

Seawater to Green Hydrogen: Future of Green Energy

Suraj Loomba,^[a] Muhammad Waqas Khan,^[b] and Nasir Mahmood^{*,[a, b]}

Water electrolysis to produce hydrogen has been viewed as the future of green energy. The reliance of current electrolyzer technologies on ultrapure fresh water is not feasible to meet increasing hydrogen demands. The abundant seawater emerged as the potential feedstock for water electrolysis, but its complex composition and chlorine chemistry make the process complicated. Recently designed effective catalysts have given hope for direct seawater splitting but need to be optimized for commercial use. Moreover, the inability of current

electrolyzer technologies with seawater requires efforts to establish this technology. In short, freshwater as feed for water electrolysis is not sustainable; the focus must be on seawater. While desalination seems to be a viable option, the economics of scale of the plant is critical in assessing its viability. Although the complex composition of seawater makes direct seawater splitting challenging, designing effective catalysts and durable electrolyzers can make it possible for a truly sustainable hydrogen industry.

In recent years, a lot of advocacies have been observed against hydrogen production *via* direct seawater splitting. While some believe that direct seawater splitting is the future, others believe that desalination of seawater can be the way to go about it, but one thing is for certain pivot from freshwater splitting. Green hydrogen is tipped to play a crucial role in decarbonizing various industries to reduce emissions, and its demand is expected to increase exponentially over the next few decades (Figure 1). To meet industry operational demands, roughly 2.3 Gt of hydrogen would be required, and to generate 2.3 Gt of hydrogen, more than 20 billion m³ of water would be needed (as 1 kg of H₂ needs 9 kg of H₂O), which is equivalent to the water consumption of a developed country with a population of 63 million.^[1] Considering limited freshwater resources (only ~3% of total water reserves) and its uneven distribution worldwide could put 80% of the world's population at high risk of water scarcity, causing more pressure on the freshwater reserves.^[2] These green technologies should not risk and compete with basic human needs.

On the other hand, seawater is an abundant resource that can be a potential feedstock for water electrolysis systems. Additionally, producing hydrogen from seawater can have the added advantage of easy access to renewable sources like tidal, wind, solar, or geothermal energy from the ocean.^[4] However, various ionic salts, undesired side reactions, and impurities like small particulates and microorganisms can create several

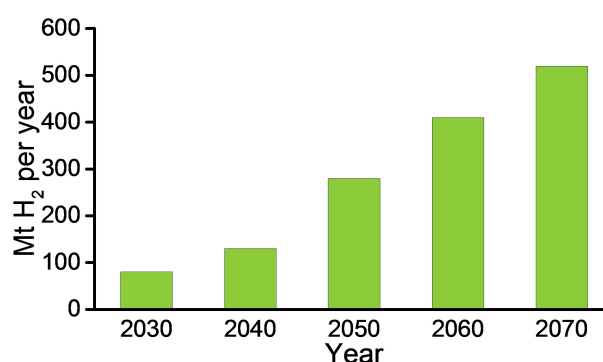


Figure 1. Global demand for hydrogen by sector 2030–2070.^[3] Data gathered from ref.[3].

challenges during electrolysis. For example, the presence of chloride anions leads to the chlorine evolution reaction (CER), generating chlorine gas, which competes with the anodic oxygen evolution reaction (OER) and tends to corrode the electrodes and deactivate the catalyst, making use of seawater inefficient.^[5]

Based on these challenges, desalination of seawater has been suggested as a plausible pathway to mitigate the chlorine chemistry as it can be carried out *via* already available technologies or by easy upgradation of matured technology of freshwater electrolyzers by integrating with desalinated systems with no significant cost increment overall at large-scale desalination process (Figure 2).^[2,5–6] The advancements in desalination technologies have led to decreased operating temperature and energy consumption while improving freshwater production and reducing the specific energy requirements from 20 kWh m^{−3} in 1970 to 2.5 kWh m^{−3} in 2021. By looking into these factors, it seems an attractive option, but this approach has several challenges in itself, like the presence of anions and cations in the desalinated water, even after the desalination process can poison the commercially available catalysts and increased cost due to the requirement of a certain level of water purity. The majority of the desalination process is carried

