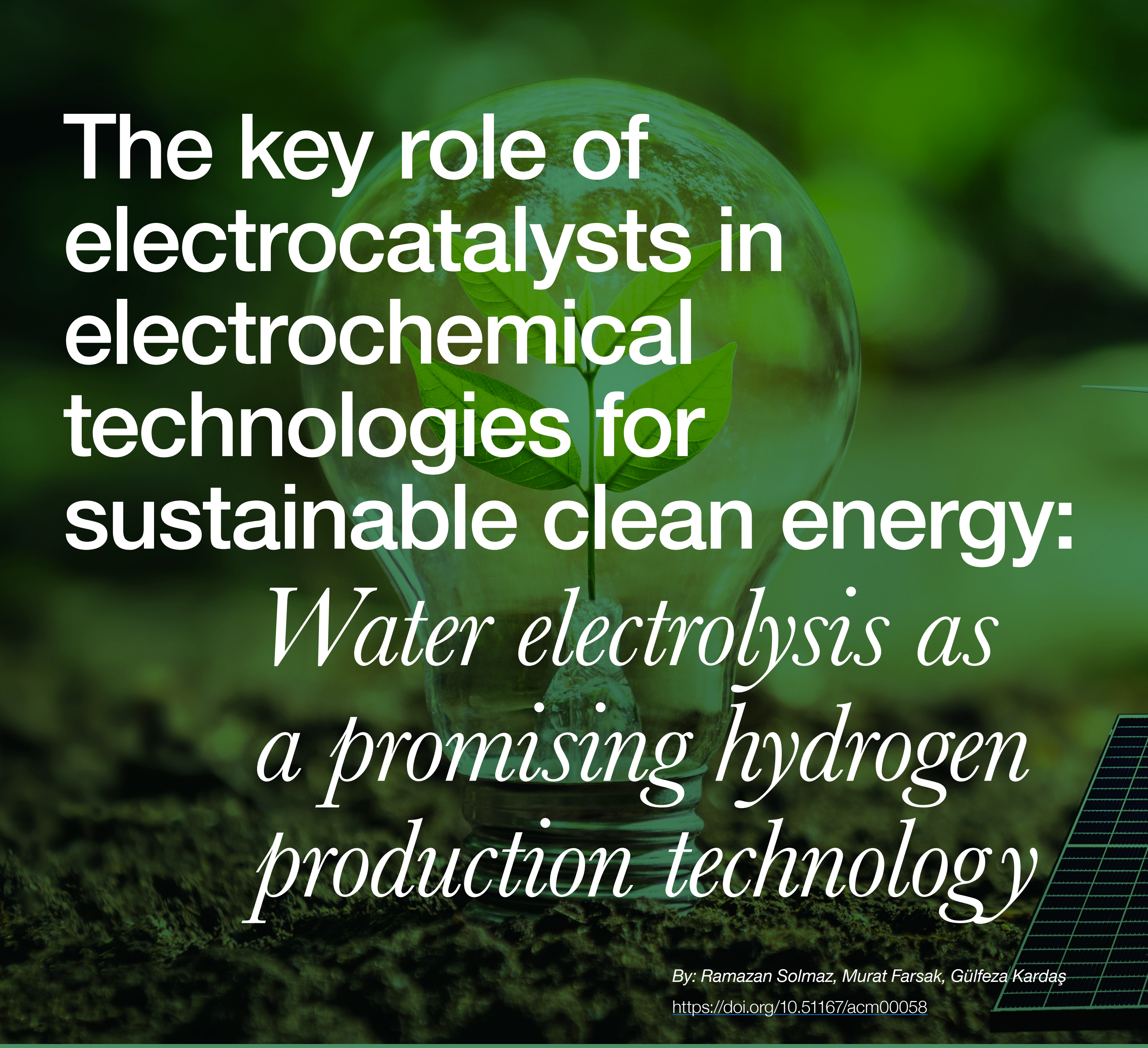

# The key role of electrocatalysts in electrochemical technologies for sustainable clean energy:

## *Water electrolysis as a promising hydrogen production technology*

*By: Ramazan Solmaz, Murat Farsak, Gülfeza Kardaş*

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Electrochemical reactions have become integral to various technological advancements and sustainable energy systems. They enable the conversion of chemical energy into electrical energy and play a crucial role in applications such as electrolyzers, fuel cells, batteries, and sensors. The electrocatalysts are central to the efficiency and performance of these electrochemical systems, which facilitate the desired electrochemical reactions by lowering the activation energy and enhancing the reaction kinetics[1].

The design and development of efficient electrocatalysts have been the subject of intense research over the past few decades. It is driven by the growing demand for clean and renewable energy sources and the need to address the environmental challenges associated with conventional energy conversion technologies. Electrocatalysts are key to unlocking the potential of electrochemical technologies as they can significantly improve energy conversion efficiency, reduce costs, and mitigate environmental impacts. Green hydrogen production by water electrolyzer with renewable electricity will be most important in transitioning to clean and sustainable energy. Developing effective catalysts for hydrogen and oxygen evolution reactions (HER and OER) is critical for advancing water electrolysis technologies[2,3]. Furthermore, hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) catalysts have crucial roles in effective fuel cells[4]. It should be a deep insight into these reactions' electrochemistry.

## 1. Fundamental Principles of Electrocatalysts

Electrocatalysts are crucial in various electrochemical processes, ranging from water electrolysis and fuel cells to battery technologies and chemical production[5]. These materials enable faster and more efficient electrochemical reactions by lowering the activation energy and facilitating the transfer of electrons[5]. By understanding electrocatalysis principles and practical applications, we can unlock the potential for groundbreaking energy storage, chemical production and environmental sustainability advancements.

To comprehend the intricacies of electrocatalysis, it is essential to understand electrocatalytic activity. Electrocatalysts are materials that facilitate the transfer of electrons during electrochemical reactions without being consumed. They provide an alternative reaction pathway with lower activation energy, thus accelerating the reaction rate and lowering the energy barriers. This allows for efficient energy conversion in electrochemical systems. It is influenced by several factors, including the nature of the catalyst, its surface structure and the reactants involved. The electrocatalytic activity of a material depends on its ability to adsorb reactant molecules, transfer electrons and desorb products. Researchers can design and optimize catalysts for specific applications by studying the mechanisms behind electrocatalytic activity[6].

Electrocatalysts typically possess high surface areas and are often composed of noble metals, metal oxides, or carbon-based materials. The

**Gülfeza Kardaş**

Gülfeza Kardaş is a professor of the Chemistry Department at Çukurova University in Türkiye. She received both her BS degree in Chemistry (1993) and her PhD degree in Physical Chemistry (1999) from Çukurova University. Her professional interests include water electrolyzers, fuel cells, batteries, polymers, and corrosion. She has published more than 100 papers. Ongoing research in her laboratory is on the development of electrocatalysts for water electrolyzers and batteries, the synthesis of polymer membrane separators for anion exchange membrane water electrolyzers and lithium-ion batteries, and the corrosion of metals.

**Ramazan Solmaz**

Ramazan Solmaz is a professor of the Occupational Health and Safety Department at Bingöl University in Türkiye. He received both his BS degree in Chemistry (2001), his PhD degree in Physical Chemistry (2009) from Çukurova University and received his second BS degree in Renewable Energy Resources at Bingöl University. Her professional interests include renewable energy, hydrogen energy, water electrolysis, fuel cells, batteries, conductive polymers, corrosion, electrooxidation, self-assembly monolayer films and electrodeposition. She has published more than 70 papers. Since 2012, he has been served as an editor at the International Journal of Hydrogen Energy.

**Murat Farsak**

Murat Farsak is an associate professor in the Battery Systems & Hydrogen Technologies Department at Osmaniye Korkut Ata University in Türkiye. His career in electrochemistry began in 2004 as an undergraduate student at Çukurova University, followed by a PhD from his alma mater in 2015. He joined Osmaniye Korkut Ata University in 2009, where he focuses on material characterization and electrochemistry, especially energy conversion and storage materials, for instance, electrode materials for Li batteries and fuel cells, and liquid electrolytes for those batteries. His recent research interests include two main topics: Li–air batteries and liquid electrolytes.

