

Revolutionizing green hydrogen production: the impact of ultrasonic fields

Revolucionando a produção de hidrogênio verde: o impacto dos campos ultrassônicos

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ABSTRACT

This paper reviews the use of ultrasonic fields in alkaline electrolysis for green hydrogen production, indicating the benefits and challenges of this emerging technology. Applying ultrasound can significantly increase electrolysis efficiency by reducing overpotentials and optimizing mass transfer. Quantitative data in Table 1 show that integrating ultrasound can reduce ohmic resistance by up to 76% and increase hydrogen production efficiency by up to 28%. For instance, under optimized conditions, hydrogen production can be increased by 45%, with energy savings ranging from 10 to 25%. The review examines the impact of ultrasound on removing gas bubbles from electrode surfaces and evaluates the use of ultrasonic transducers in different experimental setups. The effectiveness of ultrasound at specific frequencies (20–100kHz) and adjustable intensities (10–1000W/cm²) is discussed in terms of improving mass transfer and reducing ohmic resistance. Despite the benefits, technical challenges such as selecting appropriate materials and precisely controlling operating conditions are highlighted. The paper suggests that future research should focus on integrating ultrasonic technologies into renewable energy systems, combining ultrasound with advanced techniques to optimize hydrogen electrolysis sustainably and cost-effectively.

Keywords: water electrolysis; ultrasonic waves; polarization; energy efficiency; environmental sustainability.

RESUMO

Este artigo revisa a utilização de campos ultrassônicos na eletrólise alcalina para produção de hidrogênio verde, destacando benefícios e desafios dessa tecnologia emergente. A aplicação de ultrassom pode aumentar significativamente a eficiência da eletrólise, reduzindo sobretensões e otimizando a transferência de massa. Dados quantitativos da Tabela 1 mostram que a integração de ultrassom pode reduzir a resistência ôhmica em até 76% e aumentar a eficiência de produção de hidrogênio em até 28%. Por exemplo, em condições otimizadas, a produção de hidrogênio pode ser aumentada em 45%, com uma economia de energia variando de 10 a 25%. A revisão examina o impacto do ultrassom na remoção de bolhas de gás das superfícies dos eletrodos e avalia o uso de transdutores ultrassônicos em diferentes configurações experimentais. A eficácia do ultrassom em frequências específicas (20–100kHz) e intensidades ajustáveis (10–1000W/cm²) é discutida em termos de melhoria da transferência de massa e redução da resistência ôhmica. Apesar dos benefícios, desafios técnicos como a seleção de materiais resistentes e o controle preciso das condições de operação são destacados. O artigo sugere que futuras pesquisas devem focar na integração de tecnologias ultrassônicas em sistemas de energia renovável, combinando ultrassom com técnicas avançadas para otimizar a eletrólise de hidrogênio de forma sustentável e econômica.

Palavras-chave: eletrólise da água; ondas ultrassônicas; polarização; eficiência energética; sustentabilidade ambiental.

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Introduction

Hydrogen production via water electrolysis is a strategic approach to generate clean and sustainable energy. This electrochemical process, which decomposes water into hydrogen and oxygen, has been recognized not only as an alternative to reduce carbon dioxide (CO₂) emissions but also as a crucial energy vector to replace fossil fuels (Islam et al., 2019; Sazali, 2020). Hydrogen production, when powered by renewable energy sources, offers a promising path toward a global energy transition, indicating a significant shift from fossil fuel dependence to a hydrogen-based matrix (Kumar and Himabindu, 2019).

Green hydrogen production is becoming increasingly important in the current scenario, where the need to transition to clean and renewable energy sources has become a global priority (Ayar and Akin, 2023). This molecule, due to its energy efficiency and low environmental impact as an energy source, is relevant to mitigating climate change and transitioning to a sustainable energy matrix. Green hydrogen, produced through the electrolysis of water, can be used as fuel in fuel cells to produce electrical energy or heat (Marouani et al., 2023) without harmful emissions, presenting a promising alternative to fossil fuels and playing a vital role in the transition to clean energy systems and the decarbonization of several industrial and transport sectors (Kumar and Lim, 2022).

In this context, the present literature review aimed to deepen our understanding of the production of green hydrogen through water electrolysis, focusing mainly on a recent and promising innovation: the action of an ultrasonic field on water electrolysis. This technology, which involves the interaction of electrodes and electrolytes with ultrasonic waves, has been shown to have a remarkable potential to optimize the efficiency of water electrolysis, overcoming some of the challenges associated with this process (Darband et al., 2019; Ehrnst et al., 2023).

The methodology employed in this work combines a detailed literature review with a comparative analysis of different experimental setups. The examined experimental arrangements employ ultrasonic technology for hydrogen production, focusing on how different configurations may influence experimental results. Furthermore, operational parameters such as acoustic intensity, frequency, and temperature are analyzed and identified as significant determinants of hydrogen production and efficiency. Comparing these configurations reveals differences in critical parameters and illustrates how manipulating these parameters can optimize the hydrogen production process (Darband et al., 2019; Ehrnst et al., 2023).

Several studies have explored how the implementation of ultrasonic fields can influence critical factors in the electrolysis process, such as the increase in the amount of hydrogen produced, reduction in energy consumption, improvements in current density, decrease in overpotential, and drop in ohmic voltage, which is the difference between the applied potential and the real potential necessary to initiate an electrochemical reaction, increasing the surface contact and the efficiency

of the process (Sharifishourabi et al., 2024). Such studies also indicate the relevance of cavitation effects and mass transfer optimization, significantly contributing to the process efficiency and economic viability (Vincent et al., 2018; Darband et al., 2019; Burton et al., 2021).

Therefore, as we aim for a low-carbon future, continued innovation and development in hydrogen production technologies, especially those employing ultrasound, are essential to expand capabilities, reduce costs, and promote the adoption of hydrogen-based solutions as a reference for a sustainable energy matrix.

