Electrolysis: A Holistic Perspective on Methods and Applications in the Green Energy Transition

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Received November 11, 2024
Accepted March 27, 2025
Electronic access April 30, 2025

This paper presents an overarching view of the green energy transition, exploring electrolysis for fuel and chemical production, particularly water electrolysis, carbon dioxide reduction reactions (CO_2RR), and nitrogen reduction reactions (N_2RR). By connecting insights from both laboratory research and industrial applications, the study highlights the interconnectedness of these electrochemical processes. It examines atomic-scale reaction mechanisms to uncover the molecular interactions driving these processes while identifying challenges for scaling up. Key issues such as hydrogen evolution reaction (HER) selectivity and the role of gas diffusion electrodes (GDEs) in enhancing reaction kinetics and efficiency are explored through both experimental and theoretical approaches to address critical gaps in the existing literature that overlook how these mechanisms translate to real-world applications. The paper also evaluates these technologies' economic and environmental implications, emphasizing their importance in advancing sustainable energy solutions. By integrating technical and practical perspectives, this work provides a cohesive understanding of how water electrolysis, CO_2RR, and N_2RR can collectively accelerate the green energy transition, offering valuable insights for future research and industrial development.

Keywords: Green energy transition, Water electrolysis, CO_2 utilization, Ammonia, Gas diffusion electrodes, Scaling relations

The Green Hydrogen Transition and the Role of Electrolysis

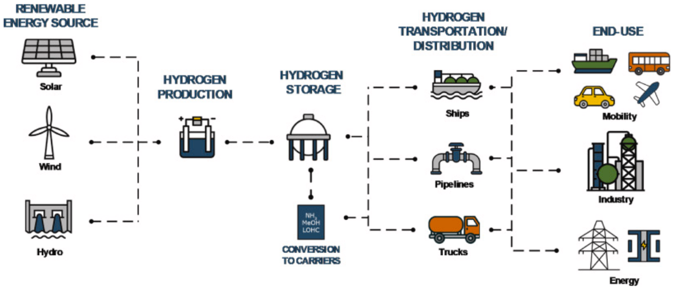
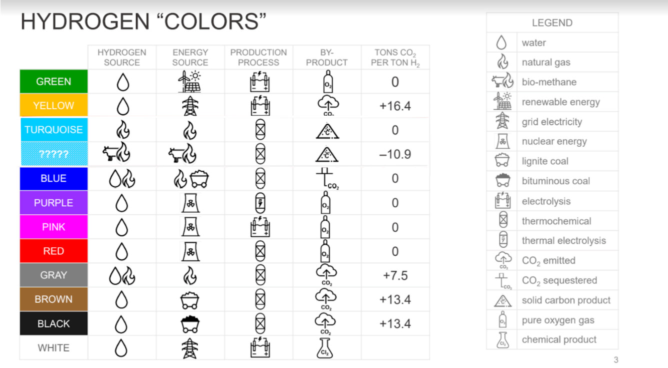


Fig. 1 : Graph that simplifies the process of industrialized hydrogen production through electrolysis. It includes the transportation methods and how the hydrogen would be utilized. Copyright Elsevier 2025 under a Creative Commons License

Due to the projected increase in energy demand, which is expected to reach 24 to 26 TW by 2040, carbon dioxide emissions are also anticipated to rise proportionally from 32 gigatonnes (Gt) per year in 2013 to as much as 44 Gt per year by 2040[1]. The heavy reliance on the combustion of fossil fuels calls for a greener alternative, with electrolysis as a promising alternative. However, economic and technical barriers prevent the adoption of the technology. Thus, its crucial to look over the theoretical and methodological perspectives in order to enhance further understanding of the mechanisms to ensure its scalability. Hydrogen has proven to be a key contributor toward achieving net-zero goals. In the future, a hydrogen-based economy is depicted in Figure one, which illustrates how hydrogen is used in various economic sectors, including transportation, industry, and energy. To mitigate global warming, hydrogen must be green (see all other possible colors ien Fig. 2); that is produced through renewable energy, and green hydrogen production includes utilizing water electrolysis as a baseline for sustainable technology. Electrolysis is a process that uses electrical power to drive a non-spontaneous chemical reaction, splitting molecules through redox reactions to store energy in the produced substances or for chemical synthesis. Its classified as an electrification method in the strategy to decarbonize industry, electrification being the process of replacing technologies or processes that use fossil fuels (like coal, oil, and natural gas) with those powered by renewable electricity, which enhances the environmental friendliness of electrolysis[2]. Thus, electrolysis has proven note-worthy when considering the green energy transition.

