostile environment. The final catalysts, identified as HER CoP-OMC (cobalt phosphide on ordered mesoporous carbon) electromagnetic catalysts, demonstrated high efficiency with an overpotential of 0.112 V versus RHE and a low Tafel slope of 0.05 V/dec at a current density of 0.010 A/cm^2. This demonstrated exceptional permanent durability. Yinbo Wu et al. created a cobalt oxide (CoO_X) catalysis for HER using straightforward hydrothermal techniques. Excellent, the CoOX catalyst demonstrates HER catalytic efficiency. The outcomes of the evaluation show that this CoO_X catalysts surface has many hydroxyl groups or vacancies in oxygen. The CoO_X exhibits a minor Tafel slope of 94 mV dec^{-1} and an over-potential of 112 mV at 20 mA cm^{-2} in alkaline conditions. A straightforward and easy technique to prepare HER catalyst production is reported in research.[43]

2.2.3 Cobalt sulfide electrocatalyst

Ananthraj et al. Created substance used in the HER electrocatalytic procedure that is equivalent in behavior to transitional metal phosphorous (TMP) and transitional metal sulfide (TMS). They believed that a relatively strong bond is formed between Sulphur and hydrogen because of the Sulphur atom's increased electronegativity rather than that of the phosphorous atom. HER electrocatalytic efficiency is lowered due to the substantial increases in excessive potential. Cobalt sulfide offers remarkable qualities, including thermal resistance in acidic conditions, yet it is rarely employed as a semiconductor or a HER catalyst.[44] Li et al. developed a cobalt sulfide nanosheet layer on carbon cloth using a solvothermal method; even though carbon fabric is a substrate that conducts electricity, it demonstrated improved catalytic activity and longer-term stability across various pH levels. It may indicate a nucleation location for the CoS nanosheet's vertical organisation expansion and boost the electrocatalysts charge transport effectiveness.[45] Tan et al. A non-porous Co9S4P4 catalyst was created using phosphating and a particular electrochemical disintegration method. The synthesised cobalt sulfide nanosheet exhibited excellent HER performance, with an overpotential of 0.058 V versus RHE in an acidic solution, 0.087 V versus RHE in a neutral solution, and 0.096 V versus RHE in an alkaline solution. It demonstrated outstanding HER catalytic efficiency at a current density of 0.010 A/cm^{2}.[46] Chao Wang et al. reported initially constructed a silk-cocoon oriented S-rich cobalt polysulfide (CoS_x, $X \approx 3.9$) catalyst exhibiting extraordinary significant HER activity by s straightforward hydrothermal procedure. The silk cocoon-shaped CoSx development technique is being carefully explored so that the critical variables for developing this framework are highlighted. This nanostructured material catalyst consists of hollow cylindrical particles connected by several sub-10 nm nanofibers to create a three-dimensional conducting network. With an onset potential of 0 V versus, the silk-cocoon structured CoSx exhibits outstanding HER activity.[47]

2.2.4 Cobalt selenide electrocatalyst

The optimal electrical configuration of cobalt selenides ($CoSe_2$) in cobalt-based electrocatalysts makes them a favourable catalyst. The primary method for creating $CoSe_2$ is the wet chemical method, which involves mixing powdered selenium to create a NaHse solution that serves as a selenium supply for the reaction.[48] During an investigation published by Anantharaj and a colleague.[44] Selenium (Se) atoms were incorporated into the metallic matrix to enhance the efficiency of the HER by improving the catalytic activity and electronic conductivity; this mechanism is comparable to that suggested for the doping of phosphorous and sulphur atoms. To support the HER electrochemical process, every substance achieved improved the electronegativity and more easily drew to positively charged protons. A cobalt-based oxide, which interacts with the catalyst during OER operation, was synthesised using a similar on-site oxidation reaction. During the HER electrocatalytic process, cobalt selenide (Co–Se) exhibits a higher hydrogen evolution rate than cobalt phosphide (Co–P) and cobalt sulfide (Co–S), despite the weaker Se–H bond strength compared to P–H and S–H bonds. Wu et al. Created a coverable foldable nanosheet that resembles a Co_{0}–$_{85}$Se arrangement on nickel foam (NF), showing excellent HER efficiency in an alkaline solution. A current density of 0.010 A/cm^{2} was reached by achieving an overpotential of 0.129 V vs RHE (V).[49] Liu et al., who created the scroll's internal hollow structure by ultrasonic, showed the scroll's internal hollow structure. An investigation of the electrodeposition procedure of an amorphous Co–Se layer on a titanium (Ti) grid was revealed to enhance the electrocatalytic activity associated with the HER process. Using a field emission scanning electron microscope (FESEM), the CO_{0}–$_{85}$Se array on nickel foam was examined for morphological structure and crystal size. As a result, a flexible nanosheet has been assembled into a scroll-like arrangement. When the final products fractured, the surface was examined using ultrasonic technology, and the inside hollow structure of the scroll was revealed.[50]