Methodology

A systematic process involving several steps was employed to ensure a comprehensive selection of studies for the literature review (Cooper et al., 2018). Precise criteria was established to include papers and prioritize studies that addressed the application of ultrasound in water electrolysis, energy efficiency, hydrogen production, and technical characteristics of ultrasonic systems. Papers that did not directly address these topics were excluded. Therefore, scientific databases such as Scopus, Web of Science, IEEE Xplore, and Google Scholar were consulted. We used specific search terms such as “ultrasonic electrolysis,” “hydrogen production,” “efficiency improvement,” “cavitation effects,” and “electrode materials.” From these, an initial list of papers was compiled. Each one was evaluated by its title and abstract to determine the relevance to the review topic. Papers that met the inclusion criteria were selected for further analysis. These were then read in full and evaluated regarding methodology, results, discussions, and conclusions. Relevant quantitative and qualitative data were gathered and organized into tables to compare and analyze them. Based on the detailed analysis, the main findings of the selected studies were summarized, highlighting the innovations, benefits, and challenges associated with ultrasound in water electrolysis. Gaps in the literature and areas requiring further research were also identified. The process was peer-reviewed to ensure the quality and relevance of the works selected. Experts in the field assessed the article choices and the synthesis of results, providing feedback and ensuring the robustness of the review. A table and two figures were developed to illustrate the most relevant points, facilitating the visualization of the benefits of ultrasound in water electrolysis and comparing different experimental configurations and results.

The described methodology ensured the careful selection and detailed analysis of the most relevant studies on ultrasound application in water electrolysis, providing a solid basis for the discussions and conclusions presented in this article. Additional references that can be consulted for methodological support include guides for conducting systematic literature reviews, such as those available in BMC Medical Research Methodology and SpringerLink.

Hydrogen Production By Conventional Electrolysis

When powered by electricity from renewable sources, such as photovoltaic, hydro, geothermal, or wind, water electrolysis becomes a

truly clean hydrogen production option, giving rise to green hydrogen (Wang et al., 2021a). Below are comments on some of the most promising electrochemical technologies at the industrial level and widely used to produce green hydrogen.

Alkaline electrolysis is a traditional and well-established method that uses alkaline solutions of sodium hydroxide (NaOH) or potassium hydroxide (KOH) as an electrolyte to improve the flow of electricity. At the anode, water (H₂O) undergoes oxidation. Each water molecule loses two electrons that are converted into gaseous oxygen (O₂), which is released. Water oxidation also produces hydrogen ions (H⁺). These react with the hydroxide ions (OH⁻) in the alkaline solution, maintaining the chemical balance (Khan et al., 2018). The loss of electrons at the anode is balanced by the gain in electrons at the cathode, where hydrogen gas (H₂) is reduced and formed. As a result of the reaction, OH⁻ are also formed, which remain in the solution. The OH⁻ production at the cathode maintains the chemical balance in the alkaline solution (Rashid et al., 2015). According to the authors, in an industrial alkaline electrolysis cell, a diaphragm acts as a physical barrier separating the anode from the cathode. Its primary function is to prevent the mixing of oxygen and hydrogen gases produced on the respective electrodes, thus avoiding the risk of explosions and maintaining gas purity. Furthermore, it allows the passage of ions between the electrodes, maintaining electrical neutrality. Generally, diaphragms are made of porous materials that allow ions to pass through, but not gases. In electrolysis, polarization, or the additional loss of voltage beyond what is theoretically necessary to drive the reaction, results in lower efficiency, as more energy is needed to produce the same amount of hydrogen (Grigoriev et al., 2020). The high resistance due to diaphragm thickness and the low operating current density can influence polarization. Therefore, reducing diaphragm thickness can help to decrease polarization and increase cell efficiency. As an advantage, alkaline electrolysis cells present technological maturity, which means they are a tested and reliable technology for hydrogen production (Rashid et al., 2015). Disadvantages include the cell's low operating current density and reduced efficiency as well as the high probability of mixing the generated gases.

Proton-exchange membrane (PEM) electrolysis is an innovative and efficient electrochemical process for hydrogen production. Unlike alkaline electrolysis, PEM technology uses a solid polymer membrane as the electrolyte to conduct protons from the anode to the cathode while blocking electrons and gases (Wu et al., 2022). This approach offers several advantages over other electrolysis methods, including operation at higher current density, high purity of the produced hydrogen, and the possibility of operating under greater pressure, which may lower the costs of compressing the hydrogen for storage and transportation (Stiber et al., 2021). Water is oxidized at the anode to form oxygen, protons, and electrons. The anodic reaction is like the reaction in the alkaline electrolysis cell. At the cathode, protons crossing the PEM membrane are reduced by electrons supplied by the external circuit to form H₂ (Zhang and Xing, 2020). Polarization in PEM electrolysis can

be influenced by several factors, including membrane resistance, electrocatalyst activity, cell heat, and water management (Salehmin et al., 2022). Optimizing electrode design and choosing advanced membrane materials are essential to minimize internal resistance and, thus, decrease polarization. This can increase the overall efficiency of the process, reducing energy consumption for hydrogen production. Although PEM technology offers many benefits, it faces challenges such as the high cost of components (especially electrocatalysts that contain precious metals such as platinum) and issues related to durability and long-term membrane stability (Ayers, 2019). Research is being carried out to develop cheaper and more efficient electrocatalysts and more durable and less permeable membranes for gases, aiming to increase the economic viability of PEM electrolysis and large-scale production of green hydrogen (Brauns and Turek, 2020).

Anion-exchange membrane (AEM) electrolysis represents an alternative to alkaline electrolysis and PEM technologies. AEM technology uses an anion exchange membrane that allows negative ions to pass through instead of protons, offering advantages in simplifying system design (Vincent et al., 2021). At the AEM-type electrolysis anode, water oxidation occurs, like PEM electrolysis, producing oxygen, protons, and electrons. At the cathode, OH⁻ are generated from water and move across the membrane to the cathode, where they are reduced by electrons from the external circuit to form hydrogen and water. Polarization in AEM electrolysis can be influenced by several factors, such as membrane resistance and the activity of electrocatalysts (Zignani et al., 2022). Furthermore, efficient water management and optimization of the electrode structure are essential to maintain low internal resistance and minimize polarization, which contribute to the energy efficiency of the process. Despite its advantages, AEM electrolysis still faces challenges related to the durability and stability of membranes and conductive polymers (ionomers), which tend to degrade faster compared to PEM membranes by an average factor of around 5 (Pushkareva et al., 2020; Liu et al., 2024). Active research involves developing more robust and resistant AEM membranes and investigating more efficient and less expensive electrocatalysts. These advances are crucial to improving the economic viability and practical application of AEM technology on a large scale.