On a broader scale, the green energy transition is to develop a circular economy, which focuses on removing waste and pollution to restore nature and circulate and reuse material goods to their highest value[3]. It represents a major overhaul of energy systems, focusing on lowering carbon emissions, improving energy efficiency, and incorporating renewable energy sources into the grid. There are many methods to achieve renewable energy through different biotic and abiotic factors.

Electrolysis presents a cleaner alternative and supports a cir-



HYDROGEN “COLORS”

	HYDROGEN SOURCE	ENERGY SOURCE	PRODUCTION PROCESS	BY-PRODUCT	TONS CO_2 PER TON H_2
GREEN					0
YELLOW					+16.4
TURQUOISE					0
?????					–10.9
BLUE					0
PURPLE					0
PINK					0
RED					0
GRAY					+7.5
BROWN					+13.4
BLACK					+13.4
WHITE					

LEGEND
water
natural gas
bio-methane
renewable energy
grid electricity
nuclear energy
lignite coal
bituminous coal
electrolysis
thermochemical
thermal electrolysis
CO_2 emitted
CO_2 sequestered
solid carbon product
pure oxygen gas
chemical product

Fig. 2 Graph illustrating hydrogen colors based on production processes, raw materials, energy sources, and carbon footprint. Black and brown indicate high CO_2 emissions, while green represents sustainable methods. CO_2 values show emissions (+) or removal (-) per ton of H_2. Adapted from Von Keitz, 2021.

cular net loop when powered by renewable energy sources like wind and solar. While solar and wind panels generate electricity, electrolysis directly produces a versatile fuel, hydrogen, which can be stored and utilized in various applications, thus decreasing dependence on weather conditions. The energy demands of electrolysis highlight the importance of consistent renewable energy inputs, such as wind or solar, to ensure the process remains both sustainable and scalable in the long term. Given that water electrolyzers are essential for the operation of CO_2 reduction reactions (CO_2RR) and nitrogen reduction reactions (N_2RR), improving implementation of electrolyzers is a critical first step. The various methods of electrolysis, whether Proton Exchange Membrane (PEM), Anion Exchange Membrane (AEM), or Alkaline electrolysis, all require significant amounts of ultrapure waterapproximately 9 kilograms for every kilogram of hydrogen produced[4,5]. Thus, desalination technologies offer potential solutions by allowing selective passage of water while blocking salts and impurities. The electrolyte composition significantly affects ion mobility and electrostatic interactions, making optimization crucial for effective desalination. While direct seawater splitting (DSS) membranes enhance desalination efficiency, their high cost and energy demands, along with seawater impurities disrupting electrolysis and requiring agents for reaction balance, highlight the importance of balancing the electrolyte in CO_2RR and N_2RR, where water is essential for eco-friendly processes.

Overall, this paper investigates the critical role of water electrolysis, CO_2RR, and N_2RR in advancing the green energy transition. Examining the interconnected concepts and mechanisms underlying these electrochemical processes enhances the understanding of their collective impact on hydrogen economy. This approach aims to provide perspectives, highlighting the significance of an integrated understanding in developing effective sustainable energy technologies and accelerating the transition to a green economy.

Basic Mechanisms of Water Electrolysis

Water electrolysis is a process that involves an anode and a cathode submerged in an aqueous solution containing water and an ionic substance, which is essential for conducting electricity. Because it is nonspontaneous, electrolysis requires an external energy source to initiate the electrochemical reaction, meaning that the supplied voltage must exceed the standard equilibrium voltagethe theoretical minimum voltage needed to split water into hydrogen and oxygen under ideal conditions[6]. During this electrolysis process, intramolecular forces within water molecules are broken, leading to the generation of hydrogen gas at the cathode through the hydrogen evolution reaction (HER) and oxygen gas at the anode through the oxygen evolution reaction (OER). The half-reaction equations are as follows:

$$\text{HER:} \quad 2\mathrm{H}^+ + 2e^- \rightarrow \mathrm{H}_2$$

$$\text{OER:} \quad 2\mathrm{H}_2\mathrm{O} \rightarrow \mathrm{O}_2 + 4\mathrm{H}^+ + 4e^-$$

The HER occurs on the negatively charged cathode, where hydronium ions (H_3O), are preferentially reduced due to their charge. However, in neutral and alkaline electrolytes, the availability of protons is limited, leading to the reduction of water molecules instead. The HER typically involves two proton-coupled electron transfer (PCET) steps and a single key intermediate, the adsorbed hydrogen, which is the transient species that forms during the reaction.