3 PEM water electrolysis and its electrocatalytic development

3.1 PEM water electrolysis

Proton exchange membrane water electrolysis (PEMWE) is a cutting-edge technology for generating high-purity hydrogen from renewable energy sources. Initially developed in 1966 to overcome the limitations of alkaline water electrolysis, this technology is also referred to as polymer electrolyte membrane electrolysis. Unlike alkaline electrolysis, PEMWE employs a polymer electrolyte that prevents liquid-phase mixing. Operating within a temperature range of 20–100 °C, it effectively splits water into hydrogen and oxygen. This system typically operates at pressures up to

40 MPa, reducing the energy required for gas compression. The membrane in PEMWE selectively permits the passage of protons (H^+ ions) while restricting other gases.[51] During electrochemical reactions, water molecules (H_2O) at the anode undergo oxidation, producing oxygen (O_2), hydrogen ions (H^+), and electrons. Meanwhile, hydrogen ions (H^+) are reduced at the cathode, forming molecular hydrogen (H_2). The overall reactions at the anode and cathode are represented by equations (3) and (4), as illustrated in Figure 4.[27]

$$2H^+ + 2e^- \rightarrow H_2\ (\text{Cathode}) \tag{3}$$

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^-\ (\text{anode}) \tag{4}$$

3.2 Electrocatalyst development for PEMWE

In PEME electrolysis, transition metal carbide has been examined as a possible replacement for expensive metal electrocatalysts because of their large surface area, widespread electronic conductivity, inexpensive price, and widespread availability. Therefore, to achieve similar electrocatalytic qualities to platinum metal, transition metal carbides are utilized. Furthermore, the transitional metals W, Ta, V. Mo, and Ti all of which are very common in nature and reasonably priced-being investigated for these uses. They cannot be utilized separately though as their excess potential was 0.300 V versus RHE (V) stronger than that of pure platinum metal.[52] Nonetheless, they serve as a backbone for precious metals, and platinum loading lowers the operational expenses of PEME electrocatalysis.[53] Kelley et al. reported a research study that examined the HER activity of palladium sustained on tungsten and molybdenum carbide. Palladium is more affordable than platinum, according to research, and its electrocatalytic qualities are comparable. It was determined to be that the palladium catalyst's underlying components, such as tungsten and molybdenum carbides, showed lower metal packing and operating costs.[54] A comparative analysis of gold (Au), palladium (Pd), and platinum (Pt) supported on metal carbides revealed promising HER electrocatalytic performance. These noble metal-supported carbides exhibited enhanced catalytic activity, highlighting their potential for efficient hydrogen evolution reactions. In order to replace platinum in potential HER electrocatalysts, carbon-supported electrocatalysts in especially, earth-rich, low-cost nanomaterial enclosed in nickel-doped graphene, are thoroughly investigated. These materials include Co–Fe nanoalloys, WO_2/C, Ni_2P/CNTs, FeS_2/CNTs, & MoS_2/CNTs.[55] Though rarely documented, these platinum-free carbon-supported HER catalysts have been studied for PEME applications. In the context of HER electrocatalysis, MoSx and palladium based nanocarbon revealed to be most effective and actives catalysts for electricity between those.