Solid oxide electrolysis (SOE) is an advanced and efficient electrochemical process for the production of green hydrogen. It is characterized by operating at high temperatures (Lei et al., 2019). This technology uses a solid electrolyte, usually ceramic, which conducts oxygen ions between the electrodes. Operating at high temperatures increases electrolysis efficiency and allows for the integration of hydrogen production with other industrial heat sources, thus optimizing energy use (Salari et al., 2022). Water is oxidized at the anode to form oxygen, protons, and electrons. At the cathode, a reduction reaction takes place, where oxygen ions are converted; these oxygen ions receive electrons from the external circuit. The catalysts most used for this reaction are generally nickel perovskites stabilized in Yttria-Stabilized Zirconia

(Nickel-Yttria-Stabilized Zirconia) (Y-ZrO₂[Ni-YSZ]) (Nechache and Hody, 2021). The resulting oxygen ions migrate to the anode, where Lanthanum Strontium Manganite+Yttria-Stabilized Zirconia (La-Sr_{1-x}MnO₃+Y-ZrO₂ [LSM-YSZ]) catalysts are used. SOE electrolysis benefits from lower polarization due to high operating temperatures, which facilitate chemical reactions and reduce electrolyte resistance (Vostakola et al., 2023). This thermally activated efficiency allows SOE to have one of the highest theoretical efficiencies, around 85%, among electrolysis technologies. However, temperature management and maintaining stable operating conditions are crucial to optimizing the performance and efficiency of this technology (Song et al., 2019).

One of the main challenges of SOE is the material stability, especially at high temperatures and aggressive operating conditions. Research is currently focused on developing more robust electrolytes and electrodes and cell designs that can withstand extreme temperature and pressure conditions without rapidly degrading (Hauch et al., 2020). According to the authors above, another challenge is the cost associated with the manufacture and operation of SOE electrolysis systems, which is currently higher than other electrolysis technologies, above US\$ 0.57/(Nm³). However, it is still in prototype scale (Lei et al., 2024). As we move towards a low-carbon future, continued innovation and optimization of these technologies will be essential to increase efficiency, reduce costs, and scale green hydrogen production, thereby meeting the growing demand for sustainable energy solutions (Oliveira et al., 2021).

Given the existing challenges for hydrogen production through water electrolysis, such as difficulties with the durability of materials under extreme conditions and the associated costs, research focused on improving these technologies is crucial. Developing stronger materials and innovative electrolytic cell designs that can operate efficiently at high temperatures and pressures is essential. Investigating new approaches, such as improving operating conditions and possibly incorporating advances such as the use of ultrasound, may offer promising strategies to overcome these limitations. This perspective points to a significant increase in efficiency, a reduction in production costs, and the expansion of alkaline electrolysis applicability to the generation of green hydrogen, contributing to a more sustainable energy matrix.

Ultrasonic Fields

Definition and basic characteristics

When a liquid medium, such as the electrolyte of an electrolysis cell, encounters an ultrasonic field, the waves create microbubbles or microcavities—a phenomenon known as acoustic cavitation (Ezzahra Chakik et al., 2017). These microbubbles grow and collapse quickly, improving mass transfer and electrolyte agitation. The agitation caused by microcavitations can increase the efficiency of electrolysis by improving the mass transfer of reactants to the surface of the electrodes. This can help overcome the limitations caused by the slow diffusion of

ions in the electrolyte (Darband et al., 2019). Therefore, ultrasonic vibration can help remove gas microbubbles from the electrodes' surface, reducing electrical resistance and polarization.

Recent studies explored the properties of ultrasonic waves and how they influence the characteristics of microbubbles on electrode surfaces. Acoustic cavitation, the result of rapid variations in pressure and temperature—with averages of hundreds of MPa and 5000 K, respectively—promotes the collapse of microbubbles, creating turbulence and liquid microjets (Nikitenko and Pflieger, 2017). This phenomenon has a “cleaning” effect on the electrode surfaces, removing adhered bubbles and, consequently, improving the efficiency of electrochemical reactions (Dehane et al., 2022). Additionally, ultrasonic waves help disperse bubbles in the electrolyte, preventing agglomeration and the formation of bubble layers that can increase overvoltage, a significant challenge in water electrolysis (Merouani and Hamdaoui, 2016). Improving efficiency and reducing overvoltage open new perspectives for optimizing electrolysis processes, especially hydrogen production. Integrating ultrasonic fields or ultrasonic electrodes directly into water electrolysis systems could represent a significant evolution in current technology. The possible applications and advantages of ultrasonic technologies should be analyzed, and how they can be strategically implemented to increase hydrogen production should be explored. Considering the promising results obtained in preliminary studies, it is necessary to evaluate the technical barriers that still need to be overcome and the potential strategies for their effective implementation.

Ultrasonic baths can interact significantly with the electrolysis process (Figure 1), causing a series of phenomena that enhance and affect the electrochemical reactions involved. This interaction is mainly based on the generation and behavior of ultrasonic waves in the liquid medium, which lead to phenomena such as cavitation, mass transfer improvement, and degassing (Islam et al., 2019).

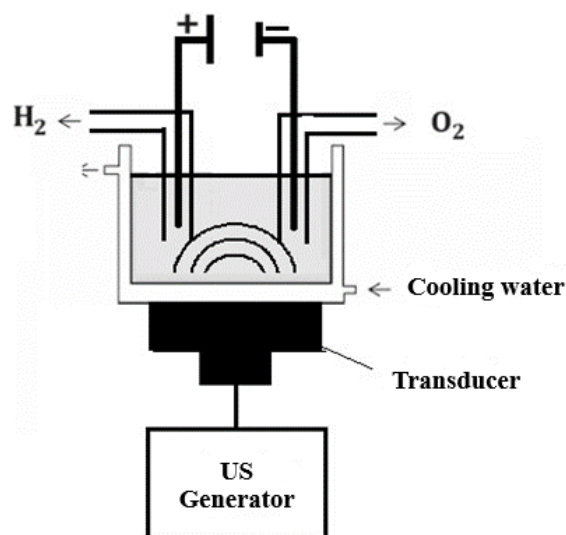


Figure 1 – Typical schematic diagram of an ultrasonic bath. H₂: hydrogen gas; O₂: gaseous oxygen; US: ultrasound.

