Hybrid seawater electrolysis for hydrogen production: Integrating anodic oxidation reactions for enhanced efficiency

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Hydrogen (H_2) plays a pivotal role in the clean energy transition, providing a viable pathway for decarbonizing sectors such as transportation, industry, and power generation. Among the various methods for H_2 production, seawater electrolysis (SWE) stands out due to the abundant availability of seawater.[1] This process involves the electrochemical splitting of water molecules into H_2 and oxygen (O_2) through the application of an electrical current. The current facilitates the hydrogen evolution reaction (HER) at the cathode and the oxygen evolution reaction (OER) at the anode. However, in chloride-rich environments like seawater, the presence of chloride ions can lead to the undesirable chlorine evolution reaction (CER), which generates chlorine and/or hypochlorite species instead of O_2.[2] This side reaction significantly reduces H_2 production efficiency, as CER requires higher voltages that increase the overall energy demand of seawater electrolysis. Additionally, the generation of chlorine and hypochlorite poses environmental and safety risks due to their toxicity and corrosiveness.

Traditional approaches to SWE have aimed to mitigate CER by employing selective electrocatalysts, optimizing electrolyte composition, and using protective coatings on electrodes. While these strategies have yielded some success, they often entail trade-offs regarding cost, complexity, and overall system efficiency. Moreover, the economic implications of managing chlorine by-products and the environmental impact of chlorine and/or hypochlorite species emissions further hinder the widespread adoption of conventional SWE.

In response to these challenges, hybrid seawater electrolysis (HSE) systems have been developed to enhance the overall efficiency of the process.[3] HSE systems incorporate anodic oxidation reactions (AORs), enabling the oxidation of various species present in seawater, such as organic compounds and pollutants introduced into the system, which can be transformed into valuable chemicals. Unlike OER, which typically requires a high overpotential and consumes considerable energy, AORs can proceed at lower potentials, reducing energy consumption and improving overall system efficiency. This thermodynamic advantage makes AORs a more energy-efficient alternative in HSE systems, offering several key benefits:

1. *Dual-Product System*: H_2 is produced at the cathode while the anode generates valuable by-products, enhancing the economic feasibility of the process. Additionally, H_2 can also be generated at the anode through the oxidation of aldehydes at ultra-low potentials, enabling bipolar H_2 generation with the cathodic HER, achieving a Faradaic efficiency of up to 200%.[4]

2. *Reduced CER*: By promoting alternative oxidation reactions, the likelihood of CER is significantly reduced, leading to a cleaner and more efficient process.

3. *Energy Efficiency*: The hybrid system can operate at lower energy inputs compared to conventional SWE, as the AORs may be more thermodynamically favorable than OER.

These benefits make HSE a promising candidate for large-scale H_2 production, especially in coastal regions where seawater is readily accessible. Additionally, this dual approach, producing hydrogen while generating valuable chemicals, aligns with circular economy principles and paves the way for more sustainable hydrogen production.

ECONOMIC AND ENVIRONMENTAL BENEFITS

The integration of AORs in SWE presents significant economic and environmental advantages, as assessed through techno-economic analysis (TEA) and life cycle assessment (LCA). The economic feasibility of HSE relies on a careful balance between capital and operational costs. Capital costs encompass the development of advanced electrocatalysts, the construction of electrolysis systems, and the integration of anodic oxidation processes. These expenses can be substantial, especially during the initial phases of technology adoption, which require considerable investment in research and development and pilot-scale projects.

Operational costs are primarily driven by energy consumption, maintenance, and raw material inputs. A notable advantage of HSE is its potential to lower energy consumption by leveraging more favorable oxidation reactions at the anode. The coupling of AOR with the HER allows SWE to operate with significantly reduced electricity demand (by 2 to 4 times), which could lower electrolysis costs by an estimated 12.5% to 25%.[3] Additionally, the value generated from H_2 at the cathode (~\$4000–\$5000 per ton) and by-products such as formic acid and glyceraldehyde can provide supplementary revenue streams, offsetting operational costs and enhancing the return on investment (Figure 1A).[5] The sale of these by-products enhances the overall return on investment and shortens the payback period for hybrid systems.