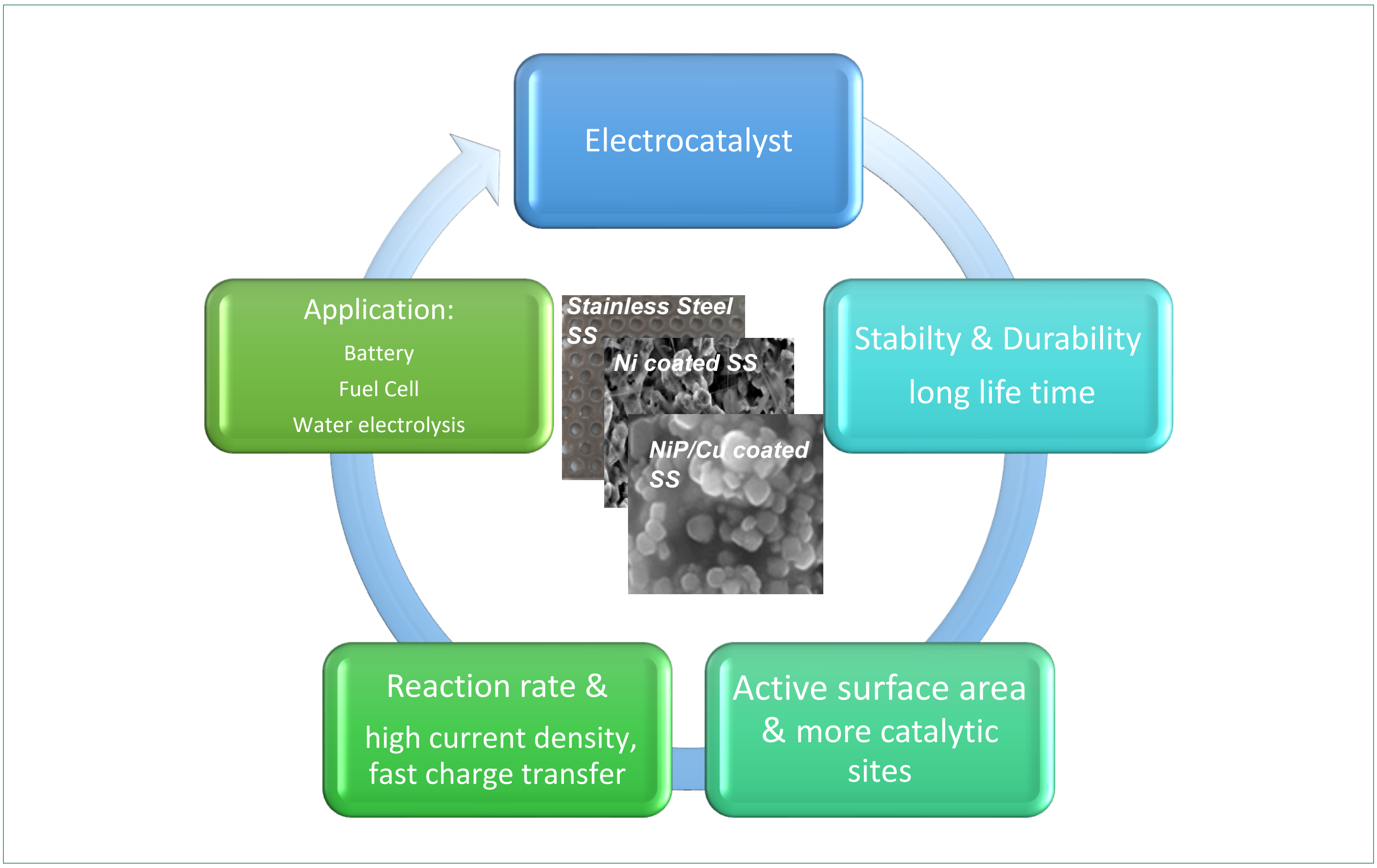

**Figure 1. Schematic illustration of critical factors affecting the performance of electrocatalysts.**

choice of catalyst depends on the specific application and the desired reaction. For example, platinum-based catalysts are commonly used in fuel cells due to their exceptional performance in the oxygen reduction reaction.

The development and optimization of electrocatalysts involve a multidisciplinary approach that combines materials science, chemistry and engineering. Researchers employ various techniques, including catalyst synthesis, characterization and testing, to design catalysts with desirable properties such as low cost, high activity, selectivity and stability. Researchers aim to enhance the electrocatalytic activity, stability and durability of electrocatalytic by tailoring their composition, morphology and structure[7–9]. Additionally, computational modeling and simulation techniques aid in understanding the underlying mechanisms and predicting the behavior of electrocatalysts. Advanced characterization techniques, such as electron microscopy and spectroscopy, enable researchers to study the catalyst's structure and understand its electrochemical behavior at the atomic level.

Researchers employ various characterization techniques to assess catalyst activity, selectivity and stability parameters. Techniques like cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy provide insights into the electrochemical behavior of catalysts. Moreover, performance metrics such as current density, faradaic efficiency and turnover frequency help quantify the catalytic activity. By evaluating the electrocatalytic performance, researchers can identify areas for improvement and guide the design of superior catalysts.

Electrocatalysts possess unique properties that enhance their electrocatalytic activity. Several factors can influence the electrocatalytic activity of a material. Some critical factors affecting the performance of electrocatalysts are shown in Figure 1 and summarized below:

***Active surface area;*** the active surface area of the catalyst is a very crucial factor, which determines the number of catalytic sites available for reactant adsorption and subsequent reaction[10]. A higher surface area provides more sites for the reactants to interact. By increasing the active surface area through various techniques such as nanostructuring or introducing porous structures, electrocatalysts can significantly enhance their catalytic reaction rate. Various techniques, such as the synthesis of nanostructured materials (i.e. nanoparticles or nanowires) and surface modification, can be employed to enhance the active surface area. Moreover, controlling the morphology and structure of catalysts can also optimize the active surface area and improve the overall performance of electrocatalysts[11].

In addition to increasing reaction rates, a larger active surface area also enhances the catalyst's stability and durability. With a higher number of active sites, the catalyst can distribute the reaction load more evenly across its surface, mitigating the degradation caused by localized high current densities. This improves the long-term performance and lifespan of the electrocatalyst.

***Catalytic reaction rate;*** another crucial factor is the catalytic reaction rate, which depends on the material's ability to facilitate charge transfer[12]. By increasing the reaction rate, we can achieve faster and more effective electrochemical processes. The rate of a reaction depends on the kinetics of the electrochemical process and the efficiency of charge transfer. The development and optimization of electrocatalysts involve tailoring their composition, optimizing reactant concentration, electrode potential, morphology and surface properties to maximize their catalytic efficiency. For example, alloying different metals can modify the electronic structure of the catalyst, promoting charge transfer and catalytic activity[13]. Additionally, controlling the morphology of the catalyst's surface can further enhance its reaction kinetics[14]. By optimizing the reaction conditions and the catalyst's properties, researchers can enhance the catalytic reaction rate, leading to faster and more efficient electrochemical processes[15].

Additionally, the catalytic reaction rate is influenced by factors such as temperature, pressure and the concentration of reactants and products. Understanding these factors allows researchers to develop strategies to improve electrocatalytic activity and overall efficiency.

***Stability and durability of electrocatalysts;*** stability, durability and lifespan are also critical factors in electrocatalyst design. These parameters are vital considerations in the practical application of electrocatalysts for long-term performance and commercial viability. Catalysts must maintain their performance over extended periods, resisting degradation and corrosion. The extreme operating conditions in many electrochemical applications can impose significant stress on catalysts, leading to degradation and loss of activity over time. Therefore, researchers focus on developing stable and durable electrocatalysts that can withstand these conditions for extended periods[16]. Factors such as catalyst composition, surface structure and reaction conditions affect the stability and durability of electrocatalysts. Researchers employ strategies like catalyst supports, protective coatings, surface modifications and alloying to enhance stability and durability. By addressing these challenges, electrocatalysts can be utilized effectively in various industries, including energy generation, chemical production and environmental applications.

Researchers employ various characterization techniques to assess parameters such as catalyst activity, selectivity and stability. Techniques like cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy provide insights into the electrochemical behavior of catalysts. Moreover, performance metrics such as current density, faradaic efficiency and turnover frequency help quantify the catalytic activity. By evaluating the electrocatalytic performance, researchers can identify areas for improvement and guide the design of superior catalysts.

Electrocatalysts have a wide range of applications in various electrochemical systems. The development of efficient and durable electrocatalysts is essential for advancing these technologies and driving their commercialization. Water electrolysis, fuel cells and batteries are important applications of the electrocatalyst which are summarized below:

***Water electrolysis;*** electrocatalysts play a pivotal role in water electrolysis, a process that converts water into hydrogen and oxygen using electrical energy. This technique is a promising technology for clean and sustainable hydrogen production. Researchers are actively exploring various electrocatalyst materials, including metal oxides, transition metals and carbon-based catalysts, to improve the efficiency and reduce the cost of water electrolysis[17–22]. Platinum and other precious metal-based catalysts are commonly used to facilitate the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER). But the development of cost-effective and earth-abundant catalysts is a significant focus of research. Water electrolysis holds immense potential for clean hydrogen production, a promising energy carrier for a sustainable future.