Cavitation is the most prominent phenomenon associated with ultrasound in liquids. High-frequency ultrasonic waves (>20kHz) generate pressure oscillations in the liquid, forming small vacuum bubbles or cavities. These bubbles can grow over several pressure cycles until they reach a critical size and collapse violently (Dong et al., 2022). The bubble collapse generates localized extreme conditions, such as high temperatures and pressures, and microjets that can rupture the diffusion layer on the electrode surface (Li et al., 2021). The ultrasonic field generated by the bath may increase mass transfer between electrolyte and electrodes. The turbulence created by the collapse of cavitation bubbles and the resulting microjets can help disperse reactants and products and remove intermediates from the electrodes' surfaces. This prevents local product or reactant saturation and improves the overall efficiency of electrolysis by allowing more electrode area to actively participate in the reaction (Plesset and Prosperetti, 1977). During electrolysis, especially in the production of hydrogen and oxygen, gas bubbles form on the electrode surfaces. Ultrasound helps to remove them faster than if it occurred naturally, which is an improvement, once the accumulation of bubbles forms a layer that prevents effective contact between the electrolyte and the electrode, increasing the resistance and overvoltage. The mechanical effects of microjets and shock waves generated by ultrasonic cavitation also physically clean the surfaces of electrodes. This removes contaminants, oxidation, or other materials that may have formed or deposited on the electrode, maintaining its activity and efficiency. Ultrasound can help reduce the overvoltage required for electrochemical reactions by improving mass transfer and keeping electrodes clean and gas-free. This not only improves the energy efficiency of the process but can also extend the life of the electrodes.

Therefore, several factors may account for the predominance of studies using ultrasonic baths instead of ultrasonic electrodes. This includes the technical complexity and higher costs associated with developing ultrasonic electrodes, the already proven efficiency of ultrasonic baths for many applications, the difficulty of efficiently interfacing the ultrasonic electrode with most conventional electrolysis techniques (PEM and SOE), and the additional difficulties in measuring and controlling ultrasound directly at the electrodes. Furthermore, it is essential to emphasize that the intensity of the ultrasonic waves must be precisely controlled. Very high intensities (10–1000 W/cm²) can lead to excessive cavitation, which can result in the erosion of electrode surfaces and possibly affect process stability (Cho et al., 2021; Foroughi et al., 2021; Kerboua and Merabet, 2023). Incorporating ultrasonic baths into the electrolysis process brings several mechanical and chemical benefits that can significantly improve the efficiency and effectiveness of the process. These phenomena contribute to faster and less costly operation, making electrolysis a more viable method to reduce gases such as hydrogen.

The concept of integrating ultrasonic electrodes (Figure 2) directly into the electrodes of an electrolysis cell is a promising idea that combines the benefits of electrolysis and sonication to improve the efficiency

of electrochemical processes (Kerboua and Merabet, 2023). However, the practical implementation of this technology faces significant challenges, mainly related to controlling vibrations and maintaining adequate voltage between the electrodes. The application of ultrasound directly through the electrodes in electrolysis implies the transmission of high-frequency vibrations directly to the electrolyte and the interface electrode-electrolyte (Shen and Tsui, 2021; Kerboua and Merabet, 2023). However, generating and controlling these vibrations within an electrolytic environment presents considerable technical challenges (Merouani et al., 2015). Kerboua and Hamdaoui (2019) stress that constant and intense vibrations can lead to mechanical wear of electrodes, reducing their lifespan and effectiveness. Therefore, electrode materials and design must be specially developed to withstand these conditions without degrading their functionality. Another necessary strategy is to ensure that the vibrations are evenly distributed throughout the electrode, which is crucial to the effectiveness of the process. Intensity variations of ultrasonic waves on the electrode surface may result in unequal reaction efficiencies, as discussed by Pollet et al. (2020) in the context of the hydrogen evolution reaction (HER). Another critical challenge for implanting integrated ultrasonic electrodes is maintaining a stable and adequate voltage between cell electrodes during electrolysis, particularly under the influence of ultrasonic vibrations. Such vibrations can cause fluctuations in current and voltage between electrodes, potentially leading to unstable operation of the electrolytic cell, as noted by Dehane et al. (2021) and Sutkar and Gogate (2009) in their study on the design aspects of sonochemical reactors. Developing electrolytic cell designs that can accommodate and maximize the benefits of sonication, including damping systems made of viscoelastic materials positioned around the cell to absorb excess vibration without affecting electrochemical operation is essential. Implementing process control systems that dynamically adjust operating conditions, such as current and voltage, in response to ultrasound-induced fluctuations, can be achieved through the use of vibration and temperature sensors, and actuators that modify operational parameters as necessary, as discussed in Gogate's (2008) study on cavitation reactors.

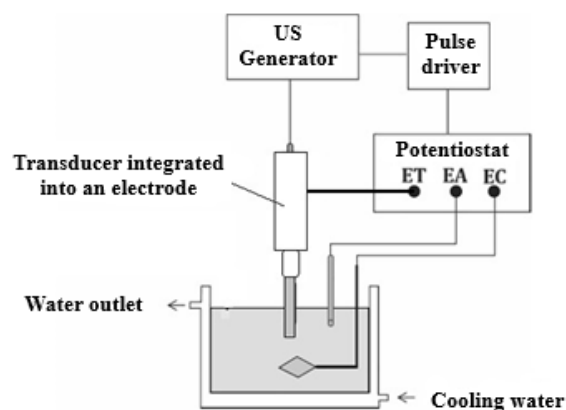


Figure 2 – Electrochemical cell with an ultrasonic electrode directly integrated into the process.

US: ultrasound.