In contrast, the OER exhibits distinct characteristics based on the solution’s pH. OER requires a higher overpotential but becomes easier in alkaline solutions, where it doesnt need as high an overpotential due to more favorable reaction kineticsspecifically, the increased availability of hydroxide ions (OH^-), which enhance electron and proton transfer. In contrast, HER is easier in acidic media than in alkaline media because the higher concentration of protons (H^+) in acidic environments facilitates the reaction more efficiently[6]. Specifically, under acidic conditions, two water molecules are converted into four protons (H^+) and one oxygen molecule, while in alkaline media, hydroxide ions are oxidized to produce water. This direct oxidation of hydroxide ions is often favored due to the attractive interactions between anions and positive ions compared to neutral water molecules[6].

Conversely, the reverse reactions of hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) they facilitate the conversion of chemical energy into electrical energy. In this context, the ORR occurs at the cathode, reducing oxygen to form water, while the HOR happens at the anode, oxidizing hydrogen to produce protons and electrons[6].

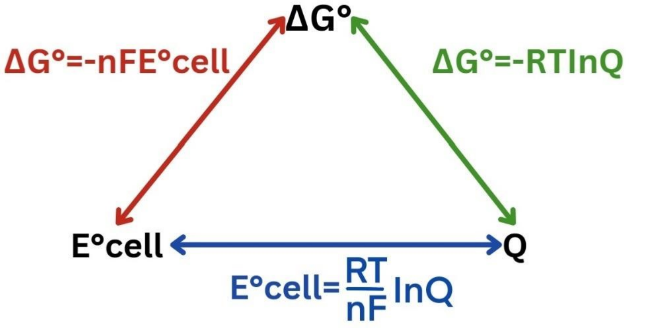


Fig. 3 The various equations used to calculate different variables, with a primary focus on Gibbs free energy (ΔG) and cell potential (Ecell). In these equations (all different variants of the same concept), F represents Faraday's constant, n is the number of electrons transferred per H_2 molecule, R is the gas constant, T is the temperature in Kelvin, and Q is the reaction quotient.

The relationship between the energy produced in a hydrogen fuel cell and the energy required for electrolysis is significant. The maximum terminal voltage of a hydrogen fuel cell, around 1.23 V under standard conditions[6], corresponds to the energy produced when hydrogen and oxygen recombine to form water, which is also the minimum voltage needed for electrolysis. This is closely tied to Gibbs free energy, illustrated in Figure 3, as $G = -nFE$ relates the free energy change to the cell potential. The Gibbs free energy determines whether a reaction occurs spontaneously, with a negative value indicating spontaneity and a positive value requiring external energy, thus determining the thermodynamic feasibility of the reaction.

The reaction quotient Q reflects the ratio of product and reactant concentrations at any point, influencing the cell's voltage and direction. When Q deviates from the equilibrium constant K, the Gibbs free energy (ΔG) shifts, with G becoming negative if $Q < K$ (favoring the forward reaction) and positive if $Q > K$ (favoring the reverse reaction), thus affecting the reaction's spontaneity.

Major Drawbacks in Electrolysis

In an electrochemical process, generally electrolysis, the reaction is controlled by how fast electrons move at the electrode, more electrons moving to the electrode leads to a higher charge which means more thermodynamic activity. Furthermore, the efficiency with which reactants and products move to and from the electrode, formally known as mass transport[1] relates to how many reactants are able to undergo chemical reactions, leading to more products. Mass transport can be understood by three factors, migration, convection, and diffusion[7]. Migration being responses to electrostatic fields in the electrolyte, ions move towards their opposite charge naturally. Convection is the mechanical movement of a solution to reduce the buildup of concentration gradients.

Diffusion includes a concentration gradient when reactants move to electrode surfaces with a lower concentration, diffusing throughout the solution. Furthermore, the series resistance also plays a major role[1]. As ions move through the electrolyte, they encounter resistance, which is the opposition to the flow of electric current. This resistance leads to ohmic losses, or voltage drops due to the energy required to push ions through the electrolyte. These losses are a key part of the series resistance, reducing the efficiency of the electrochemical process by necessitating higher applied voltage to maintain the desired current. However, increasing the current leads to alternate obstacles. The higher the current going through the electrolyte, the more bubbles form on the surface of the electrodes. Bubbles lead to voltage loss and poor ion transfer. On either hand, bubbles that are on the catalyst surface reduce effectiveness since they block the active sites necessary for the electrochemical reactions, and bubbles in the solution increase resistance to ion movement[8].

Understanding Catalytic Efficiency: The Volcano Plot in Electrolysis

Moreover, catalysts play a crucial role in reducing activation barriers in electrochemical reactions like OER and HER, where improved electrocatalysts can lower these barriers and enhance reaction efficiency. The activation energy shows the energy required to initiate a reaction, and a good catalyst reduces this energy by providing an optimal surface for reactions. Volcano plots, which graph catalytic activity against properties like binding energy, as shown in Figure 4 (for HER), illustrate that catalytic performance peaks at an optimal pointhighlighting the need for a balance in catalyst properties to achieve maximum efficiency. When there is a peak, it depicts the optimal range of binding energy for maximum efficiency.