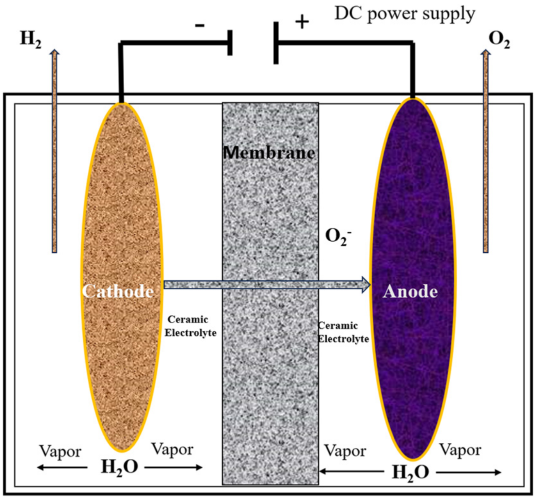

Figure 4: Solid-oxide water electrolysis technology graphical illustration.

4 Solid-oxide electrolysis and its electrocatalytic development

4.1 Solid-oxide water electrolysis

The efficient synthesis of ultra-pure hydrogen and the transformation of electrical energy into chemical energy have attracted a lot of interest in solid–oxide electrolysis. First presented by Donitz and Erdle in 1980, the techniques is currently being developed because further study is needed.[32,56] Solid ceramic electrolyte, which is employed in SOE, is compact and responds quickly, much like PEME cells. It is unique because it necessitates a high temperature, which requires both an electrical and thermal input. This method has the potential to be industrialized and applied to the routine production of hydrogen, and it may work high pressures of up to 3 Mpa.[57] Figure 4 displays the SOE schematic diagram. Two H_2 and two O_2 ion atoms are generated when the molecules of water (H_2O) decrease at the cathode side. One molecules of oxygen (O_2) are subsequently created at the anode by oxidizing the two O_2 ion molecules. Equations (5) and (6) depict the electrochemical reactions occurring at the cathode and anode in solid oxide electrolysis (SOE), outlining the fundamental processes involved in hydrogen and oxygen production.[27]

$$2H_2O + e^- \rightarrow 2H_2 + O_2\ (\text{Cathode}) \tag{5}$$

$$O_2^- \rightarrow O_2 + e^-\ (\text{Anode}) \tag{6}$$

Strontium-doped lanthanum manganite and nickel-zirconia are among the most widely used cathode materials in solid oxide electrolysis (SOE) due to their excellent electrochemical performance and stability. At the anode, zirconia is typically utilized.[58] The anodes interchange current density is 5.3×10^{-1} A/cm^2, while the cathode is 2×10^{-1} A/cm^2. Due to cooling require, the use of water is typically about 83.3 times greater than hydrogen output. Currently, a lot of investigation is being done to create ceramic proton conducting material that can be utilized to create SOE. Furthermore, compared to O_2 conductors, these materials show remarkable ionic conductivity and great efficiency. Figure 4 displays the SOE process schematic diagram. In contrast to significant temperature SOE technology devices, that remains in its invention stage, temperature below freezing technologies like AWE and PEME offer an elevated degree of technological capability.[59] Some disadvantages of the SOE approach include the application of ceramic electrolytes at temperature that are higher than 1,000 °C and electrode deterioration. Something demonstrated poor stability and strength. But compared to SOE, PEME technology can manufacture hydrogen of greater quality using a solid ceramic membrane that operates between 500 and 1,000 °C.[17] Recent studies have demonstrated significant improvements in SOE performance, including the use of advanced perovskite materials for electrodes, such as $La_{0\cdot6}Sr_{0\cdot4}CoO_3$-δ, which achieved a current density of 1.5 A/cm^2 at 800 °C, showcasing enhanced catalytic performance compared to previous materials. Additionally, novel ceramic electrolytes like cerium-doped yttria-stabilized zirconia (YSZ) have increased ionic conductivity by 20 % at 900 °C, improving overall efficiency. Furthermore, recent experiments report that SOE systems operating at temperatures above 800 °C can achieve hydrogen production rates of up to 2.3 Nm^3/h, with new nickel-zirconia and perovskite cathodes boosting hydrogen production by 30 % compared to traditional systems. These findings underscore the potential of SOE technology to produce high-efficiency hydrogen while advancing the stability and performance of electrocatalysts, demonstrating the viability of SOE for industrial-scale hydrogen production.[60]