Effects of ultrasonic waves on electrochemical reactions

Recent studies have focused on the influence of ultrasonic waves on electrochemical reactions, as these waves have the potential to improve the efficiency and kinetics of reactions in these systems (Su et al., 2024). Essential parameters include frequency, intensity, ultrasonic power, and the ultrasound emission source. The frequency, generally between 20 and 800kHz, influences the current intensity of a redox process less than the ultrasonic power (Islam et al., 2021). High frequencies generate more hydroxyl radicals in aqueous media, favoring chemical mechanisms involving radicals. In contrast, lower frequencies are efficient for mechanical effects, such as removing gases and cleaning electrode surfaces.

One of the main forms in which ultrasonic waves impact electrochemical reactions is through optimizing mass transfer. Ultrasonic waves can increase the efficiency of this process and can also affect the polarization of electrochemical reactions (Kacem et al., 2021; Ren et al., 2021). More effective removal of bubbles adhering to electrode surfaces reduces overvoltage. According to Angulo et al. (2020), this results in lower energy consumption of 10–25% to achieve the same reaction rates. However, as suggested by the authors, it is essential to consider that the inappropriate application of ultrasonic waves can lead to adverse effects. For example, ultrasonic intensities above 1.6 W/cm² can cause excessive cavitation, which can damage electrode surfaces or lead to extreme temperature and pressure fluctuations near the electrodes.

Using ultrasonic fields involves applying frequency waves above 20kHz to the electrolyte during electrolysis (Burton et al., 2021). Zhang and Xing (2020) and Liu et al. (2024) also studied the operation of an ultrasonic electrode, where acoustic waves caused complex interactions between the physical behavior of ultrasonic waves, the properties of the electrolyte, and electrochemical reactions. Villagrán et al. (2005) also tested probe-shaped ultrasonic transducers; data showed that, at any given time, the charge transferred under electrolysis with ultrasound was 2.2 times higher than under operating conditions without ultrasound.

When ultrasonic fields are employed, some associated disadvantages must be considered. The formation and collapse of bubbles may generate pressure and temperature fluctuations near the electrodes, leading to excessive cavitation phenomena and erosion of the electrode surfaces (Fang et al., 2023). Introducing ultrasonic waves into the electrolyte may require careful control to avoid unwanted effects such as interference with electrochemical reactions or changes in the composition of the electrolyte. Thus, it is important to note that the intensity of ultrasonic waves must be controlled in order to avoid harmful impacts such as erosion of electrode surfaces or reaction interference (Dotan et al., 2019). Optimizing ultrasonic parameters is essential to achieving benefits without compromising the stability and durability of the electrodes. The occurrence of cavitation and turbulence can have cascading effects on the chemical and physical characteristics of the electrolyte, requiring careful analysis of long-term effects (Darband et al., 2019; Islam et al., 2019). Therefore, the inadequate application of ultrasonic waves can lead to unwanted phenomena such as erosion of the electrodes and impacts on the characteristics of the electrolyte.

Case studies

Several experiments studied the effects of ultrasonic fields on hydrogen production via electrochemical processes to improve the efficiency and sustainability of this vital reaction (Foroughi et al., 2021). These studies focused on a wide range of parameters, from the intensity and frequency of ultrasonic waves to the composition of the electrolyte and the types of electrodes employed, analyzing the practical use of the developed processes.

Cataldo (1992) investigated the effect of ultrasound on the production of hydrogen and chlorine during the electrolysis of aqueous solutions of sodium chloride (NaCl) or hydrochloric acid (HCl), carrying out studies on the impact of ultrasound on electrolysis with the aid of a Hoffmann coulometer and a precise device for measuring gases electrolytically generated, immersed in an ultrasonic bath Ney Ultrasonik 100. The axis of each carbon electrode inserted into the coulometer was positioned perpendicular to the surface of each piezoelectric transducer in the ultrasonic bath. This meant that the ultrasonic wavefront had the same direction as the gas bubbles released at the electrodes. The experiment was conducted using a constant frequency of 30kHz and a constant acoustic intensity, estimated between 1 and 2 W/cm², under stable cavitation conditions. Electrolysis was carried out under continuous potential, and the measurements of the volume of the gases released at the electrodes were taken when the gas burettes were reset to zero (t=0). During electrolysis, the temperature of the gases and the electrical current flowing through the coulometer were monitored. Each experiment was performed under the same general conditions, with and without sonication. The volume of measured gases in the coulometer was corrected for the partial pressure of water and converted into mass. A saturated NaCl solution (about 6 M), an acidified 5.0 M NaCl/1.1 M HCl solution, and a 6.0 M HCl solution were used as electrolytes. The study compared the results of experiments with and without sonication. The results indicated that the hydrogen generation efficiency improved by 5–18% at high current density with the application of an ultrasonic field. Under experimental conditions, the energy consumption for hydrogen production was reduced by about 10–25%, with significant energy savings. Although the study evaluated electrolysis at different current densities, the author did not directly compare current densities with and without ultrasound. The overpotential and ohmic voltage drop resulted in a reduction in cell voltage. Cavitation and mass transfer effects were improved due to reduced bubble coverage over the electrodes, although specific details of cavitation were not commented on. The author suggested that there was energy saving, but did not directly address operational costs or economic viability.

To understand how ultrasonic fields can improve the efficiency of water electrolysis, potentially reducing energy consumption and improving the efficiency of hydrogen production, Li et al. (2009) investigated the energy efficiency of water electrolysis under the influence of an ultrasonic field. The main objective was to evaluate the effects of the ultrasonic field on cell voltage, gas generation efficiency, and electrolysis energy consumption. The experimental setup consisted of an electrolytic

cell made of stainless steel, with two compartments and an internal capacity of around 300 cm³ each. Two dimensionally stable anodes (DSA) of ruthenium(IV) oxide (RuO₂) and iridium dioxide (IrO₂) coated with titanium (Ti) were used as working electrodes and counter electrodes, respectively. The surface area of the DSA electrode was approximately 2.5 cm². A silver/silver chloride (Ag/AgCl) reference electrode was used, and water electrolysis was carried out galvanostatically with current densities of 20–400 mA/cm². The ultrasonic field was generated with a power of 50 W and a frequency of 60 Hz. Alkaline NaOH solutions (0.1, 0.5, and 1.0 M) were used as electrolytes. The experimental temperature was maintained at 303 K. The results showed that applying ultrasonic fields in water electrolysis increased hydrogen production efficiency by 5–18% at high current densities. In comparison, energy consumption was reduced by about 10–25% under experimental conditions, indicating significant savings. The research also observed improvements in cavitation and mass transfer effects attributed to decreased bubble coverage over the electrodes, which resulted in reduced cell voltage. Although energy savings were suggested, the study did not directly address the technique's operational cost or economic viability.