Binding energy refers to the strength of interaction between an intermediate or reactant to a catalyst surface. It influences how strongly a substance adheres to the catalyst, impacting the efficiency of catalytic reactions[9]. In the context of catalysis, an optimal binding energy ensures that reactants are neither too weakly nor too strongly bound.

CO_2 Reduction Reactions and Nitrogen Reduction Reactions: A Comparative Analysis

Both carbon dioxide reduction reactions (CO_2RR) and nitrogen reduction reactions (N_2RR) are pivotal electrochemical processes that offer sustainable pathways for producing valuable chemicals while addressing pressing environmental challenges. The direct electrochemical reduction of CO_2, coupled with the sustainable generation of hydrogen from water electrolysis, approaches the net-zero production of various hydro-

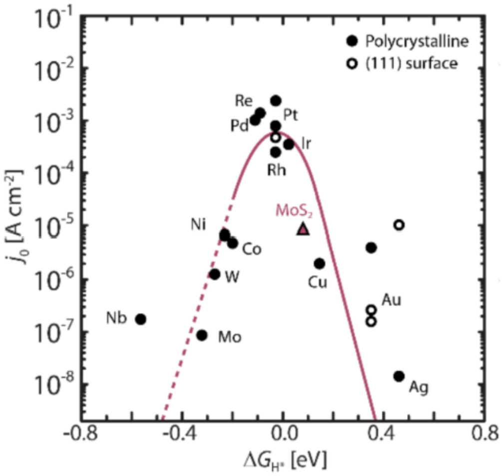


Fig. 4 The graph illustrates the relationship between catalyst efficiency and reaction energy (ΔG_H) for the hydrogen evolution reaction (HER). The x-axis (ΔG_H) represents hydrogen adsorption energy, while the y-axis (j_0) measures intrinsic catalyst activity. A 'volcano' trend appears, with peak catalysts achieving optimal efficiency. A similar pattern occurs in oxygen evolution reactions (OER), where iridium oxide is positioned near the peak. Copyright Royal Society of Chemistry 2022 under a Creative Commons License

carbons, methane, and multi-carbon[10], effectively closing the carbon cycle while using renewable energy sources as described in Figure 5. Moreover, Table 1 shows the equilibrium potential of such products of CO_2RR, together with the number of proton-electron pairs needed to produce 1 mol of the listed products. Most products fall within a close range of equilibrium potential, indicating the difficulty of selectively targeting the production of a specific product. The number of proton-electron pairs indicates how energy-intensive the production of a given product is because each pair contributes to the reduction of CO_2 into a specific product. More pairs required for a reaction means more energy is needed to transfer those electrons and protons to the reactant. For example, the production of CO or formic acid requires - in principle - a quarter of the energy input needed to produce methane or acetic acid. Given the challenges in the scale up of renewable energy production, storage, and transmission, low-electricity-intensity products should receive a priority in industrialization. Thus, CO (which is bolded) proves to be especially attractive as it is a platform chemical and an important intermediate in many, well-established industrial chemical processes. In contrast, N_2RR focuses on converting atmospheric nitrogen (N_2) into ammonia (NH_3) using protons and electrons, presenting a sustainable alternative to the energy-intensive Haber-Bosch process[1]. These notably leverage renewable energy sources and water as essential components, facilitating the generation of electrons and protons needed for the reduction processes.

Table 1 The table lists the different outcomes of CO_2RR along with the Eo going along the different electrochemical reactions. The right-hand column depicts water electrolysis as well as CO_2RR for different value-added products. The similarity of the Eo illustrates the selectivity problem, meaning it is difficult to differentiate the possible products; the right-hand column involves the energy/electricity intensity, thus depicting the favorability of industrial scale-up (being that CO is a clear favorite for industrial CO_2RR).

Products	**Cell potential (V vs RHE)**	$H^+ + e^-$ **Ions Needed**
Carbon monoxide (CO)	**-0.1**	**2**
Formic acid (HCOOH)	-0.12	2
Methane (CH_4)	0.17	8
Methanol (CH_3OH)	0.03	6
Acetic acid (CH_3COOH)	0.11	8
Ethanol (C_2H_5OH)	0.09	12
Ethane: C_2H_6	0.14	14