4.2 Electrocatalyst development for SOWE

Since the operational mechanism of a solid oxide electrolysis (SOE) cell differs from that of a solid oxide fuel cell (SOFC), components such as the anode and cathode in a fuel cell can also function as the cathode and anode in an electrolysis cell. For instance, nickel-yttria stabilized zirconia (Ni-YSZ) is commonly used as a cathode in SOE for hydrogen production and as an anode in fuel cells. However, Ni-YSZ exhibits limited stability and requires a high hydrogen concentration to prevent nickel oxidation. This explains why nickel aggregates during the hydrogen generation procedure's prolonged elevated temperatures.[61,62] Redox perovskite oxides can be used as the electrodes in the method of producing hydrogen in order to resolve this issues.[63] Cao et al. demonstrated the incorporation of $La_{0\cdot3}Sr_{0\cdot7}$–$Ti_{0\cdot3}Fe_{0\cdot7}O_3$-σ (LSTF), a specialized symmetrical electrode, into the $Sm_{0\cdot2}Ce_{0\cdot8}O_{1\cdot9}$-YSZ electrolyte. The LSTF electrode exhibited enhanced redox stability and superior electrocatalytic activity, achieving maximum power densities of 0.215, 0.293, and 0.374 W/cm^2 at 800 °C, 850 °C, and 900 °C, respectively. Since the cathode in a solid oxide electrolysis (SOE) cell operates effectively at both medium and high temperatures, materials such as perovskites, double perovskites, and modified ABO_3 perovskites are considered promising candidates for application in SOE technology.

By lowering the excessive potential, the best HER electrocatalysts might reduce the energy and expense required for the electrochemical division of water. Thus, it is crucial and difficult to conduct study and development in order to create effective non-precious electrocatalysts for HER. The water electrolysis process is currently making substantial use of cobalt and nickel based electrocatalysts as HER electrocatalysts. The study provides a comprehensive understanding of the latest Ni- and Co-based electrocatalysts, including nickel-based alloys, cobalt oxides, cobalt sulfides, cobalt selenides, nickel-yttria-stabilized zirconia (Ni-YSZ), nickel phosphides, and cobalt phosphides. Additionally, it explores advanced materials such as cobalt-doped iron disulfide CNTs (FeS_2/CNTs), nickel phosphide-supported carbon nanotubes (MoS_2/CNTs and Ni_2P/CNTs), and tungsten dioxide-supported carbon nanowires (WO_2/C). These materials have demonstrated exceptional activity and efficiency as electrocatalysts for the hydrogen evolution reaction (HER).

5 Discussion and future scope

SOE operates at high temperatures (700–900 °C), offering high efficiency in hydrogen production. However, material degradation at these temperatures remains a significant challenge. Recent studies have focused on improving the ionic conductivity, chemical stability, and mechanical strength of solid oxide electrolytes by developing novel materials and control strategies. For instance, Liang et al. (2023) proposed a novel control strategy to neutralize heat sources within SOECs under variable solar power conditions. Their approach modulates heat generation by adjusting the fuel flow rate, effectively reducing temperature gradients and enhancing the longevity of the SOECs. Additionally, Bloom Energy and Shell have collaborated to develop scalable solid oxide electrolyzer systems for hydrogen production, aiming to replace conventional grey hydrogen with cleaner alternatives.[64] PEM electrolysis is known for its high efficiency and rapid response to dynamic power inputs. However, the reliance on scarce and expensive materials like iridium for catalysts poses economic and scalability challenges.

Recent advancements have explored the development of alternative catalysts and membrane materials to reduce costs and improve performance. For example, researchers have investigated the use of non-precious metal catalysts and durable membrane materials to enhance the sustainability of PEM electrolysis systems. Furthermore, studies have highlighted the importance of addressing gas crossover issues, which can lead to efficiency losses and safety concerns. Innovations in membrane technology aim to mitigate these challenges by improving selectivity and reducing permeability. AWE is a mature and cost-effective technology for hydrogen production. However, it faces challenges related to lower current densities and higher overpotentials compared to PEM systems. Recent research has focused on developing advanced electrocatalysts to enhance the performance of AWE. Liu et al. (2024) designed a novel cobalt-based metallic heterostructure ($Co_3Mo_3N/Co_4N/Co$) that exhibits high activity for both HER and OER in alkaline media. This catalyst demonstrated a low cell voltage of 1.58 V at 10 mA cm^{-2} and maintained approximately 100 % retention over 100 h at 200 mA cm^{-2}, outperforming commercial Pt/C and RuO_2 catalysts. These advancements underscore the potential of innovative catalyst designs to overcome the limitations of AWE and enhance its viability for large-scale hydrogen production.[65]