A comparative analysis with conventional SWE indicates that hybrid systems may be more economically viable due to their capacity to generate additional revenue from by-products and their lower energy costs. Nonetheless, the initial capital investment remains a significant barrier. Strategies for cost reduction, including scaling up production, optimizing reaction conditions, and integrating renewable energy sources, can help mitigate these challenges. For instance,

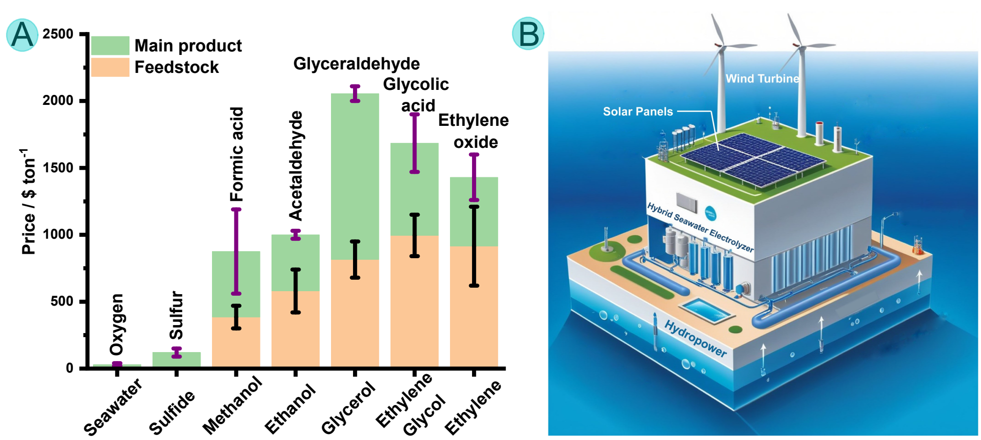

Figure 1. (A) The market prices of feedstock and primary products from the anode side utilized in hybrid seawater electrolysis.[3] (B) Applications of hybrid seawater electrolysis for hydrogen production.

coupling HSE with solar or wind energy can substantially reduce electricity costs, enhancing competitiveness with other H_2 production methods (Figure 1B).

The market dynamics for H_2 and its by-products are crucial to the economic viability of HES. The increasing demand for clean H_2 across various sectors, combined with the potential for valuable by-products, positions hybrid systems as a competitive option within the H_2 economy. However, fluctuations in the market, regulatory policies, and competition from alternative H_2 production methods may influence the economic feasibility of this technology.

The TEA indicates that while hybrid systems necessitate significant initial investment, their ability to generate additional revenue from by-products and operate at reduced energy costs renders them competitive with other H_2 production methods. Concurrently, the LCA highlights the environmental benefits of HSE, particularly when powered by renewable energy sources and aligned with circular economy principles.

A comprehensive LCA of HSE reveals numerous environmental advantages over traditional SWE and steam methane reforming, the predominant method for H_2 production. The LCA evaluates various factors, including greenhouse gas emissions, energy consumption, water usage, and pollutant generation. HSE can significantly diminish greenhouse gas emissions, especially when utilizing renewable energy sources. Furthermore, the avoidance of CER and their associated by-products mitigates the environmental impact of the process. However, the energy-intensive nature of electrolysis remains a challenge, particularly when reliant on non-renewable energy sources.

Resource efficiency in HSE is another vital aspect of its environmental sustainability. This process primarily utilizes seawater, an abundant and readily available resource, which offers a considerable advantage over steam methane reforming that depends on natural gas (Figure 1B). The incorporation of renewable energy further enhances resource efficiency, reducing dependence on non-renewable resources and minimizing overall environmental impact.

One of the key environmental benefits of HSE is its potential for by-product utilization. By facilitating AORs that yield valuable chemicals, the process not only minimizes waste but also contributes to the circular economy. For example, the production of formic acid as a by-product of methanol oxidation serves as a valuable chemical feedstock for various industries, decreasing the necessity for its production from fossil fuels (Figure 1A).[5] The long-term sustainability of HSE hinges on its capacity to operate efficiently while minimizing environmental impact. The integration of circular economy principles, such as recycling and by-product valorization, is essential for achieving this objective. Additionally, the scalability of the technology and its compatibility with renewable energy sources are critical factors in ensuring its sustainability.