Zadeh (2014) investigated the effects by adding an ultrasonic field to optimize hydrogen production efficiency, aiming for an improvement in mass transfer and energy savings between 10 and 25%. The experimental setup consisted of a conventional electrolysis cell with nickel (Ni) electrodes separated by 7.5 cm and temperature control. The author used a Hoffmann coulometer immersed in a Ney Ultrasonik 100 ultrasonic bath. A stable acoustic cavitation was achieved with a constant frequency of 20kHz, amplitude of 30%, and acoustic intensity of approximately 1–2 W/cm². Measurements of the volumes of gases released at the electrodes were corrected for the partial pressure of water and converted into mass. NaOH and KOH solutions, both 0.1 M, were used as electrolytes. The electrolysis cell showed an average efficiency of 80%, which is in line with literature values of 70–96% (Lamy and Millet, 2020). The use of ultrasound increased the efficiency of H₂ production by 4.5%, close to the range of 5–18% reported in the literature (Li et al., 2009). The 43.75% increase in the active electrode area improved current generation by 70% and hydrogen production by 50% for potentials from 2 to 5 volts. The decomposition potential and overvoltage of KOH were lower than those of NaOH. Ultrasound reduced these values, resulting in an energy saving of 1.3%, lower than the 10–25% range found in the literature (Li et al., 2009).

Foroughi et al. (2022) investigated the impact of the ultrasonic field (408kHz) on the hydrogen and oxygen evolution reactions (HER and OER) in Raney-Ni electrodes in 30% aqueous KOH solution. Linear sweep voltammetry and electrochemical impedance spectroscopy techniques were used to evaluate the electrochemical behavior of the Raney-Ni electrode. The methodology applied in this study used a potentiostat/galvanostat with a three-electrode cell, where the Raney-Ni electrode served as the working electrode, a Ni mesh as the counter electrode, and a reference electrode mercury/

mercury oxide (Hg/HgO). Electrolyte solutions were prepared with 30 wt % KOH and ultra-high purity deionized water (Millipore, 18.2 MΩ cm in resistivity). During the experiments, ultrasound was applied to the electrochemical cell to investigate its impact on HER and OER. Linear voltammetry and electrochemical impedance spectroscopy techniques were employed to study the electrodes' behavior and evaluate the reactions' efficiency. The data concerning the ERHE (potential referring to the reversible hydrogen electrode) were analyzed and corrected for internal resistance compensation. This methodology allows a detailed assessment of the effect of ultrasound on electrochemical reactions in a controlled environment. All electrochemical experiments were performed with a BioLogic-SP 150 potentiostat/galvanostat in a conventional three-electrode configuration, using a 30% m/m KOH solution (Sigma-Aldrich, 99.99% purity) at 25°C, 40°C, and 60°C. Raney-Ni alloy electrodes synthesized by Fraunhofer IFAM were utilized as working electrodes (Bernäcker et al., 2019). A new Raney-Ni electrode was used for each sonoelectrochemical experiment. A Ni mesh (40 mesh woven from 0.13 mm diameter wire, 99.99% metal base, Alfa Aesar, Germany) was cut into a rectangular shape (20.67 × 10.76 mm) and placed as a counter electrode. The reference electrode was made of Hg/HgO filled with 30% KOH solution (the same one used as an electrolyte). All potentials in this work were reported concerning ERHE (ERHE=Hg/HgO+0.90V). The experiments were conducted at different temperatures (25, 40, and 60°C), and ultrasound was applied at 408kHz. The electrolyte was a 30% by weight KOH solution, and the work did not mention specific pressure or potential of hydrogen (pH) data. They employed linear voltammetry and electrochemical impedance spectroscopy. The ultrasonic field significantly changed the HER overpotential by -300 mA·cm⁻² (+34 mV at 25°C), especially at low temperatures and mainly due to the effective removal of gas bubbles from the electrode surface. There was no significant influence on the OER overpotential. Ultrasound did not significantly alter the structure of the Raney-Ni electrode, maintaining its quality and stability. There was an increase in current density under ultrasound, indicating improved electrolysis efficiency. Ultrasound improved mass transfer and reduced bubble resistance, contributing to greater electrolysis efficiency. Compared to conventional conditions, the study presented 10–25% energy savings for hydrogen production in an ultrasonic field. Ultrasound did not affect the stability of the Raney-Ni coating, as evidenced by scanning electron microscopy (SEM) images, which presented no signs of delamination after exposure to ultrasonic conditions. These results confirm that the electrodes' structural integrity is maintained, allowing the use of this operational condition without risk of deterioration. The authors observed that ultrasound power and temperature affect the HER in electrolysis. They found that HER activity in Raney-Ni under ultrasonic conditions increased at low temperatures (e.g., 25°C), while the effect of ultrasound on OER was negligible. Furthermore, it was observed that the effect of ultrasound on both reactions de-

creases with higher temperatures. The authors suggested that ultrasound improves the electrocatalytic performance of Raney-Ni for HER mainly by efficiently removing gas bubbles from the electrode surface and dispersing them in the electrolyte. This effect depends on the behavior of hydrogen and oxygen gas bubbles in alkaline media. As for challenges and limitations, the researchers warned of the need to adjust ultrasonic conditions to optimize the effects on hydrogen production. Regarding the economic viability of the process, they suggested improvements in energy efficiency with the application of ultrasound but did not provide a detailed analysis of future commercial viability.