***Fuel cells;*** fuel cells are electrochemical devices that convert the chemical energy of a fuel directly into electrical energy. Electrocatalysts, typically based on platinum or platinum alloys, are crucial components in fuel cells, facilitating the electrochemical reactions that occur at the anode and cathode of fuel cell. By optimizing the electrocatalytic activity and stability, fuel cells offer a promising way for clean and efficient energy generation. Advancements in electrocatalyst design aim to enhance the efficiency and durability of electrocatalyst as well as reduce the cost of fuel cells for widespread adoption and commercial viability of fuel cell technologies.

***Battery technologies;*** batteries are essential for energy storage. Electrocatalysts can significantly impact battery performance and play a crucial role in the development of advanced battery technologies. In rechargeable batteries, electrocatalysts enhance the kinetics of charge transfer reactions, leading to faster charging and discharging rates that improve the overall performance and their energy storage capabilities. Additionally, catalysts can improve the stability of battery materials and prevent unwanted side reactions. Researchers are actively working on developing electrocatalysts for various battery chemistries, including lithium-ion batteries, sodium-ion batteries and flow batteries, to improve their energy density, cycle life and overall performance. Developing electrocatalysts with high activity and stability is essential for advancing battery technologies.

## 1.1. Recent Developments and Future Directions of Electrocatalysts

Electrocatalysis continuously evolves, with researchers discovering novel materials, innovative synthesis techniques and advanced characterization methods. Recent developments include the discovery of single-atom catalysts, the design of self-supported catalysts and the exploration of new catalytic mechanisms. These advancements aim to improve electrocatalyst performance, durability and economic viability.

While electrocatalysts hold great promise for a sustainable future, several challenges need to be addressed. These include the development of cost-effective catalysts, understanding complex reaction mechanisms, improving long-term stability and scaling up production for commercial applications. Developing cost-effective and abundant catalyst materials is crucial for widespread adoption. Additionally, exploring novel electrocatalytic materials and catalyst designs as well as understanding their fundamental properties will drive innovation in the field. Integrating electrocatalysts into practical devices and addressing scalability and commercialization challenges are vital for realizing the full potential of electrocatalysis. By overcoming these challenges, such as stability, scalability and commercialization, electrocatalysis can pave the way for sustainable energy systems and environmentally friendly chemical synthesis. Thus, we can revolutionize energy conversion, storage and utilization for a greener and more sustainable future.

The commercialization of electrocatalysts is vital for their widespread adoption and integration into future energy transition. It requires addressing technical, economic and regulatory challenges to ensure the viability and market competitiveness of catalyst materials. Collaborations between academia, industry and policymakers are essential for accelerating the commercialization process and facilitating the widespread adoption of electrocatalysts in real-world applications. By optimizing the catalyst synthesis methods, scalability, manufacturability and cost-effectiveness of electrocatalysts, we can accelerate their commercialization and drive the transition towards a sustainable future energy transition.

## 1.2 Current Energy Sources, Limitations and Need for Sustainable and Renewable Alternatives

In today's world, the energy demand is constantly increasing. Currently, the world heavily relies on traditional energy sources such as including fossil fuels such as coal, oil and natural gas for its energy needs. These non-renewable energy sources have been instrumental in powering our industries, transportation and homes for decades. However, their use has significant drawbacks. Fossil fuels contribute to air pollution, greenhouse gas emissions and climate change. These pollutants not only affect air quality but also contribute to global warming. Additionally, the limited availability of fossil fuels poses a significant challenge for future generations. Moreover, their extraction and production often lead to environmental degradation.

The limitations of our current energy sources, coupled with the urgent need to transition to more sustainable and environmentally friendly options, have led to the search for alternative energy sources. Renewable energy sources are becoming increasingly popular in recent years, with the cost of production and installation steadily decreasing[23]. These alternatives aim to address the shortcomings of fossil fuels while providing a reliable and sustainable energy supply. Solar panels, wind turbines and hydroelectric power plants are becoming increasingly common sights as we strive to transition to a more sustainable energy future. Unlike fossil fuels, renewable energy sources are abundant and have a lower environmental impact. They can provide a significant portion of our energy needs.

The global energy landscape is profoundly transforming in pursuing a sustainable and carbon-neutral future. As the effects of climate change become increasingly evident, the need to reduce greenhouse gas emissions and shift towards renewable energy sources has never been more urgent. In this endeavor, the production of green hydrogen has emerged as a promising solution with the potential to revolutionize how we generate, store and utilize energy.

Green hydrogen as an energy carrier can solve the challenges of renewable energy sources like solar and wind intermittency. As energy storage, it converts surplus renewable energy into hydrogen during periods of excess production. This hydrogen can then be stored and used to generate electricity when renewable generation is low, thus providing stability to the grid and enabling a more reliable energy supply. Green hydrogen also has the potential to decarbonize sectors that are difficult to electrify directly, such as heavy industries like steel, cement and chemicals. These sectors are responsible for significant global carbon emissions and often lack viable renewable alternatives. These industries can significantly reduce their carbon footprint using green hydrogen as a feedstock or energy source. It can be crucial in decarbonizing transportation, particularly in sectors where battery-electric solutions, such as long-haul freight and aviation. Fuel cell electric vehicles (FCEVs) powered by hydrogen offer longer ranges and shorter refueling times than battery-powered vehicles, making them suitable for various applications. It has the potential to transform the energy landscape on a global scale. Countries with abundant renewable resources can produce green hydrogen and export it to regions with limited renewable capacity, thus enabling a more equitable distribution of clean energy and reducing reliance on fossil fuels.

## 2. Green Hydrogen as a Future Energy Source: Advantages, Limitations and Challenges

Hydrogen has emerged as a promising future energy source among the various alternatives. Hydrogen is the most abundant element in the universe and can be produced from various sources, including water, using renewable energies. Hydrogen can power fuel cells, which produce electricity through an electrochemical reaction between hydrogen and oxygen. It can also be utilized in other applications, including transportation, heating and industrial processes.

Hydrogen offers several advantages that make it an attractive energy source. Firstly, it is clean-burning, producing only water vapor as a byproduct when used in fuel cells. This eliminates harmful emissions, reduces the impact on air quality and mitigates climate change. Additionally, hydrogen can be produced from renewable sources, making it a sustainable option. It also has a high energy density, meaning it can store much energy in a small volume[24]. Moreover, hydrogen has a high energy content, making it an efficient choice for energy storage. This makes hydrogen an excellent choice for energy storage applications.

However, there are also challenges and limitations associated with hydrogen as an energy source. Firstly, storing and transporting hydrogen is challenging due to its low density, which requires high-pressure containers or cryogenic temperatures[25]. The production of hydrogen is still largely dependent on fossil fuels, hindering its environmental benefits. This process releases greenhouse gases, undermining the environmental benefits of hydrogen. Also, hydrogen infrastructure is still underdeveloped and widespread adoption requires significant investment and technological advancements. The production methods for hydrogen, such as water electrolysis, require significant energy input, which can limit the overall efficiency and environmental benefits. Electrolysis, a process that uses an electric current to split water into hydrogen and oxygen, relies on the efficiency and effectiveness of electrocatalysts. These catalysts play a crucial role in enhancing the electrocatalytic activity, active surface area and catalytic reaction rate, thereby improving the overall efficiency of the process.

Overcoming the challenges and commercializing hydrogen as an energy source will require significant advancements in electrocatalytic technologies and infrastructure. Developing and optimizing electrocatalysts are ongoing research areas aiming to improve their electrocatalytic performance, stability and durability. These advancements will make hydrogen production more efficient and economically viable on a large scale.

### 2.1 Production Methods for Hydrogen

Researchers are actively exploring alternative production methods to overcome the limitations and challenges associated with hydrogen as an energy source. There are several methods for hydrogen production, such as steam methane reforming, partial oxidation of hydrocarbons, electrolysis, photoelectrochemical water electrolysis, biological hydrogen production, thermochemical water electrolysis, coal gasification, biomass gasification, high-temperature solid oxide electrolysis, etc[26]. One promising method is water electrolysis, which utilizes an electrochemical process to split water molecules into hydrogen and oxygen. This process requires electrocatalysts, materials that enhance the electrocatalytic activity and catalytic reaction rate. This method utilizes a renewable resource and does not release harmful byproducts. The efficiency and performance of water electrolysis depend on the catalysts' electrocatalytic activity and active surface area.

Researchers are actively working on developing and optimizing electrocatalysts for water electrolysis. The goal is to enhance these materials' catalytic performance, stability and durability. Materials science and nanotechnology advancements have paved the way for the design and synthesis of efficient and cost-effective electrocatalysts. The development and optimization of electrocatalysts, particularly in water electrolysis, play a vital role in advancing hydrogen as an energy source and driving the commercialization of various energy-related technologies by improving the efficiency of water electrolysis and hydrogen production.