In recent studies, hybrid materials, which combine metal-based catalysts with carbon-based materials or metal-organic frameworks (MOFs), have demonstrated superior stability and efficiency compared to traditional electrocatalysts used in Solid Oxide Electrolysis (SOE). Traditional catalysts, such as nickel (Ni) and cobalt (Co)-based alloys, are commonly used in SOE due to their favorable catalytic properties. However, they are prone to issues like oxidation, phase instability, and reduced performance at high temperatures, which limits their long-term stability and efficiency. For example, nickel-based catalysts, particularly Ni-YSZ (yttria-stabilized zirconia), while efficient, tend to undergo structural degradation at elevated temperatures, leading to performance loss over extended use. On the other hand, hybrid materials like cobalt selenide ($CoSe_2$) supported on carbon nanotubes (CNTs) have shown significant improvements. Recent studies have demonstrated that these hybrids exhibit higher hydrogen evolution rates (HER) and increased stability during prolonged electrolysis. $CoSe_2$/CNTs, for instance, maintain their catalytic activity over 1,000 h of electrolysis, whereas traditional Ni-YSZ catalysts experience a notable decline in activity after just a few hundred hours due to oxidation and phase changes. The combination of the transition metal catalyst ($CoSe_2$) with CNTs provides enhanced conductivity and a stable support structure, which reduces the degradation typically seen in pure metal catalysts. Furthermore, hybrid materials often show a higher resistance to high-temperature-induced sintering, allowing them to perform more efficiently at the operational temperatures required for SOE. Table 1 shows the comparisons of key electrolysis technologies for hydrogen production, Alkaline Water Electrolysis (AWE), Proton Exchange Membrane Electrolysis (PEME), and Solid Oxide Water Electrolysis (SOWE) exhibit distinctive features and limitations. AWE, one of the most mature technologies, typically operates at 60–90 °C and employs nickel-based catalysts with potassium hydroxide as the electrolyte. Its hydrogen production rate ranges from 0.2 to 0.4 Nm^3/h per cell, with an efficiency of about 65–70 %. The technology benefits from long operational lifespans and low catalyst costs but suffers from slower kinetics and lower current densities.[32] PEME operates at slightly higher temperatures (50–80 °C) and uses precious metals such as platinum (Pt) or iridium (Ir) as electrocatalysts within a solid polymer electrolyte, allowing for high current densities and system compactness. It delivers high-purity hydrogen with energy efficiency ranging from 70–80 %, although the high cost and scarcity of noble metals remain significant barriers.[66] In contrast, SOWE operates at much higher temperatures (700–1000 °C), leveraging ceramic electrolytes and perovskite-type materials such as LSTF ($La_{0\cdot3}Sr_{0.7}$–$Ti_{0.3}Fe_{0\cdot7}O_3$-σ) and Ni-YSZ composites. SOWE achieves higher efficiency due to improved thermodynamic favorability and faster electrode kinetics, making it suitable for integration with industrial waste heat or solar thermal energy systems. However, challenges include electrode degradation, limited durability under redox cycling, and complex thermal management.[67,68] These comparative insights highlight that while PEME currently leads in commercial viability and compact design, ongoing research in SOWE catalyst stability and non-precious metal-based PEME catalysts is vital for future scalability and cost reduction.[69]

Additionally, hybrid materials often benefit from synergistic effects between the metal catalyst and the support material. For instance, the interaction between $CoSe_2$ and CNTs results in improved electron transfer and more active catalytic sites, further enhancing the efficiency of the hydrogen evolution reaction. This is in contrast to traditional materials, where the catalytic sites are limited and less stable under prolonged operational conditions. Overall, while traditional catalysts like Ni-YSZ continue to be important for SOE applications, the development of hybrid materials offers substantial improvements in both catalytic efficiency and stability, making them a promising alternative for large-scale, long-term hydrogen production via electrolysis.