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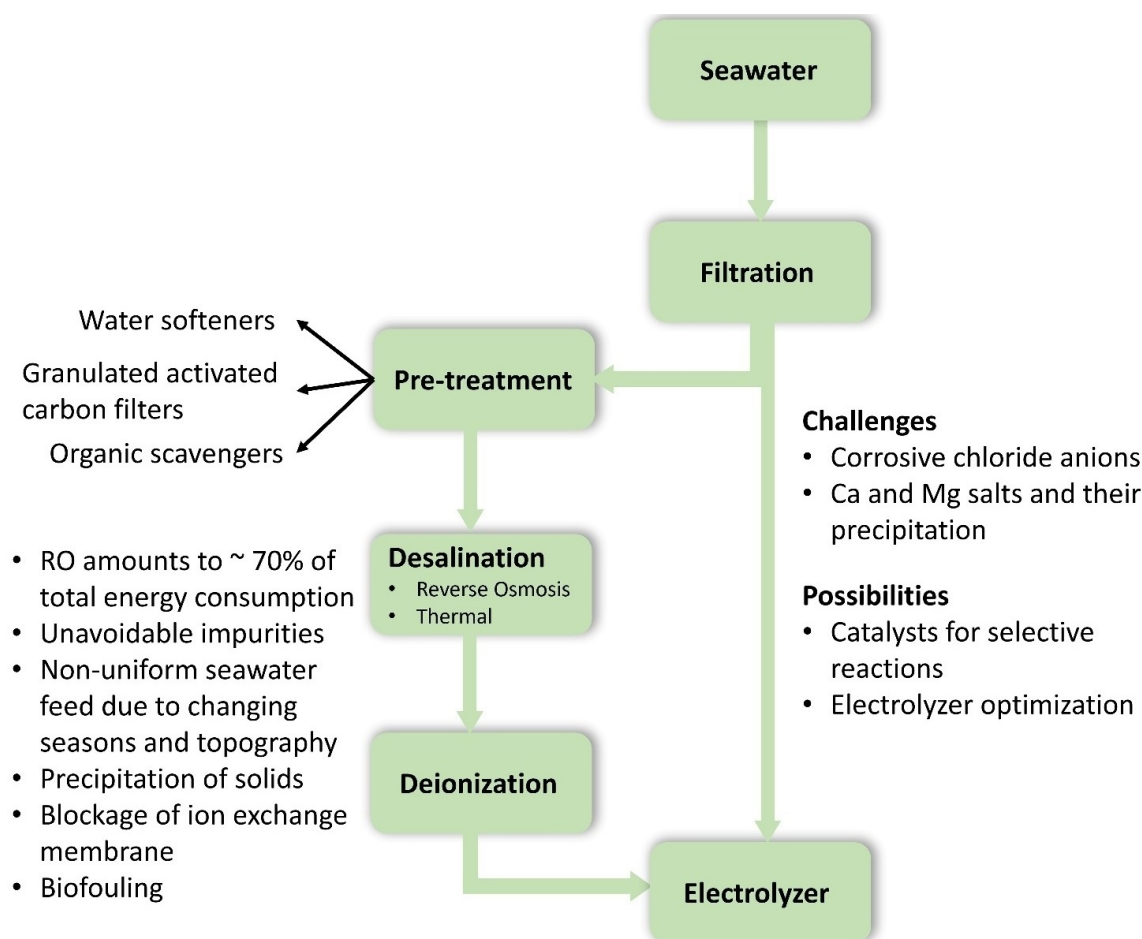
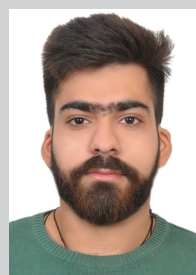


Figure 2. Operational challenges of present and proposed technologies for direct seawater splitting.



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out *via* reverse osmosis, which amounts to about 70% of the total energy consumption of the desalination plant. Even though reverse osmosis has high overall efficiency and can be economically feasible in countries with high fossil fuel costs, its electricity consumption is high (4–5 kWh m⁻³).^[7] Furthermore, an additional deionization step is also required wherein all the remaining anions and cations are removed using a mixed bed filter (which needs to be regenerated or exchanged once saturated) or an electro-deionization unit. Still, there is a possibility that some unwanted particles or precipitates remain in the feed, causing biofouling or the blockage of the ion exchange membrane. There are also problems associated with the upscaling of this two-step technology and expandability across different demographical regions across the globe.^[8] The desalination plant's requirement for seawater treatment along with the deionization step is not only an energy-intensive process but also requires huge capital, operational and maintenance costs, and a large land area for setup, making it unfeasible for export markets linked with busy ports or renewable energy generation sites.^[9]