### 2.2 Water Electrolysis: Green Hydrogen Production

Clean energy has become a pressing concern as the world grapples with the challenges of climate change and the need to reduce greenhouse gas emissions. Electrocatalysis is crucial in developing sustainable clean energy technologies, enabling cleaner and more efficient energy conversion processes. These technologies rely on

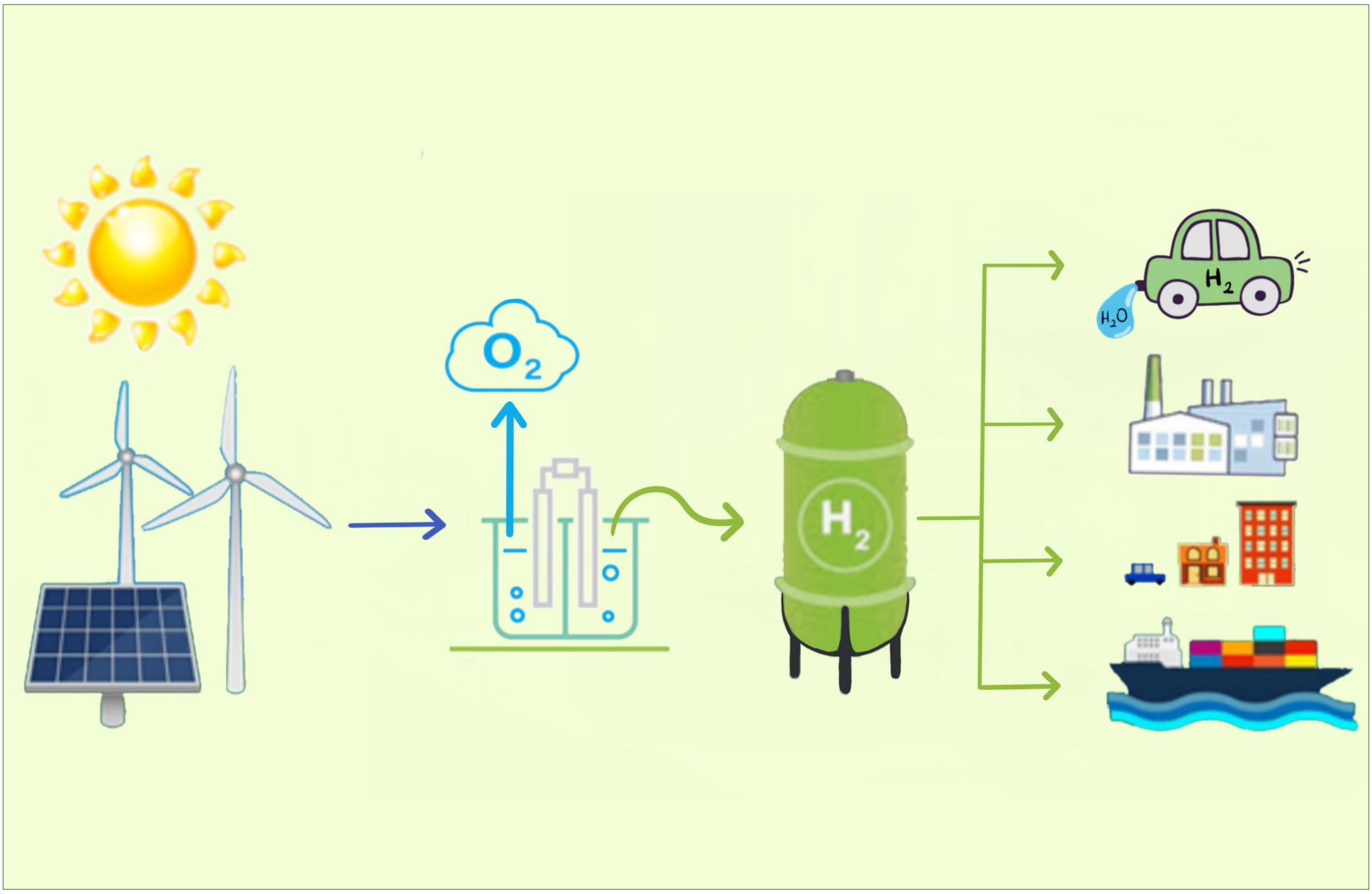

**Figure 2.** Schematically illustration of the green hydrogen production, storage, and usage.

the electrocatalytic activity of certain materials to facilitate catalytic reactions, enhancing the efficiency and performance of the systems. As we strive to reduce our dependence on fossil fuels and mitigate the environmental impact of traditional energy sources, electrocatalysts offer a promising solution for developing clean energy technologies. These catalysts facilitate electrochemical reactions, such as water electrolysis and fuel cell reactions, by lowering the activation energy required. This results in enhancing the efficiency and performance of the systems. By understanding the potential of electrocatalysts, we can discover new opportunities for clean energy generation and storage.

One of the most promising electrocatalysis is water electrolysis (or electrolysis), particularly for hydrogen production. Water electrolysis is a clean and efficient process that utilizes electrocatalysts to split water molecules into hydrogen and oxygen gases by applying an a direct current. Using renewable energy sources such as solar or wind power to drive the water electrolysis reaction, we can produce green hydrogen without harmful emissions, making it an ideal solution for a carbon-neutral future.

The basic principles of water electrolysis involve the use of an electrocatalyst to facilitate the splitting of water molecules into hydrogen and oxygen gases, lower the energy barrier for these reactions and enabling faster and more efficient hydrogen generation. Electrocatalysts are crucial in facilitating these reactions by providing active sites for the adsorption and activation of water molecules. Platinum-based catalysts are known for their high electrocatalytic activity and stability, making them ideal candidates for water electrolysis applications[27]. However, platinum's scarcity and high cost have prompted researchers to explore alternative catalysts. Several alternative electrocatalysts, such as nickel, molybdenum, copper, iron and cobalt-based materials, have been extensively studied to enhance the efficiency and kinetics of water electrolysis reactions. These catalysts increase the electrocatalytic activity and provide a larger active surface area, resulting in faster catalytic reaction rates. Other transition metal oxides and sulfides, such as nickel oxide and cobalt sulfide, have also shown promising results as electrocatalysts for electrolysis[28]. Carbon-based materials, such as graphene and carbon nanotubes, have also been explored for their potential as cost-effective and sustainable electrocatalysts. These examples highlight the diversity and potential of electrocatalysts in advancing water electrolysis technologies. However, stability and durability remain, as these catalysts can be prone to degradation over time. Research efforts are focused on developing more stable and durable electrocatalysts to ensure the long-term viability of water electrolysis technologies.

The kinetics of water electrolysis process are influenced by factors such as the electrocatalytic activity, active surface area and catalyst stability. Therefore, developing and optimizing efficient electrocatalysts are crucial for improving the efficiency and scalability of water electrolysis technology.

Water electrolysis offers several advantages for hydrogen production compared to conventional methods. Firstly, it provides a clean and sustainable source of hydrogen, with water being an abundant and readily available resource on Earth. Additionally, water electrolysis can be integrated with renewable energy sources, such as solar and wind power, to produce hydrogen in a carbon-neutral manner. Furthermore, hydrogen produced through water electrolysis can be used in various applications, including fuel cells, battery technologies and even to replace fossil fuels in transportation. The versatility and scalability of water electrolysis make it a promising technology for achieving a sustainable, clean energy future. Green hydrogen production and usage are schematically illustrated in Figure 2.

## 2.3 Water Electrolysis Reactions and Kinetics

The potential benefits of green hydrogen are substantial and several challenges must be addressed. While the allure of its potential benefits is undeniable, the journey towards its full realization is not without its share of challenges. Among the foremost is the cost of electrolysis, a cornerstone of green hydrogen production. Bridging the gap between ambition and affordability demands technological leaps and economies of scale that render the process economically viable. Yet, addressing these challenges becomes imperative as the world collectively pivots towards a more sustainable future. Understanding the kinetics and mechanisms of electrochemical reactions of the water electrolyzers and hydrogen fuel cells is essential for optimizing the performance of these technologies. Recent research on the HER/HOR and OER/ORR focuses on the catalysts used and the mechanisms involved[6,10,11,20].

### *Hydrogen Evolution Reaction (HER) and Hydrogen Oxidation Reaction (HOR)*

The hydrogen evolution reaction (HER) and hydrogen oxidation reaction (HOR) are two electrochemical processes that involve the generation by water electrolysis and consumption of hydrogen gas ($H_2$) by fuel cells. These reactions are fundamental to energy conversion technologies for clean and sustainable energy transition.