5.1 Future scope

Looking ahead, the development of efficient, cost-effective, and durable electrocatalysts for water electrolysis is expected to advance through several strategic directions. One of the primary goals is to establish scalable and environmentally sustainable synthesis techniques for transition metal-based and carbon-supported catalysts. Green chemistry approaches and energy-efficient methods such as solvothermal synthesis and electrospinning are anticipated to support industrial-scale production while minimizing ecological impact. Additionally, enhancing the long-term operational stability of non-precious metal electrocatalysts under industrial current densities is critical. This will require comprehensive durability assessments and degradation studies that simulate real-world conditions. Another promising area lies in integrating these catalytic systems with intermittent renewable energy sources like solar and wind. For this, the development of catalysts that maintain performance under variable voltage inputs and dynamic load cycles is essential. There is also growing interest in dual-functional materials that can effectively catalyze both the hydrogen and oxygen evolution reactions, thus simplifying cell architecture and reducing overall system costs. Advanced *in situ* and operando characterization techniques, such as X-ray absorption spectroscopy and Raman spectroscopy, will continue to play a vital role in uncovering the mechanistic pathways and active sites responsible for catalytic behavior. Furthermore, the inclusion of techno-economic analyses and lifecycle assessments in future research will be key to determining the commercial viability and sustainability of newly developed electrocatalysts. These efforts, when combined, will not only drive innovation in hydrogen production technologies but also accelerate the transition toward a clean, hydrogen-based global energy infrastructure.

Table 1: Comparisons of hydrogen production technologies.

Parameter	AWE	PEME	SOWE
Catalyst (Anode/Cathode)	Ni-based/Ni-based	Iridium/Platinum	LSM/Ni-YSZ
Electrolyte	30–40 % KOH	Solid polymer (e.g., Nafion)	Solid ceramic (e.g., YSZ)
Operating temperature (°C)	60–80	50–80	700–900
Current density (A/cm^2)	0.2–0.4	Up to 10	0.5–1.0
Cell voltage (V)	1.8–2.4	1.75–2.2	1.3–1.5
Energy efficiency (%)	62–82 (HHV)	67–82	>90
Specific energy consumption	4.2–5.9 kWh/Nm^3	4.2–5.6 kWh/Nm^3	~3.5–4.0 kWh/Nm^3
Advantages	Low cost, mature technology	High purity H_2, compact size	High efficiency
Challenges	Lower current density	Expensive catalysts	High operating temperature

6 Conclusions

Electrochemical water electrolysis presents a highly effective and sustainable pathway for generating pure hydrogen and oxygen, positioning it as a key technology for clean energy production. Among the various electrolysis methods, proton exchange membrane electrolysis (PEME) has advanced significantly, while solid oxide electrolysis (SOE) continues to be explored at the experimental level. However, the practical deployment of water electrolysis still faces challenges related to sluggish kinetics and the dependency on expensive precious metal electrocatalysts. These limitations restrict broader adoption and increase the cost of green hydrogen production.

In recent years, transition metal-based catalysts – particularly those involving Fe, Mn, Co, and Ni and their corresponding oxides – have emerged as promising alternatives to noble metals for the hydrogen evolution reaction (HER). Several engineering strategies, including heterostructure formation, carbon hybridization, and bimetallic synergism, have been employed to boost their conductivity, stability, and overall catalytic performance. Despite progress, durability concerns and high overpotentials remain major technical barriers, especially in high-temperature SOE systems. Enhancing ionic and electronic conductivity, along with maximizing the electrochemically active surface area, remains critical. A notable insight is the repurposing of fuel cell anodic materials as cathodic electrodes in SOE, offering a potential route to reduce costs and simplify system integration.

From a commercial perspective, several companies, including NEL Hydrogen, ITM Power, and Siemens Energy, are now deploying PEM electrolyzers at industrial scale, while research-driven startups are actively testing non-precious metal catalysts for pilot-scale applications. Governments and energy companies worldwide are also investing in green hydrogen hubs, with the goal of replacing grey hydrogen and fossil fuels in refining, ammonia production, and heavy transport. Looking forward, the integration of renewable energy with scalable, low-cost, and durable electrocatalyst systems will be instrumental in realizing a hydrogen-based economy. This review underscores the importance of continuous innovation in catalyst design and deployment strategies, which are essential for overcoming the final hurdles to industrialization and ensuring long-term commercial viability.

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