Seawater splitting and water purification have recently been combined into an integrated system as a potential alternative to the current desalination system. For instance, Xie et al. developed a system that integrated the in-situ water purification process into the seawater electrolysis based on a self-driven phase transition mechanism. The system consisted of a gas-path interface comprising a hydrophobic porous polytetrafluoroethylene (PTFE)-based waterproof breathable membrane and a self-dampening electrolyte of concentrated KOH solution. The system is designed to allow the transfer of water vapours but prevents seawater ions or liquid from moving through it with claims of 100% ion-blocking efficiency.^[10] Proton exchange membrane (PEM) electrolyzers have also been integrated with seawater reverse osmosis, requiring a small fraction of energy as compared to the total energy requirements of the water electrolysis process. This integration can cost an additional US\$ 0.1 per kg of hydrogen generated, which does not seem much, but operational complexity is still a question.^[11] Furthermore, these are still in the initial stages and have some concerns regarding membrane stability and whether it can have the same ion-blocking efficiency after long operations. Also, some unwanted microbes or precipitates might pass through the membrane, potentially harming electrolysis. In comparison, catalysts designed for direct seawater splitting would have the ability to tackle such ions and/or impurities, making it much simpler and adaptable at a large scale.

Direct seawater splitting systems can be made more desirable *via* potential integration with the chlor-alkali systems. In the chlor-alkali process, caustic soda (NaOH) is obtained as one of the products at the cathode, which can be a potential feedstock for the water electrolysis where the chlorine has already been removed and would not interfere with the anodic OER. About 12 kg of NaOH is produced per hour from 1000 kg of brine feed to the process, which can contribute to the feed for electrolysis. Integrating a chlor-alkali unit can also lead to an increased water recovery from 50 to 58% while reducing the brine volume by 29% and saving on any pretreatment cost for

seawater, which can cost around US\$ 2 per kg of hydrogen.^[12] However, this can be very localised and restricted supply and may not be enough to meet the world's hydrogen needs, but can be used where available as value added product to reduce the cost of hydrogen.

Moreover, hydrogen installation units also require restricted zones around units for safety. Suppose we consider the argument of overall no or less cost difference for desalinated seawater electrolysis as compared to direct seawater electrolysis as correct. In detail, on average, a reverse osmosis plant can cost roughly US\$ 2 to produce 1 kg of desalinated water per day, when operated at scale. Since the water requirement for hydrogen production is far less than the plant capacities, it can increase the costs beyond the average due to the large scale, which can range somewhere between US\$ 2–4 per kg water.^[2] This technology mismatch and initial high capital cost makes it difficult for early start-ups and small-scale companies to establish green hydrogen production installations. In this way, since direct seawater splitting can shunt these costs, it will attract efforts from more participants towards achieving the net-zero target and boosting the green hydrogen sector. Also, looking critically into the reported economic comparison claiming the low cost of desalinated seawater vs. real seawater, we need careful reassessment due to the alarming mismatch of the size of a desalination plant and the water supply required for the electrolyzer. For example, a well-established desalination process like reverse osmosis plants requires a large installation capable of producing 10,000 to ~1 million m³ of water per day so it is cost-effective, while a 10 MW commercial electrolyzer needs only ~125 m³ of water per day.^[13] Large-size desalination plants also require more renewable energy, which puts strain on the entire system. This type of huge mismatch should be considered to compare the cost of desalinated water. The reinstallation of the desalination plants is not a practical approach, and more research is required for the capacity and mobility plants. Furthermore, the research on technological challenges arising from the complex seawater composition may also provide solutions to the present technologies, which rely on highly pure water for electrolysis. Thus, the financial and large land space bottleneck for expanding the green hydrogen sector can be eliminated by utilizing direct seawater electrolysis.

One-step seawater electrolysis alleviates the capital cost and other challenges assigned to the water treatment, but the electrolytic cell performance is still critical for this early-stage technology. Moreover, there is a dearth of catalysts that can carry out direct seawater splitting without being affected by chlorine chemistry. Additionally, the current commercial electrolyzers are not designed for direct seawater splitting as the membranes used are prone to blockage, while the system itself can corrode due to corrosive chlorine chemistry.^[11a] In recent years, significant efforts have been made to develop active and stable electrode materials to support the direct seawater electrolysis technology to avoid undesired side reactions. Strategies like heteroatom doping,^[14] surface coating,^[15] alloying,^[5] etc., have been used to develop catalysts for direct seawater splitting, which can tackle the corrosive chlorine