The following half-reaction in acidic and alkaline solutions can represent the:

In acidic electrolyte;

$$2H^+ (aq)+2e^- \rightleftharpoons H_2 (g) \qquad E^o=0.000V\ (SHE)$$

In alkaline electrolyte;

$$2H_2O(l)+2e^- \rightleftharpoons H_2(g)+2OH^-(aq) \qquad Eo=0.828V\ (SHE)$$

In these half-reactions, hydrogen ions in the acidic solution and liquid water in the alkaline solution are reduced by gaining electrons to form one mole of hydrogen gas ($H_2$). The half-cell reactions depend on the electrolyte or the mobile ion e.g., solvated hydroxide, solvated proton, carbonate, or oxide ion. The HOR is the reverse process of the HER. It occurs at the anode of a fuel cell, where hydrogen gas is oxidized to release protons and electrons. The HOR is a key process in fuel cells, where hydrogen fuel is converted into electricity by combining it with oxygen (from the air) in the presence of a catalyst.

The HER and HOR are essential reactions in energy conversion technologies. The HER is pivotal in processes like water electrolysis, which produces hydrogen gas as a clean and renewable energy carrier. On the other hand, the HOR is a critical step in fuel cells, facilitating hydrogen fuel conversion into electricity with minimal environmental impact. Both reactions contribute to advancing the development of sustainable and efficient energy systems.

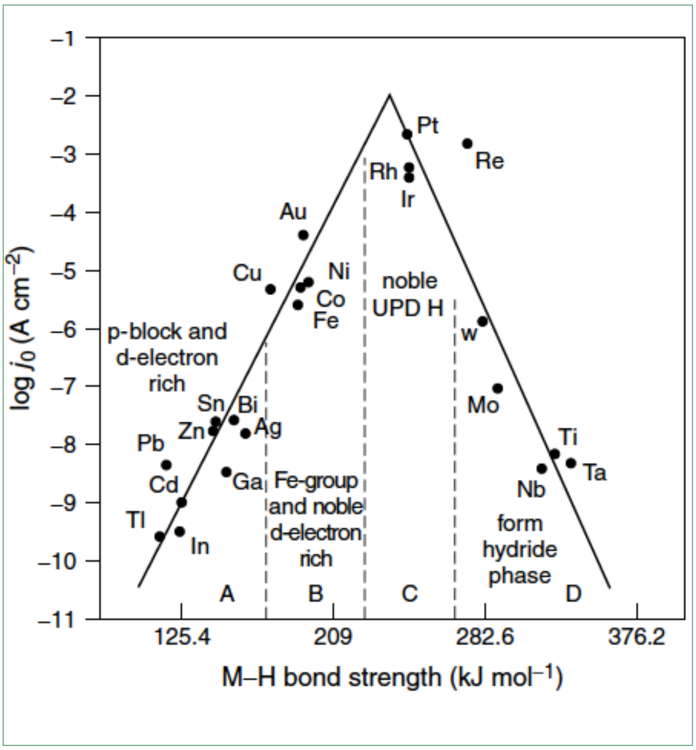

**Figure 3. Volcano curve for various transition metals** [29]

HER reaction rate is expressed in terms of the exchange current density, which is proportional to the reaction rate at the equilibrium potential. There is no net current under the above conditions, even though the concept is useful for representing rates at equilibrium. Theoretical considerations of fundamental kinetic equations for the HER predict the volcano curve in the plot of the logarithm of the exchange current density versus the enthalpy of hydrogen adsorption for various transition metals[29]. the parabolic bilinear volcano-type curve in the dependence of the logarithm of the exchange current density on the intermediate transition metal-hydrogen bonding strengths.

It is seen from Figure 3 that Pt is the most active metal for HER and is located on the top of the volcano plot. However, it is expensive. Using a volcano plot can produce cheap and effective catalysts for HER. It should be measured this catalyst behavior under the polarization condition. Platinum group metal (PGM) catalyst is one option for the acidic solution because of the corrosion. The efficient composite catalyst can be prepared with transition metals cheaper than PGM in an alkaline solution. The rational design of efficient and durable electrocatalysts for HER in alkaline media is paramount for enhancing alkaline electrolyzers' performance and commercial viability. Electrocatalysts for HER in alkaline conditions should exhibit high catalytic activity, excellent stability and a low overpotential, enabling the efficient and sustained production of hydrogen. Furthermore, these catalysts should be cost-effective, environmentally friendly and scalable to meet the demands of large-scale hydrogen production. The HER is a fundamental electrochemical process during water electrolysis in alkaline conditions. The key principles governing the HER process in alkaline conditions involve the thermodynamics and kinetics of the reaction.

The kinetics of the HER process in acid and alkaline conditions refer to the reaction rate and the associated factors that influence it. The

HER involves three reaction steps, including the adsorption of reactants, the formation of reaction intermediates and their subsequent desorption to generate hydrogen gas. These reaction steps are given below in acidic and alkaline solutions:

In acidic solution:

$H^+ (aq)+M+e^- \rightleftharpoons MH_{ads}$ (Volmer step)

$MH_{ads}+H^+ (aq)+e^- \rightleftharpoons H_2+M$ (Heyrovsky step)

$MH_{ads}+ MH_{ads} \rightleftharpoons H_2+2M$ (Tafel step)

In alkaline solution:

$H_2O(l)+M+e^- \rightleftharpoons MH_{ads}+OH^-(aq)$ (Volmer step)

$MH_{ads}+H_2O(l)+e^- \rightleftharpoons H_2+M+OH^-(aq)$ (Heyrovsky step)

$2MH_{ads} \rightleftharpoons H_2+2M$ (Tafel step)

The first step is the formation of the adsorbed hydrogen on the metal. The second step is the formation of hydrogen gas by desorption of the adsorbed hydrogen with the reduction of hydrogen ions in the acidic solution (reduction of the water molecule in the alkaline solution). The third step is the formation of hydrogen gas by chemical desorption of the adsorbed hydrogen. The strength of metal hydrogen bond has a key role in the reaction mechanism and the rate of hydrogen evolution.

The rate-determining step of the HER in alkaline media is often associated with the Volmer step, which involves the initial adsorption of a water molecule on the catalyst surface and its subsequent dissociation into adsorbed hydrogen species (H*). This step is typically followed by the Tafel and Heyrovsky steps, which involve the transfer of electrons and the desorption of hydrogen gas, respectively[30]. The overall rate of the HER is influenced by various factors, including the electrocatalyst's surface area, composition, morphology, active site availability and the efficiency of charge transfer at the electrode-electrolyte interface[31]. Moreover, the concentration of hydroxide ions ($OH^-$) in alkaline electrolytes can affect the HER kinetics by facilitating the reaction steps or promoting side reactions such as water dissociation[32].

In alkaline conditions, efficient HER electrocatalysts should possess several characteristics to enhance the kinetics of the reaction. These include high catalytic activity, excellent electrochemical stability, efficient charge transfer kinetics, suitable adsorption/desorption properties and optimized reaction pathways. Materials such as transition metal-based compounds (e.g., nickel, cobalt), metal oxides, metal sulfides and carbon-based materials have been extensively studied for their potential as electrocatalysts for the HER in alkaline media. Additionally, nanostructuring, surface modifications and heteroatom doping have been explored to enhance the active surface area, improve charge transfer and modulate the adsorption and desorption processes during the HER[33].

Understanding the key principles governing the HER process in alkaline conditions is crucial for designing and developing efficient electrocatalysts to facilitate sustainable hydrogen production. By fine-tuning the thermodynamic and kinetic factors, researchers aim to optimize the efficiency and performance of alkaline electrolyzers, contributing to the advancement of clean and renewable hydrogen energy technologies.

In recent years, significant progress has been made in the development of novel electrocatalysts specifically tailored for the HER in alkaline electrolyzers. Researchers have explored a range of materials, including transition metal-based compounds (such as nickel, cobalt and their alloys), metal oxides, metal sulfides and carbon-based materials[34,35]. These materials offer diverse catalytic properties and surface functionalities that can be finely tuned to achieve high catalytic activity and stability.