Due to the need for expensive electrocatalysts to compensate for the ohmic losses associated with the kinetic overvoltage potential of conventional green hydrogen production systems, Ehrnst et al. (2023) investigated in detail a new strategy employing high-frequency (10 MHz) sound waves to enhance the HER. The authors above worked with neutral electrolytes, modifying the coordination of the network of water molecules, that is, changing how the water molecules are arranged and interact with each other. In water, molecules form a complex network of hydrogen bonds. By applying high-frequency sound waves, it is possible to disrupt this network. This perturbation can lead to the formation of more “free” or less constrained water molecules, which are more available to participate in chemical reactions such as the HER. The research focused on high-frequency hybrid sound waves to alter the coordination of the water network in electrolytes to improve HER performance. The experimental setup involved using an electrochemical cell with sound waves reflected from the surface—SRBW (Rezk et al., 2016). For the experiments, a 0.1 M solution of sodium phosphate ($\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$) with a pH adjusted to 7.2 was used as the electrolyte, utilizing polycrystalline gold electrodes. The results highlighted a significant improvement in the HER efficiency. The choice of a neutral electrolyte enabled in-depth investigations into the interfacial structure of water using Raman spectroscopy, as documented by Wang et al. (2021b). This contributed to a better understanding of hydronium ion generation and improved mass transport, as well as helping to prevent the accumulation of bubbles on the electrodes. The authors showed that incorporating high-frequency hybrid acoustic wave excitation into the water electrolysis process can substantially increase the HER rate, especially in neutral media, using polycrystalline gold (Au) or silver (Ag) electrodes. This increase, approximately 14 times in current density, is due to the reduction in overvoltage and the increase in current density facilitated by the excitation of the SRBWs. These waves help to “thwart” the water’s hydrogen bond network, generate H^+ and hydronium ions (H_3O^+) *in situ*, and produce a solid convective flow that quickly removes bubbles from the electrodes. The energy consumption required to generate the SRBWs resulted in a net energy saving of 27.3%, greater than the energy efficiency reported in conventional sonoelectrochemistry (5–25%). This highlights the

potential of this approach as a practical and cost-effective way to produce green hydrogen using cheap, generic electrode materials.

Duan et al. (2024) investigated the impact of using ultrasound to prevent bubbles accumulation on the surface of the electrodes. Such bubbles can act as a barrier to ion transport, hindering electrochemical reactions and requiring more energy to maintain the reactions (Fu et al., 2020). This work used practical tests to observe bubble behavior and measure the direct effects of ultrasound and computational models to understand processes at levels that are not easily accessible by direct observation. This model helps predict how bubbles behave and how ultrasound influences electrolyte dynamics and mass transfer (Mladenović et al., 2022). Both the interaction between the liquid and gaseous phases and acoustic effects such as cavitation are considered here. Firstly, the polarization curves and bubble flow patterns under different positions of the ultrasonic transducer and electrode were obtained through experiments. Then, the flow model of the electrolytic cell with ultrasound was constructed, considering the mass transfer between the gas and liquid phases and the acoustic flow phenomenon caused by cavitation. The results revealed that the location of the ultrasonic transducer significantly affects how the ultrasound propagates and interacts with the bubbles due to wall reflection and the ultrasound transmission process in the electrolyte. An ideal position of the ultrasonic transducer may significantly increase the current density, demonstrating the importance of planning the configuration of electrolytic cells. Through simulations, the flow within the electrolytic cell was visualized and optimized, identifying the best operational conditions for the application of ultrasound, aiming to maximize its effectiveness. The position of the ultrasonic transducer as an electrode significantly impacts the current density when the transducer is located on the right side of the electrolytic cell. Compared to those without ultrasound, the current density can be increased 2.40–22.70% at different electrode positions. The influence of operational parameters on the flow field inside the electrolyzer was obtained through numerical simulation. As a result, appropriate charging methods and operating conditions could maximize ultrasound effectiveness.

To investigate ultrasound’s influence on removing bubbles from electrode surfaces and on ohmic resistance, Merabet and Kerboua (2024) used an alkaline electrolyzer without a membrane powered by photovoltaic solar energy (Tam et al., 2024). The objective was to quantify the effect of sonication on the bubble coverage on the electrodes and, consequently, on the electrical parameters of the electrolysis cell. The research combined laboratory-scale experiments with numerical modeling. The electrolysis system was configured with a glass hydrogen cell and nickel plate electrodes using a degassed KOH solution. Experiments were performed with continuous and pulsed sonications (60W, 40kHz) and compared with conditions without sonication (Kobus et al., 2022). A solar panel model ET-M53640 was used to power the system, and its performance was also mathematically modeled. The integration of continuous sonication showed a 76% reduction in bubble resistance compared to the system without

sonication and 52% compared to pulsed sonication. The experiments were repeated three times to check the repeatability of the results in terms of supply currents and resulting voltages under the photovoltaic power supply. The study demonstrated that sonication, especially in continuous mode, effectively reduces bubble resistance and, consequently, ohmic resistance in an alkaline electrolyzer without a membrane. The lowest electrode coverage was achieved with continuous indirect sonoelectrolysis, with a value of 37%, compared to 82% in sono-free conditions, corresponding to a reduction of approximately 54.8%. The resulting bubble resistance varied from 569.81 mΩ without ultrasound to 132.54 mΩ with integrated continuous sonication. In fact, it is assumed that ultrasound produces an agitation effect in the bulk electrolyte, and close to the electrode surface, promoting the desorption of gas bubbles from the electrode.

Aiming to analyze the use of ultrasonic technology for the electrochemical generation of hydrogen, Sharifishourabi et al. (2024) studied the key mechanisms and techniques involved. The study particularly sought to understand how cavitation bubbles, induced by ultrasonic waves, could be generated and detected and how these bubbles influence the efficiency of hydrogen production (Cho et al., 2021; Zore et al., 2021). The review also aimed to compare different experimental setups that use ultrasound to produce hydrogen, analyzing fundamental parameters

such as acoustic intensity, liquid temperature, and frequency. A comparative analysis of experimental setups showed the variation in objectives, frequencies, and temperatures used in studies on hydrogen production, soil remediation, and water treatment. The diversity in acoustic intensities and container sizes suggested no single ideal approach, highlighting the need to understand the parameters to optimize hydrogen production. Using ultrasound to improve hydrogen production has shown high potential on a laboratory scale, but more research is needed to improve and scale up the process for industrial use. Sono-hydrogen, although still in the experimental phase, has great promise as an energy resource. Despite challenges like the cost of ultrasound equipment and the need for efficient catalysts, the benefits make this a promising area for future research and development. With continued innovation, sono-hydrogen production could become important for a sustainable, low-emission energy future.