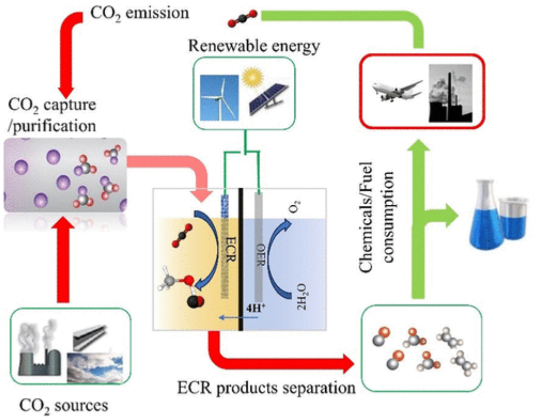


Fig. 5 Illustration simplifying the processes of producing value-added products from CO_2 in the atmosphere or emissions as a reactant, using renewable energy (solar panels and wind turbines) to conduct electrochemical CO_2 reduction (eCO_2RR). Copyright American Chemical Society 2024 under a Creative Commons License

- **Reaction Mechanisms: $CO_2$and N_2Pathways**
  The mechanisms underlying CO_2RR and N_2RR are distinct yet interconnected. CO_2RR primarily involves the generation of carbon monoxide (CO) as a critical intermediate, whose binding strength to the catalyst surface significantly influences further reductions to hydrocarbons and alcohols. Conversely, N_2RR can follow associative or dissociative pathways, depending on the catalyst. In the associative mechanism, molecular nitrogen is hydrogenated, weakening its bonds en route to N-N bond dissociation, while the dissociative pathway cleaves nitrogen first, leading to intermediates that can be subsequently hydrogenated[11].

  The competition for catalyst active sites is pronounced in both processes, with CO and NH_2 acting as crucial intermediates that must bind to the catalyst with optimal strength. Inadequate binding can lead to stalled reactions or premature desorption, ultimately hindering product formation [10,12]. Thus, the design and optimization of catalysts remain paramount for enhancing the selectivity and efficiency of both CO_2RR and N_2RR.

- **Obstacles in Industrial Application of CO_2RR and N_2RR: The Selectivity Challenge Against Hydrogen Evolution**
  A significant challenge in both CO_2RR and N_2RR is the selectivity towards the desired products amidst competing reactions, particularly hydrogen evolution reactions (HER). The mechanisms governing HER, complicate the overall reaction dynamics [13]. When protons and electrons are abundant, hydrogen evolution tends to dominate, inhibiting the desired product formation. In the context of N_2RR, the selectivity for ammonia synthesis can be hindered by the presence of protons, as the kinetics of HER become favored under high proton concentrations. To enhance selectivity in electrochemical reactions, it is essential to maintain adequate control over the delivery rate of protons or electrons. While improved control over proton supply increases selectivity for both processes, it also results in a reduced overall reaction rate. Another method to improve selectivity against HER is through organic solvents, particularly aprotic solvents, as they create environments that involve a surrounding medium that lacks protons (hydrogen ions) available for donation, thus suppressing proton-driven reactions, thereby enhancing selectivity in reduction reactions [14]. Additionally, incorporating an insulator or photoabsorber can selectively generate electrons by ensuring they are produced only when specific wavelengths of light are absorbed, further enhancing the efficiency of these processes. The methods mentioned are effectively illustrated in Figure 6.

  To mitigate these challenges, inhibiting proton transfer and reducing HER activity through the strategies allow for a more favorable environment for the subsequent reduction [13]. A delicate balance is required in both CO_2RR and N_2RR processes to ensure efficient product formation while minimizing undesired side reactions.

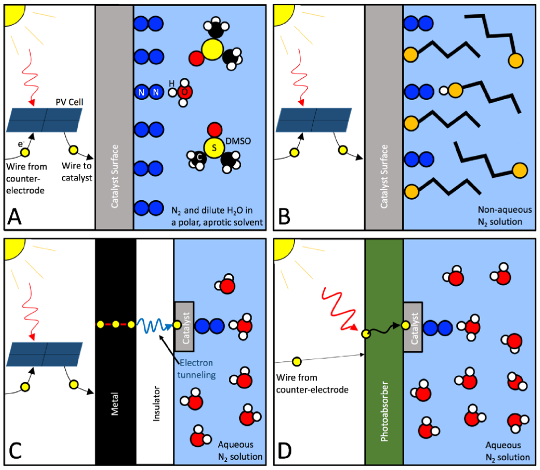


Fig. 6 Depicting the selectivity challenge in N_2RR (applicable to CO_2RR), A and B demonstrate the control of H supply via the use of aprotic solvents, which suppress proton-driven reactions. In contrast, C illustrates the availability of infinite electrons, while D highlights the use of a photo-absorbent to drive the reaction. Reprinted with permission from Singh et al. (2017). Copyright 2017 American Chemical Society.