Various strategies have been employed to improve the performance of electrocatalysts for HER in alkaline electrolyzers, including nanostructuring, surface modification and heteroatom doping. These approaches aim to increase the active surface area, enhance charge transfer kinetics and improve the adsorption and desorption of reaction intermediates during the HER process. Additionally, efforts have

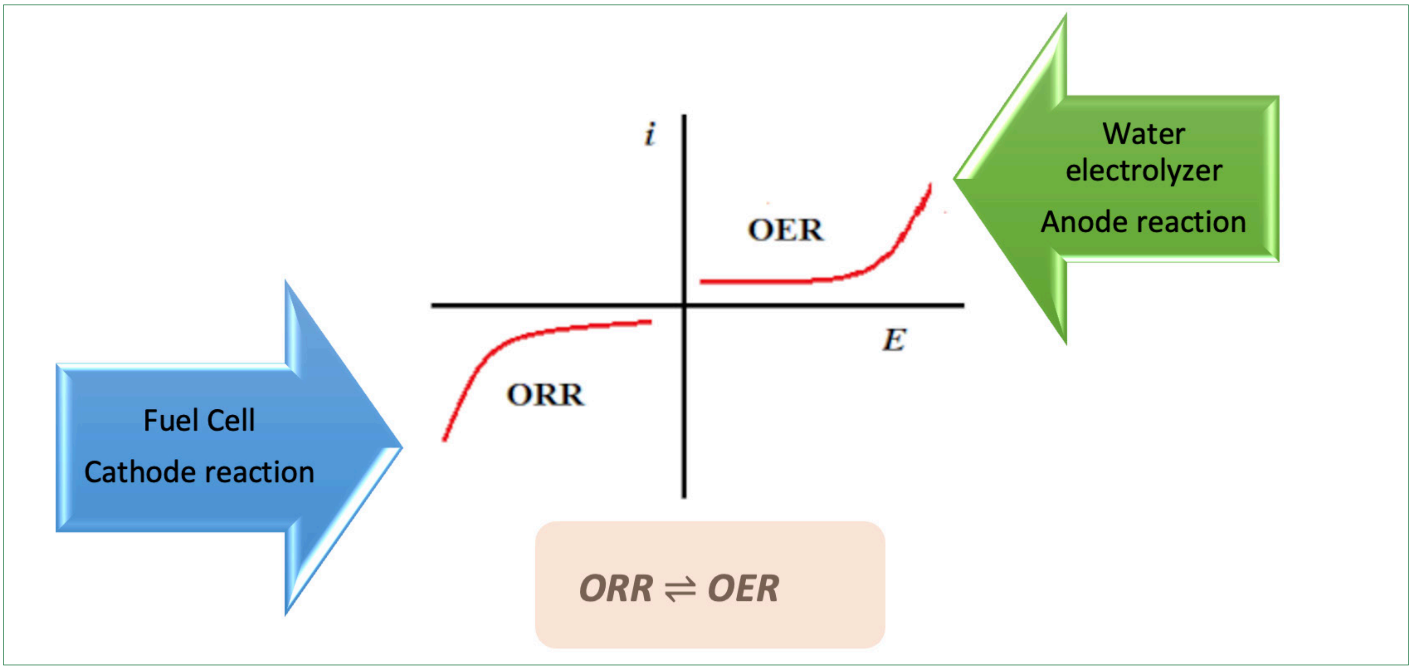

**Figure 4.** OER/ORR electrochemical reactions for fuel cell and water electrolyzer.

been directed toward exploring advanced synthesis techniques, such as solvothermal, hydrothermal and electrodeposition methods, to precisely control the catalyst materials' composition, morphology and crystallinity.

### *Oxygen Evolution Reaction (OER) and Oxygen Reduction Reaction (ORR)*

The oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR) are vital electrochemical processes for the water electrolyzer and fuel cell. The OER typically occurs at the anode of electrolysis cells, where water is split into oxygen and hydrogen ions during water electrolysis. The OER can be represented by the following half-reactions in acidic and alkaline solutions:

**In acidic electrolyte;**

$$2H_2O(l) \rightleftharpoons O_2(g)+4H^+(aq)+4e^- \qquad E^o=+1.229\ V\ (SHE)$$

In alkaline electrolyte;

$$4OH^-(aq) \rightleftharpoons O_2(g)+4H_2O(l)+4e^- \qquad E^o=+0.402\ V\ (SHE)$$

In these reactions, 2 moles of water ($H_2O$) in an acidic solution and 4 moles of hydroxide ions are oxidized, yielding one mole of oxygen gas ($O_2$) along with 4 moles of electrons ($e^-$). The oxygen reduction reaction (ORR) is the reverse reaction of the OER and an electrochemical process that involves the reduction of oxygen, which is the cathode reaction of the fuel cell which is given schematically in Figure 4. This reaction is central to generating electricity in fuel cells, facilitating the conversion of hydrogen fuel and oxygen into water and electrical energy.

While the OER/ORR is thermodynamically feasible, it often requires a catalyst to significantly reduce the overpotential (the additional voltage needed) for the reaction to occur efficiently. OER catalysts accelerate the process by providing an alternate reaction pathway with lower activation energy. Developing effective catalysts is critical for improving efficiency, performance and economic viability of electrolysis and fuel cell technologies.

Developing catalysts that can enhance the efficiency of ORR and OER is a critical challenge. Many catalysts are based on expensive materials like platinum, which poses cost and scalability concerns. Researchers are actively developing cost-effective and durable catalysts that can enhance the kinetics of these reactions.

### *Thermodynamics of water electrolysis*

The overall reaction is the decomposition of the water to produce hydrogen and oxygen. The reaction is given below:

$$H_2O(l) \rightleftharpoons H_2(g)+1/2O_2(g) \qquad E^o_{rev(decomp.)}=1.229\ V \cong 1.23V\ (SHE, 25^o\ C)$$

The standard reversible decomposition voltage for the electrolysis E¯rev^o can be calculated, at standard conditions $\Delta G^o = 237.13$ kJ mol $^{-1}$ as:

$$E^o_{rev} = -\frac{\Delta G^o}{nF} = -\frac{\Delta H^o - T\Delta S^o}{nF} = -1.23V$$

The positive value of change in Gibbs free energy indicates that the reaction is non-spontaneous. This is reflected in the negative sign in reversible decomposition voltage. An absolute value of $E^o$ of 1.23 V is commonly reported.

The thermoneutral decomposition voltage ($E^o_{th}$) can be determined using at standard conditions.

$\Delta H^o$ is the enthalpy of liquid water decomposition or known as the molar high heating value (HHV) enthalpy of hydrogen combustion for the reverse reaction of water formation:

$$|E^o_{th}| = \left|\frac{\Delta H^o}{nF}\right| = 1.48\ V$$

Typically, electrolyzer cells are operated above the thermoneutral voltage. $E^o_{th}$, (but above the reversible decomposition potential, $E^o_{rev}$,), an energy from the surrounding in heat equal to nF ($E^o_{th}$ - $E^o_{cell}$) will be required to maintain a constant operating temperature.

## 3. Types of Water Electrolyzers

There are four types of water electrolyzers for large-scale hydrogen production are shown in Figure 5. These are alkaline water electrolyzer (AWE), proton exchange membrane water electrolyzer (PEMWE), anion exchange membrane water electrolyzer (AEMWE) and solid oxide water electrolyzer (SOWE)[31]. AWE uses an alkaline solution (usually potassium hydroxide) as the electrolyte. It has a long history and is a well-known technology, making it reliable for hydrogen production. PEMWE employs a solid polymer electrolyte membrane to separate the anode and cathode. This design allows for faster reaction rates, higher efficiency and greater flexibility in operation. It is known for its rapid start-up and shutdown capabilities, making it suitable for applications where dynamic response is essential. However, the catalyst for HER and OER should be platinum group metals and oxides. AEMWE is a cutting-edge electrochemical process that employs an anion exchange membrane as a solid electrolyte. Through the application of an electric current, water is split into hydrogen and oxygen. In AEMWE, the anion exchange membrane facilitates the migration of negatively charged ions (anions), allowing hydroxide ions ($OH^-$) to move from the cathode to the anode. At the cathode, these hydroxide ions react with water molecules to generate hydrogen gas, while oxygen gas is evolved at the anode. The key distinction of AEMWE lies in its use of the anion exchange membrane, which eliminates the need for corrosive acids typically used in traditional electrolysis. SOWE is a high-temperature electrochemical process that employs a solid oxide material as the electrolyte to conduct ions. This process occurs in a solid oxide electrolyzer cell consisting of an anode and a cathode separated by the solid oxide electrolyte material. At the cathode, oxygen ions are reduced to oxygen gas, while at the anode, water molecules are split into hydrogen ions and oxygen. The separated hydrogen ions can then combine to form hydrogen gas. The beauty of SOWE lies in its capacity to directly produce hydrogen from steam while efficiently separating oxygen, all with the added benefit of high conversion efficiency.

AWE and PEMWE are commercially available to produce large-scale green hydrogen production by renewable electricity. Catalysts are pivotal components of these electrolyzers, playing a crucial role in accelerating the electrochemical reactions that drive the conversion of water into hydrogen and oxygen gases. These catalysts are essential for making electrolysis more efficient, cost-effective and sustainable. Here, we delve into the world of catalysts in water electrolyzers, exploring their functions, types, significance and recent advancements.