chemistry and prevent electrode corrosion. In our recent work, porous ultrathin sheets of nitrogen-doped nickel molybdenum phosphide (N-NiMo₃P) were synthesized with a polyanion layer on its surface consisting of phosphate and nitrate anions, which repels the negatively charged chloride anions and prevents the formation of chlorine gas, thus enhancing the performance and stability of the catalyst in seawater electrolyte.^[14] In another work, a Lewis acid layer was introduced over the surface of CoO_x to manipulate the local reaction environment. The CoO_x was coated with a layer of Cr₂O₃, which assisted in splitting the water molecule with in-situ generation of hydroxyl anions surrounding the catalyst. The in-situ generated anions cater to local alkalinity while repelling the chloride anions present in seawater, thus preventing CER and electrode corrosion.^[15] A RuMoNi electrocatalyst was synthesized for a highly efficient anodic OER having a corrosion-resistance layer consisting of NiMoO₄ with in-situ generated MoO₄²⁻, which are absorbed on the surface of the catalyst and repels the chloride anions.^[5] In recent years, there has been increasing efforts towards the development of bio-inspired catalysts. Biological enzymes have currently been the inspiration for these kinds of catalysts possessing electrocatalytic active sites with enhanced intrinsic properties. These catalysts can also be designed to have a larger surface area, improved mass transfer, and reaction efficiency. However, efforts still need to be put into developing efficient synthesis strategies with a focus on improving the stability and activity of catalysts before realizing their commercial applications.^[16] Developing efficient catalysts for direct seawater splitting has been a real challenge, but we are finally seeing the light at the end of the tunnel. The recent progress has brought us closer to the reality of a world powered by sustainable green hydrogen, still a lot of effort is required to modify and improve these materials and systems for large-scale applications, especially their compatibility in large system.

However, developing efficient and durable catalysts for direct seawater splitting has not been the only hurdle. Developing and designing low-cost and efficient electrolyzers for direct seawater splitting is also crucial. On a commercial scale, PEM, anion exchange membrane (AEM), high-temperature, and alkaline water electrolyzers (AWE) are available, but they require highly pure de-mineralized water, which means that some of the non-purified feed could be rejected.^[4,17] Moreover, the membranes used in the electrolyzers are not compatible with the complex composition of seawater, as the chloride anions can interfere with the ion transfer and corrode the metal components, which is a concern in AEMs. Furthermore, the Mg²⁺ and Ca²⁺ present in seawater can also compromise the membrane (especially in PEM) by producing salts or metal deposition, leading to performance degradation. In contrast, diaphragm materials used in AWEs are robust, and there are fewer concerns for blockage, but they either allow cations or anions to pass, which is a key hurdle to its application. High-temperature water electrolyzers, on the other hand, allow accelerated reaction kinetics and low energy loss, leading to improved efficiency. However, issues like catalyst degradation, limited availability of materials, and durability hinder its applications.^[18] Considering each type of electrolyzer's

advantages and disadvantages, electrolyzers need to be suitable and durable for direct seawater splitting. Therefore, designing the catalysts alone cannot overcome the problems associated with seawater; compatible electrolyzers also need to be designed to meet the global hydrogen demand and realize large-scale and practical applications.

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Conflict of Interests

The authors declare no conflict of interest.

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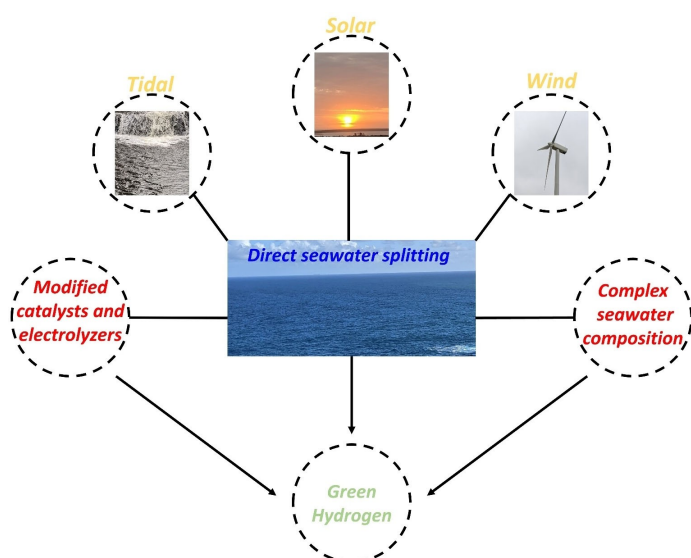
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CONCEPT



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Seawater to Green Hydrogen: Future of Green Energy

Direct seawater splitting can only be a true approach for sustainable green hydrogen production; however, it

needs a lot of effort to manipulate internal chemistry at electrodes and develop durable electrolyzers.