The Role of Gas Diffusion Electrodes in CO_2 and N_2 Reduction Reactions

The solubility of the reactants plays a crucial role in the efficiency of both CO_2RR and N_2RR. According to Henrys Law, the concentration of dissolved gases like CO_2or N_2 can be enhanced by lowering temperatures or increasing pressures, which facilitates their dissolution in the electrolyte [12]. Increasing pressure not only enhances gas solubility but also shifts the equilibrium toward product formation, promoting the conversion of CO_2 to hydrocarbons and $N_2$to ammonia. However, it is essential to note that while higher temperatures can improve kinetics in CO_2RR, they can also lead to the decomposition of ammonia in N_2RR, thus complicating reaction dynamics [12]. This highlights the necessity of carefully optimizing reaction conditions to favor the desired pathways while maintaining high efficiency in both systems.

Due to the gaseous nature of these reactants and their implications for electrochemical reactions, gas diffusion electrodes (GDEs) are critical for enhancing the efficiency of both carbon dioxide reduction reactions (CO_2RR) and nitrogen reduction reactions (N_2RR). The gas diffusion electrode (GDE) is a physical structure, which is shown in Figure 7, that facilitates electrochemical reactions, while the gas diffusion layer (GDL) serves as a medium for gas diffusion into the liquid coating the solid catalyst. GDEs boost catalytic activity and lower cell potentials by keeping high concentrations of reactants (CO_2/N_2) close to the catalyst. Their porous, multi-layered structure allows for efficient gas transport, enabling optimal interaction with the catalyst [15,16]. Key components include a gas diffusion layer made of carbon fibers, which provides pathways for gas diffusion, and a catalyst layer where electrochemical reactions occur. To ensure good electrical contact and minimize resistance, a conductive tape is wrapped around the entire electrode, facilitating easy electron flow to the catalyst, especially at high currents. This design increases the electrochemically active surface area, granting better access to CO_2due to shorter diffusion pathways compared to H-cell systems.

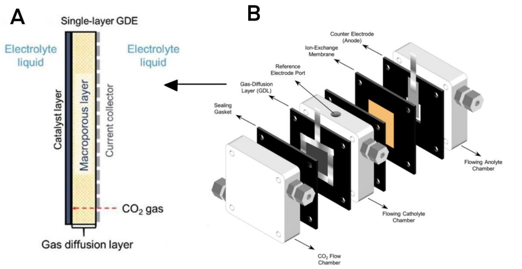


Fig. 7 (A) The gas diffusion layer zoomed in from the apparatus. (B) The structural components of the Gas Diffusion Electrode (GDE) within a three-cell electrode configuration designed for CO_2 reduction. It highlights the arrangement of the components. Adapted from Kamat & Christopher, 2022.

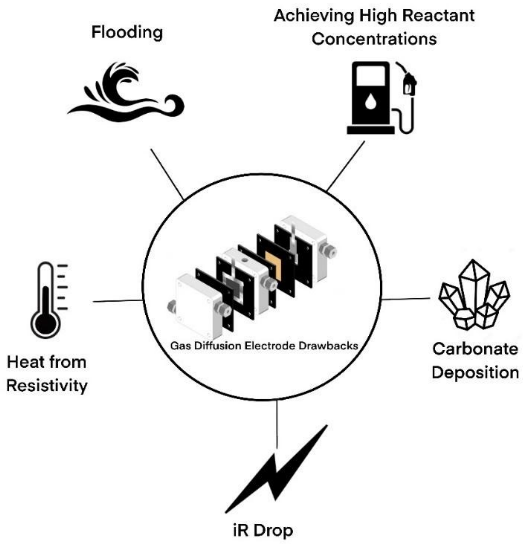


Fig. 8 Illustration that depicts the industry's common gas diffusion electrode drawbacks. The GDE apparatus illustration is taken from Kamat & Christopher, 2022

- **Gas Diffusion Electrodes in Industry: Considerations for Improved Performance**

  It has been proven that gas diffusion electrodes play a crucial role in industries with significant potential for reduction reactions in climate change mitigation. However, their applications face challenges (shown in Figure 8) that, if addressed, could enhance their efficiency and expand their utility across various sectors, improving their value in electrochemical engineering.

One of the most pressing challenges in electrochemical reduction reactions is the deposition of carbonates, which block electrode pores, reduce reactivity, and hinder mass transport[15]. Coupled with the accumulation of impurities on catalyst surfaces, these issues diminish activity and complicate performance assessment, particularly at the highly negative potentials required for effective operation[16]. These interferences point to a fundamental problem in system durability and reactivity. To combat this, potential cycling, a self-cleaning mechanism, has been proposed as a dynamic way to reverse electrochemical reactions, clearing carbonate deposits and restoring reaction efficiency which addresses the immediate challenges of maintaining clean surfaces but also suggests an avenue for more adaptive systems that self-regulate, enhancing long-term operational stability. In hindsight, the core of this issue connects to how efficiently reactants reach the electrode interface. Traditional calibration methods, relying on low-concentration data, fall short under gas diffusion electrode (GDE) conditions, where high reactant concentrations are key to maintaining reaction rates and yields[15]. Calibrating gas chromatography (GC) instruments to better reflect these high-concentration environments ensures a more accurate understanding of catalyst behavior. This adjustment moves beyond fine-tuning experimental setups and towards replicating real-world conditions where commercial scalability depends on precise data, especially under the high-stress environments in which GDEs typically operate.