## 3. Electrocatalyst Functions in Water Electrolyzers

Electrocatalysts in water electrolyzers lower the energy barrier required for splitting water molecules into hydrogen and oxygen gases. They facilitate the oxidation of water at the anode and the reduction of protons at the cathode. Essentially, catalysts enable the electrochemical reactions to occur significantly faster than they would without catalysis. This enhances the efficiency of the

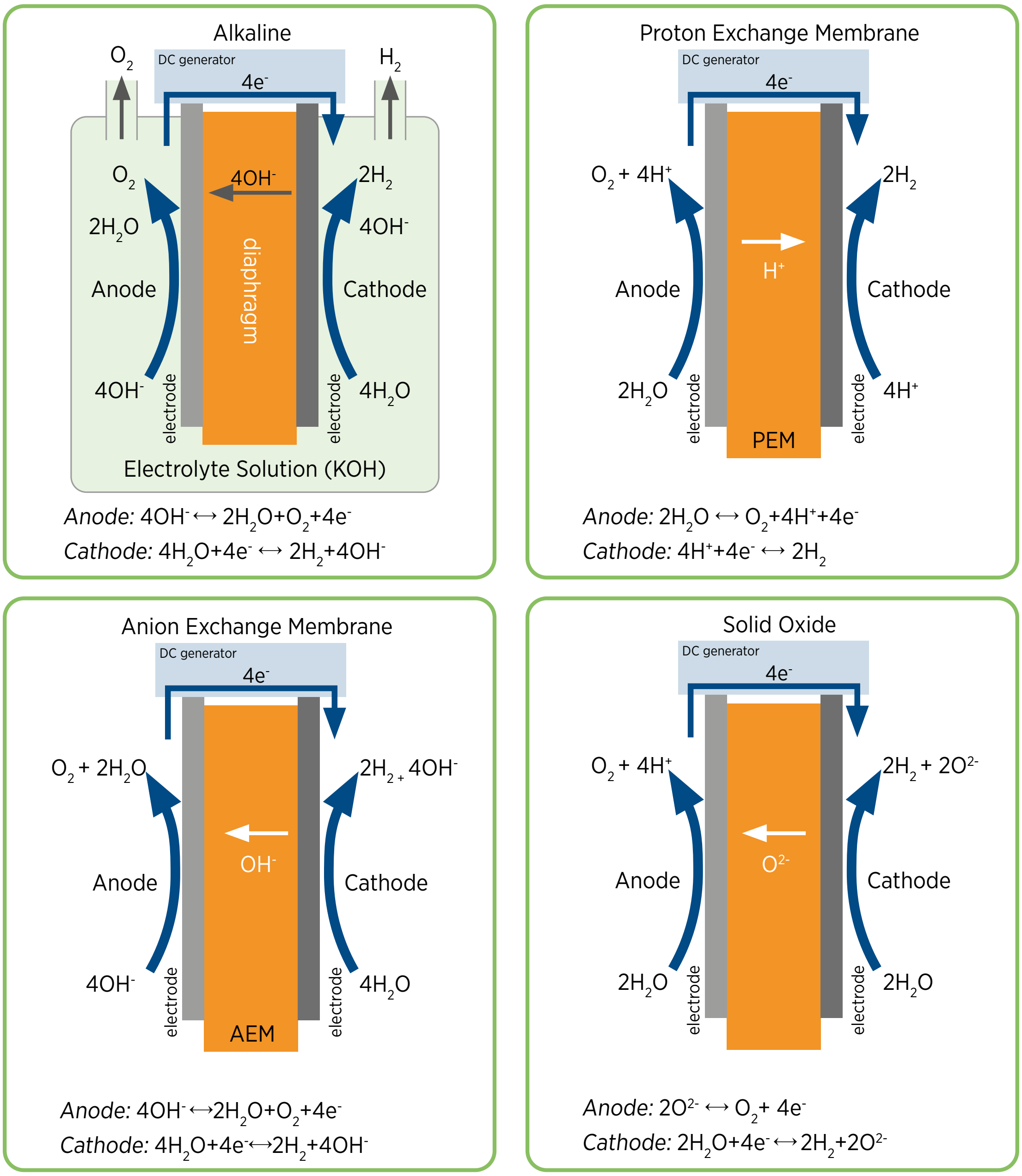

**Figure 5. Four types of water electrolyzer technologies. Source: IRENA (2020), Green Hydrogen Cost Reduction: Scaling up Electrolysers to Meet the 1.5⁰C Climate Goal, International Renewable Energy Agency** copyright (© IRENA).

electrolysis process and reduces the energy input required for hydrogen production.

### *OER Electrocatalyst*

The OER is known to be the major bottleneck in improving the overall efficiency of water electrolyzers[36]. To address this challenge, extensive research has been conducted to develop highly efficient OER catalysts that can reduce the kinetic limitations. Two main mechanisms have been proposed for the OER: the conventional adsorbate evolution mechanism and the lattice oxygen-mediated mechanism[37]. In the adsorbate evolution mechanism, the OER involves four concerted proton and electron transfer steps, producing oxygen molecules from water. The reaction pathway includes the adsorption of hydroxide anions on the metal active site, forming metal-hydroxide species, converting metal-hydroxide to metal-peroxide intermediates and releasing oxygen gas[37]. The adsorbate evolution mechanism has been extensively studied and provides valuable insights for the rational design of OER electrocatalysts.

On the other hand, the lattice oxygen-mediated mechanism suggests that lattice oxygen in the catalyst material directly participates in the OER. This mechanism is less understood compared to the adsorbate evolving mechanism but offers alternative pathways for the OER. Further research is needed to fully understand and exploit the potential of the lattice oxygen-mediated mechanism in catalyst design.

Noble-metal based electrocatalysts, such as ruthenium dioxide ($RuO_2$) and iridium dioxide ($IrO_2$), have long been considered the most efficient OER catalysts[38]. These catalysts exhibit excellent activity and stability, especially in acidic electrolytes. However, their high cost and limited availability hinder their widespread use. To address these challenges, researchers have focused on improving the performance of noble-metal based catalysts and exploring alternative materials. One approach to enhance the catalytic activity of noble-metal based catalysts is heteroatom doping. By introducing foreign atoms into the catalyst structure, the binding energies of reaction intermediates can be modified, leading to improved performance. For example, Cu-doped $RuO_2$ catalysts have been synthesized and exhibited enhanced OER activity. Incorporating copper into the $RuO^2$ lattice creates unsaturated Ru sites, reducing the OER overpotential[39]. Another strategy is alloying noble metals with other transition metals. Alloy catalysts have been shown to modify the catalyst's electronic structure and optimize the reaction intermediates' adsorption energy. For instance, IrM (M=Ni, Co, Fe) catalysts have been developed and IrNi catalysts have demonstrated superior OER activity compared to pure Ir or Ni catalysts. The alloying of Ir with Ni shifts the d-band center of Ir, leading to enhanced OER performance. Surface structure modifications, such as morphology control, have also been explored to improve the catalytic activity of noble-metal based catalysts. Hollow nanoparticles, nanocages, nanoshells and nanoframes have been synthesized and exhibited enhanced catalytic activity. For example, an Ir-based multimetallic double-layered nanoframe catalyst has been developed, which prevents particle coarsening and agglomeration, leading to improved OER performance.

Non-noble metal based electrocatalysts have received significant attention due to their abundance and lower cost compared to noble metals[22]. Among non-noble metal catalysts, earth-abundant oxide and (oxy)hydroxide catalysts, such as nickel-iron (Ni-Fe) based catalysts, have shown promising OER performance. These catalysts are widely employed in industrial-scale developments. Ni-Fe based oxide and (oxy)hydroxide catalysts exhibit excellent activity and stability in alkaline electrolytes[22]. Both Ni and Fe in the catalyst structure enhance the catalytic activity through synergistic effects. Various strategies, such as morphology control and surface modification, have been employed to improve the performance of Ni-Fe based catalysts[40].

### *HER Electrocatalyst*

While the OER is the major bottleneck in water electrolyzers, the HER also plays a crucial role in achieving high overall efficiency[41]. The HER involves reducing water to generate hydrogen gas at the cathode. Similar to the OER, efficient catalysts are required to overcome kinetic limitations and improve the performance of the HER. Platinum-based catalysts, such as Pt/C, have long been considered as the most efficient catalysts for the HER[40]. However, platinum's high cost and limited availability hinder their widespread use. To address these challenges, researchers have focused on developing alternative catalysts, including non-noble metal and hybrid catalysts[42].

Non-noble metal catalysts, such as molybdenum diselenide ($MoSe_2$), have shown promising HER activity. $MoSe_2$ exhibits a layered structure with excellent electrocatalytic properties. The incorporation of $MoSe^2$ into heterostructured catalysts has enhanced the HER performance. For example, LSC/K-$MoSe_2$ heterostructured catalysts have been synthesized and exhibit significantly higher HER activity than LSC or K-$MoSe_2$ alone[43].

Hybrid catalysts, combining noble and non-noble metals, have also shown excellent HER performance. These catalysts use the synergistic effects between different metals to enhance the catalytic activity[44,45]. For instance, AgPt alloyed nanocrystals have been synthesized and exhibited enhanced HER activity compared to pure Pt catalysts.