Table 1 clearly demonstrates the significant benefits of employing ultrasound in electrolysis processes for ultrasound-assisted hydrogen production such as reducing ohmic resistance, increasing gas production efficiency, and reducing the voltage required for cell operation. These benefits are mainly attributed to the efficient removal of bubbles from electrode surfaces, which is promoted by the effects of cavitation and microjets generated by sonication.

Table 1 – Benefits of the ultrasonic field in water electrolysis.

Study	Experimental setup	Benefits of the ultrasonic field	Quantitative results
Cataldo (1992)	NaCl or HCl aqueous solution, ultrasonic bath at 30 kHz, 1 to 2 W/cm ² and electrolysis over constant potential	Increases Cl ₂ yield, reduces overvoltage	0.7–0.8 V reduction in H ₂ deposition potential, increased efficiency of H ₂ production from 5 to 18%
Li et al. (2009)	Alkaline NaOH solution (0.1, 0.5, and 1.0 M) at 303 K, sonication at 60 kHz and 50 W	Reduced cell voltage, increased H ₂ efficiency	Current 10–25% reduction in energy consumption for H ₂ , increase in H ₂ efficiency by 5–18% at high densities
Zadeh (2014)	Cell with 1000 cm ³ and nickel electrodes separated by 7.5 cm, sonication of 20 kHz, and amplitude of 30%	Bubble removal, increased active area, reduced overpotential	Increase of 43.75% in the effective area, 4.5% increase in H ₂ production, 1.3% energy reduction
Foroughi et al. (2022)	Raney-Ni mesh electrodes, 30% KOH electrolyte (25, 40, and 60°C), 408 kHz sonication with 100% amplitude	Increased H ₂ production efficiency at low temperatures and reduced gas bubble resistance did not significantly alter the Raney-Ni structure	Energy savings of 10–25% in H ₂ production
Ehrnst et al. (2023)	Glass electrochemical cell containing neutral electrolyte (0.1 M sodium phosphate: Na ₂ HPO ₄ /NaH ₂ PO ₄), Au working electrode, frequency 10MHz	Use of 10 MHz frequencies prevents corrosion of electrodes, replaces complex and expensive electrocatalysts	An approximately 14-fold increase in current density demonstrates a net energy saving of 27.3%
Duan et al. (2024)	Electrolyzer with ultrasonic transducer coupled to the electrode, frequency of 20 kHz	An ideal position of the ultrasonic transducer can significantly increase the current density	Current density increases between 2.4 and 22.7% at different transducer positions
Merabet and Kerboua (2024)	Type hydrogen electrolyzer without membrane, nickel electrodes, 25% KOH, working area 13.5 cm ² , 40kHz, 60 W, PV	Reduced bubble coverage, lower ohmic resistance in the presence of sonication due to streaming, microjets, and shock waves	54.8% reduction in bubble coverage, 9.32% reduction in cell voltage

NaCl: sodium chloride; HCl: hydrochloric acid; NaOH; sodium hydroxide; Ni: nickel; KOH: potassium hydroxide; Na₂HPO₄: sodium phosphate dibasic; NaH₂PO₄: sodium dihydrogen phosphate; Cl₂: chlorine gas; H₂: hydrogen gas.

Future perspectives

The future perspectives to develop these techniques are broad, also covering the improvement of materials due to greater resistance to cavitation (Theerthagiri et al., 2020; Islam et al., 2021; An et al., 2023). As the search for more efficient and sustainable energy technologies advances, the introduction of electrodes and ultrasonic baths in green hydrogen production emerges as a notable innovation. However, by employing it, not only technical and environmental considerations must be made but also economic viability (Ehrnst et al., 2023).

In addition to the direct costs, the environmental benefits and indirect costs associated by reducing greenhouse gas emissions must be considered. While these benefits may not directly translate into immediate monetary savings, they meet global sustainability goals and can be highly valued in a regulatory context that favors green technologies. The choice of probes and electrodes, such as the titanium sonotrode used by McMurray (1998), can significantly impact the process efficiency. The cost ratio of titanium and stainless-steel electrodes reaches 3.4 times (Turton et al., 2012). However, this selection must be based on the material's ability to withstand prolonged ultrasonic exposure and its effectiveness in facilitating desired chemical reactions. In large industrial facilities, efficiency gains may justify the high initial cost, while in smaller operations, the return on investment may be less attractive (Nnabuife et al., 2022). Therefore, a cost analysis must consider different scale scenarios and evaluate the economic viability of small, medium, and large electrolysis operations.

Conclusions

The application of ultrasonic fields in the production of green hydrogen has proven to be a revolutionary innovation, significantly improving the efficiency of the electrochemical process. Analysis of the case studies demonstrated that optimizing mass transfer and reducing overvoltage and ohmic voltage drop directly contribute to greater hydrogen production efficiency. These improvements are reflected in significant reductions in energy consumption, with efficiency gains between 5–45% and energy savings of 10–25%.

However, implementing ultrasonic fields in electrolysis faces challenges, such as selecting materials resistant to acoustic erosion and precisely controlling ultrasonic conditions. Cavitation and microbubble collapse require fine adjustments to prevent electrode damage and ensure component durability. Based on the results presented, it can be concluded that, despite these challenges, ultrasonic fields offer a promising route to more sustainable hydrogen production. Furthermore, adopting this technology can significantly advance electrolysis's economic and environmental viability, especially when integrated with renewable energy sources.

Further exploration of the interactions between ultrasonic fields and electrode materials and the development of advanced process control and optimization strategies are recommended for the future. New cavitation-resistant materials can further improve efficiency. Ultimately, the combination of electrochemistry and ultrasound represents an innovative solution that could be crucial in transitioning to a clean and sustainable energy matrix.

Authors' Contributions

Menezes, C.M.B.: conceptualization; methodology; investigation; writing – original draft. **Sobral, D.M.:** conceptualization; methodology; investigation; writing – original draft. **Santos, L.B.:** validation; supervision. **Benachour, M.:** validation; writing – review and editing; funding acquisition. **Santos, V.A.:** conceptualization; methodology; investigation; writing – review and editing; project administration; funding acquisition.

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