As current densities increase in these systems, another interconnected challenge emerges: the interplay between resistivity, heat generation, and system stability. High resistivity in GDLs causes significant ohmic drops across the catalyst layer, which in turn leads to uneven local reactions and inefficiencies in current collection[15]. This resistivity isn't just an abstract problem since it's directly linked to heat buildup within the electrochemical cell. At elevated current densities, the unwanted heat can become substantial, further impacting performance and potentially compromising safety. Ohmic heating becomes a major contributor to cell potential, especially as larger charges pass through the electrolyte in two-electrode setups. Without effective cooling systems and high-volume electrolyte circulation, this heat can lead to runaway temperatures that threaten both efficiency and the structural integrity of the system.

Thus, addressing one aspectresistivityhas a cascading effect. Implementing real-time electrochemical impedance spectroscopy (EIS) for continuous monitoring of ohmic drops allows for precise adjustments in cathodic conditions, improving both reactivity and temperature management. This dual solution not only ensures the system runs at peak efficiency but also extends its operational limits, making higher current densities achievable without sacrificing control or safety.

Flooding, while a separate operational issue, ties into this overall picture of system management. Maintaining a stable gas-liquid interface is critical for gas reduction reactions, and slight pressure imbalances between gas and liquid phases can lead to flooding, disrupting the reactant flow to the catalyst layer. By regulating pressures and integrating automated control systems, it's possible to prevent these disruptions. However, just like with resistivity and heat, managing flooding is not just about preventing a single issueits about creating a balanced, self-regulating system where pressure, reactant concentration, and thermal conditions all align to optimize performance.

Electrochemical Challenges: The Interconnectedness of Electrolysis

Water electrolysis, along with CO_2RR and N_2RR, faces economic and scientific challenges that impact overall performance. The movement of electrons at the electrode is crucial, as it directly influences the energy required for reactions across all three processes[1,17]. Efficient transport of reactants to the electrode surface and timely removal of products is vital; this ensures that reactants are replenished, and product formation is optimized, preventing the development of a diffusion layer that can hinder reactant access and slow down reactions. A key aspect of these processes is system resistance, particularly concerning the movement of ions through the electrolyte. High resistance can impede ion flow, reducing reaction efficiency for water electrolysis, CO_2RR, and N_2RR, and requiring more energy to drive these processes. This resistance comprises several factors, including the conductivity of the electrode material, surface quality, and ion transport resistance, which is influenced by ion concentration and the distance ions must travel. Thus, high resistance in any of these areas can ultimately impact the performance of the electrochemical system[7,17]. At the molecular level, this study examines how key catalytic properties, such as binding energy and intermediate stability, dictate reaction efficiency across all three processes. Furthermore, the role of GDEs has also proven to be central, as their multi-layered structure improves mass transport efficiency by maintaining high local reactant concentrations. This enhancement is critical in CO_2RR, where carbonate deposition and flooding can reduce catalytic effectiveness, and in N_2RR, where nitrogen solubility presents a fundamental challenge to achieving high reaction rates. A key takeaway is that the energy demands of electrolysis require stable and intermittent energy supply strategies, while the efficiency of CO_2RR and N_2RR depends on proper electrolyte balance and gas-phase reaction control.

Challenges in Hydrogen Production via Electrolysis: Addressing Supply Chain Bottlenecks

Despite its promise, large-scale electrolysis remains hindered by both technical and economic barriers. Capital and operational expenditures (CAPEX and OPEX) for electrolyzer systems, particularly those utilizing platinum-group metals like iridium, present a significant cost challenge, with iridium demand projected to exceed global supply by 2040[12]. While alkaline water electrolysis is considered the most mature and durable technology for large-scale hydrogen production, the costs remain high, with investment costs ranging from \$800 to \$1500 per kilowatt[5]. Hydrogen production via electrolysis is further constrained by electricity prices, requiring integration with low-cost renewable energy sources to remain competitive. Current estimates place electrolytic hydrogen production costs at three to six dollars per kilogram, with ongoing reductions in renewable energy costs expected to drive these figures lower[12].