Researchers are continually seeking cost-effective and abundant catalysts, aiming to surpass the performance of platinum (Pt), the most widely used catalyst for HER[46]. While promising catalysts have been reported, their intrinsic activity needs to be more rigorously assessed and mass-transport limitations are frequently overlooked[47]. This article explores the significance of measuring intrinsic catalytic activities, the impact of mass-transport limitations on observed activity and the challenges faced in accurately determining the intrinsic activity of catalysts for HER.

To evaluate the true potential of catalysts for HER, it is essential to measure their intrinsic catalytic activities, specifically turnover frequencies (TOFs)[48]. While geometric current densities provide useful information from an applied perspective, they do not reflect the intrinsic catalytic activity that arises from tuning the electronic structure of the catalyst[49]. TOF represents the number of molecules produced per second per site and is the most relevant scientific metric for comparing intrinsic activity. However, many studies need to consider this metric and instead focus on geometric current densities. This oversight leads to inaccurate comparisons and conclusions about the performance of catalysts.

Mass-transport limitations can significantly influence the observed activity of catalysts for HER. Increasing the catalyst loading can reduce the overpotential required to reach a certain current density by increasing the number of active sites. However, this increase in geometric current density does not necessarily indicate improved intrinsic catalytic activity. In fact, as catalyst loading increases, the TOF decreases significantly. This reduction in TOF with higher loading indicates the prevalence of mass-transport limitations, where the observed current is entirely limited by the mass transport of hydrogen to or from the electrode surface. Consequently, the intrinsic activity of the catalyst does not affect the measured activity and the reported Tafel slope of 30 mV/dec for HER is simply the apparent Tafel slope of the diffusion overpotential. It is crucial to recognize and account for mass-transport limitations to assess the intrinsic activity of catalysts accurately.

Determining the true intrinsic activity of catalysts for HER is a challenging task due to the presence of mass-transport limitations. Mass-transport limitations persist even at ultra-low catalyst loadings, making it difficult to obtain an accurate measure of intrinsic activity. The reported activity at low loadings may represent a lower bound estimate than the true intrinsic activity. The combination of fast mass-transport techniques and ultra-low catalyst loading can help mitigate the influence of mass-transport effects. However, even measurements using fast mass-transport techniques may still be limited by mass transport, resulting in an underestimation of the intrinsic activity. Therefore, claims of developing catalysts that surpass the intrinsic activity of platinum should be supported by rigorous characterization and consideration of mass-transport limitations.

Despite efforts to find alternatives to platinum for HER, no earth-abundant catalyst material has demonstrated intrinsic activity comparable to platinum. Catalysts based on metal sulfides and phosphides have shown promising results and follow a volcano-like trend in terms of activity, with the highest activity observed when the hydrogen adsorption-free energy is close to zero[50]. However, their intrinsic activities are at least three orders of magnitude lower than platinum at room temperature. Achieving catalysts that can compete with platinum on intrinsic activity requires further exploration of kinetic barriers and coverage effects.

### *Hysteresis in Polarization Curves*

The presence of hysteresis in polarization curves of HER at ultra-low catalyst loadings can serve as an indicator of mass-transport limitations[51]. Hysteresis refers to the phenomenon where the activity

Unlocking the full potential of green hydrogen hinges on our ability to delve deep into the intricate world of electrochemical reactions within water electrolyzers and hydrogen fuel cells. These reactions are at the core of green hydrogen production and utilization, making it imperative to comprehensively understand their kinetics and mechanisms. Recent advancements in research have led to a more profound comprehension of these processes, shedding light on the catalysts used and the underlying mechanisms at play. This knowledge is proving instrumental in optimizing the performance of green hydrogen technologies, bringing us closer to harnessing its benefits on a broader scale.

One of the key areas of focus in recent research has been the development of advanced electrocatalysts. Catalysts are essential in speeding up the electrochemical reactions in green hydrogen production, making the process more efficient. Researchers are exploring novel materials and designs for catalysts that can operate effectively under various conditions, including high temperatures and pressures[52–56]. These breakthroughs in catalyst development not only enhance the efficiency of electrolysis but also contribute to reducing the energy input required, thereby lowering the cost of green hydrogen production.

Understanding the underlying mechanisms of electrochemical reactions is equally critical. By delving into the intricacies of these processes, scientists can identify bottlenecks and areas for improvement. This knowledge enables fine-tuning electrolysis and fuel cell systems, resulting in higher performance and increased reliability. As research advances in this field, optimizing green hydrogen technologies becomes increasingly achievable, paving the way for a cleaner, more sustainable energy future.

## 5. Developments, Sustainability and Future Directions in Electrocatalysts for Water Electrolyzer

Continuous research and development efforts are being made to overcome the challenges associated with electrocatalysts and improve their performance in water electrolysis. Scientists and engineers are exploring novel materials, nanostructured catalysts, catalyst designs and hybrid catalyst systems to enhance the electrocatalytic performance and stability of the catalysts. Furthermore, studies are being conducted to understand the fundamental principles governing the electrocatalytic activity and selectivity of different catalysts. Also, computational modeling and experimental techniques are used to gain deeper insights into the electrocatalytic mechanisms. This knowledge allows for the rational design and optimization of electrocatalysts, making them more efficient and cost-effective. Recent studies have shown promising results in improving the efficiency and durability of electrocatalysts, bringing us closer to realizing the full potential of water electrolysis for clean hydrogen production.

Electrocatalytic water electrolysis systems hold great promise in achieving sustainable clean energy. Hydrogen production becomes even more environmentally friendly by utilizing renewable energy sources and can contribute to reducing greenhouse gas emissions. Integrating electrocatalytic water electrolysis with renewable energy technologies ensures a carbon-neutral cycle, as the energy required for water electrolysis is derived from clean sources, significantly reducing greenhouse gas emissions. Furthermore, integrating water electrolysis with renewable energy sources, such as solar and wind power, can enhance the overall sustainability of clean energy systems by providing a continuous and reliable energy supply and significantly reducing the carbon footprint of hydrogen production. Hydrogen produced through water electrolysis can be used in various clean energy applications, such as fuel cells and energy storage, enabling the transition to a low-carbon economy. Additionally, the use of environmentally friendly electrocatalysts and the optimization of system efficiency contribute to the sustainability of the electrolysis process. Therefore, efforts are being made to develop sustainable and eco-friendly electrocatalysts using earth-abundant materials and green synthesis methods.

As we continue to explore the potential of electrocatalysis in clean energy technologies, the future holds exciting possibilities for improving water electrolysis technology. Researchers are focused on developing earth-abundant, cost-effective and environmentally friendly electrocatalysts with higher activity, stability and durability. Future directions for improving water electrolysis technology generally include catalyst design, materials engineering, electrode architecture, system integration and scale-up and commercialization. By addressing these key areas, researchers aim to make water electrolysis a viable and cost-effective method for clean hydrogen production on a large scale.

The commercialization of water electrolysis technologies is also a major goal for the future. The scalability and cost-effectiveness of these systems will determine their widespread adoption and integration into our clean energy infrastructure. Industrial-scale water electrolysis plants can provide a consistent and reliable source of hydrogen for various applications. Government support, investment in research and development and collaborations between academia and industry are crucial in driving the commercialization of water electrolysis technologies and making clean hydrogen a viable and accessible energy source. The advancements in electrocatalyst development and optimization will continue to play a pivotal role in making hydrogen a viable and environmentally friendly energy option.

## CONCLUSION

Studying electrocatalysts for water electrolysis is crucial for advancing renewable energy production. Accurately assessing the intrinsic activity of catalysts is essential but often needs to be noticed, leading to misleading comparisons and conclusions. Mass-transport limitations significantly impact the observed activity of catalysts, making it challenging to determine their true intrinsic activity. The search for alternatives to platinum continues, but no earth-abundant catalyst has demonstrated intrinsic activity comparable to platinum. Hysteresis in polarization curves can serve as an indicator of mass-transport limitations. Overcoming these challenges and accurately evaluating catalysts for HER and OER requires a comprehensive understanding of kinetic barriers, coverage effects and mass-transport phenomena.

Recent research on catalysts for water electrolyzers has focused on developing more efficient and affordable alternatives to precious metal catalysts. Scientists have made significant progress in discovering new materials with promising catalytic properties. For example, some studies have explored using earth-abundant materials like nickel, cobalt and iron as catalysts. Additionally, advancements in nanotechnology have enabled the design of catalysts with tailored structures and increased surface areas, further enhancing their performance.

The ongoing research and development of catalysts for water electrolyzers hold tremendous promise for the widespread adoption of green hydrogen as a clean energy carrier. Future prospects include the continued exploration of non-precious metal catalysts, integrating advanced materials and nanotechnologies and scaling up production processes to reduce costs. These endeavors are essential for driving the transition to a more sustainable and carbon-neutral energy future, where green hydrogen plays a pivotal role in decarbonizing various sectors of the economy.

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