CHALLENGES AND LIMITATIONS

HSE holds significant promise for H_2 production; however, several challenges and limitations must be addressed to unlock its full potential. A primary technical challenge is optimizing the balance between H_2 production and the oxidation of other species at the anode. Achieving this balance is crucial to maximizing hydrogen output while selectively driving AORs over the less desirable OER/CER, thus enhancing system efficiency and sustainability. This necessitates the careful selection of catalysts and operating conditions to ensure that desired reactions occur efficiently and selectively.

Current electrocatalysts face limitations, particularly regarding their durability and selectivity. Although substantial progress has been made in developing selective catalysts, there remains a pressing need for materials that exhibit both high efficiency and durability under the harsh conditions of HSE.

Scaling up HSE systems for industrial applications introduces additional challenges. The complexity of integrating multiple reactions within a single system demands sophisticated control strategies, which may incur extra costs and technical hurdles. Furthermore, addressing potential regulatory challenges and ensuring public acceptance of the technology are critical for its successful deployment.

SUMMARY AND PROSPECTS

HSE represents a promising approach to H_2 production, addressing many challenges associated with traditional SWE. By integrating AORs, these systems can enhance efficiency, reduce CER, and generate valuable by-products, making them both economically and environmentally attractive.

Economically, the dual-product nature of hybrid systems allows for additional revenue streams from by-product sales, which can offset H_2 production costs. This feature enhances competitiveness with other H_2 production methods, such as steam methane reforming. Environmentally, HSE minimizes the production of harmful by-products, such as chlorine and/or hypochlorite species, which would otherwise necessitate costly and energy-intensive treatment processes. Additionally, operating the system at lower energy inputs reduces the overall carbon footprint of H_2 production.

Despite the significant challenges that remain, particularly in catalyst development and system optimization, the potential of HSE to contribute to the H_2 economy is substantial. Continued research and innovation in this field could lead to the development of commercially viable systems that play a crucial role in the global transition to clean energy.

To advance HSE for H_2 production, several key areas require further research and innovation:

1. *Development of More Selective and Stable Catalysts:* Continued exploration of electrocatalysts that can selectively promote desired AORs while suppressing CER is essential. This includes investigating new materials and fine-tuning catalyst structures to enhance both selectivity and durability, particularly under the challenging conditions of long-term hybrid seawater electrolysis. To improve catalyst longevity in practical applications, it is crucial to address issues such as chloride-induced corrosion, which can lead to catalyst dissolution, delamination, and reduced efficiency over time.

2. *Optimization of Reaction Conditions*: Further studies are necessary to optimize the operating conditions of hybrid systems, including temperature, pressure, and electrolyte composition, to maximize efficiency and selectivity. Research should also explore the integration of novel reaction conditions, such as high-temperature or high-pressure environments, to enhance process efficiency.

3. *Integration with Renewable Energy*: Combining HSE with renewable energy sources, such as solar or wind power, could significantly reduce environmental impacts and enhance sustainability. This integration requires the development of flexible systems capable of operating efficiently under variable power inputs, as well as exploring energy storage solutions to ensure a stable energy supply.

4. *Commercialization and Scale-Up:* Research efforts should focus on scaling up HSE systems for commercial applications. This includes addressing engineering challenges associated with large-scale production and developing cost-effective solutions for system integration. To enable commercial viability, attention must be given to designing scalable synthesis methods for catalyst fabrication, as well as scalable electrode and cell preparation techniques. While laboratory-scale synthesis methods often focus on milligram quantities, industrial applications require electrode sizes on the scale of square meters. This scale-up introduces new challenges, such as shunt currents and material inhomogeneities, which must be carefully managed to ensure uniform cell performance. Additionally, exploring modular systems that can be easily scaled to meet varying demand is crucial.

5. *Policy Support and Incentives*: The successful deployment of HSE will depend on supportive policy frameworks and incentives that encourage the adoption of clean H_2 technologies. Potential measures could include subsidies for renewable energy, tax incentives for H_2 production, and regulatory frameworks that promote the use of green H_2 across various industries.

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DECLARATION OF INTERESTS

The authors declare no competing interests.