CO_2RR and N_2RR face similar economic challenges, with Faradaic efficiency and catalyst stability dictating their industrial feasibility. In CO_2RR, the need for selective product formation and mitigation of competing HER presents a major obstacle[18]. Industrial-scale carbon capture and storage projects remain limited, with only 18 large-scale operations worldwide, separating about 40 megatonnes of CO annually, which accounts for less than 0.1 percent of global emissions[10]. Meanwhile, N_2RR must overcome the energy-intensive activation of nitrogen triple bonds, making it difficult to compete with the Haber-Bosch process unless electrocatalytic efficiency and energy requirements improve[12]. Current studies suggest that electrochemical ammonia synthesis, while promising, is still significantly impacted by high electricity costs, with estimated production costs of approximately 776 dollars per metric ton, only slightly higher than traditional ammonia production methods at 560 dollars per metric ton[12].

Discussion

To shape the future of electrochemical systems across both established and emerging industries, it is essential to evaluate various factors that optimize these systems, with critical takeaways being listed in Table 2. Understanding transport phenomena and maintaining effective current and potential distribution are crucial for consistent performance, especially as cell designs evolve with new technologies. Thus, a combined approach can mitigate some of the individual drawbacks associated with different electrochemical reactions. For example, lessons learned in scaling up CO_2RR can be applied to improve technology readiness for nitrogen N_2RR, as both face similar technological and chemical challenges. Key considerations should also include economic and geographical aspects, such as placing electrolyzers near renewable energy sources and sourcing raw materials sustainably. Assessing the lifecycle of processes, including energy consumption and waste management, is essential for minimizing environmental impact and ensuring resource efficiency. This holistic perspective could foster the development of innovative electrochemical systems that maximize the utility of renewable resources while minimizing waste and energy consumption.

Table 2 A comprehensive summary of the fundamental concepts and mechanisms underlying electrocatalytic technologies, highlighting their major drawbacks and challenges. Additionally, it outlines potential approaches and innovative strategies for advancing the implementation of these technologies, paving the way for enhanced efficiency and broader adoption in various applications.

Electrochemical Processes	Reactions Mechanism	Drawbacks	Approaches
Water Electrolysis	• OER: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	• Kinetics and thermodynamics limit overall efficiency	• Nanostructured MoS_2 catalysts to enhance surface area and active sites
	• HER/HOR: $2H^+ + 2e^- \rightarrow H_2$	• Geographical (e.g., water sources) and economic considerations for industrialization	• Improves overall catalytic efficiency
CO_2 Reduction Reaction (CO_2RR)	• $CO_2 + 2H_2O + 2e^- \rightarrow CO + 2OH^-$	• Selectivity for products (CO, HCOOH, etc.) are hindered by similar E^0	• Gas diffusion electrodes (GDEs)
	• Product dependent on specific reaction conditions	• HER could dominate the overall reaction, posing a selectivity challenge.	• Considerations include EIS, passive cooling, and use of aprotic solvents and photoabsorbers
N_2 Reduction Reaction (N_2RR)	• $N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$	• Energy intensive due to strong N_2 triple bonds which requires many proton-electron pairs.	• Considering similarity to, utilize GDEs
	• Dissociative Mechanism: $N_2 + 2H^+ + 2e^- \rightarrow 2NH^*$	• HER could dominate the overall reaction, posing a selectivity challenge.	
	• Associative Mechanism: $N_2 + 3H_2 \rightarrow 2NH_3$		

Methods

In this study, resources were utilized from the American Chemical Society (ACS), Google Scholar, and ScienceDirect to conduct a comprehensive review of existing electrochemical concepts, establishing a foundation for advanced fundamental principles. Emphasizing modern perspectives, the research focused on literature published from 2012 onward, ensuring the incorporation of recent advancements and methodologies. The investigation progressed systematically from foundational literature to an examination of experimental studies, which were subsequently linked to economic evaluations. Throughout this process, relevant articles were critically analyzed to identify gaps in the current knowledge and potential areas for further exploration (with key fundamental concepts, such as the electrochemical double layer, Tafel slope, cyclic voltammetry (CV) graphs, diffusion layer, and DFT (density functional theory) scaling relations, explored implicitly but not explicitly mentioned in the text). Proper citations were provided for all figures and tables, ensuring academic integrity, while original figures and tables were developed and adapted to enhance clarity and facilitate understanding. Additionally, a thorough synthesis of the findings was conducted to integrate theoretical insights with practical applications, ultimately contributing to a holistic understanding of the subject matter.

Acknowledgments

This paper represents the individual work of the author. However, I would also like to express my gratitude to Dr. Ahmed Elnabawy (Cairo University, Giza, Egypt) for his guidance and invaluable support throughout the research and writing process. Through discussions and teachings provided, complex concepts were simplified and further developed, with various recommen-

dations and opinions taken into consideration.

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