

Enabling the use of seawater for hydrogen gas production in water electrolyzers

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Hydrogen gas will play an increasingly critical role in developing a carbon-neutral energy infrastructure, but it will need to be produced by water splitting using renewable electricity sources. A recent study by Veroneau and Nocera in *Proceedings of the National Academy of Sciences (PNAS)* suggests an electrolyzer that produces desalinated water from abundant seawater by using forward osmosis.

Hydrogen gas production currently contributes to over 2% of global CO₂ emissions given that it is mostly produced from fossil fuels.¹ About half of the pure H₂ gas produced is used to manufacture ammonia for fertilizers, with the balance primarily used in refineries. The production of H₂ gas is expected to greatly increase to replace petroleum products used for large vehicles, ships, and airplanes. One way to reduce the carbon footprint of H₂ gas production is generating it by water splitting, using renewable energy as a source of the electricity, and evolving pure H₂ gas from the cathode and O₂ from the anode. The costs for producing H₂ by water electrolysis, however, are currently about two to four times higher than conventional methods using natural gas.¹ The main operating expense for water electrolyzers is the electricity used, but low prices of solar and wind electricity have greatly reduced costs of H₂ production from water splitting in recent years. Although the capital expenses for water electrolyzers stacks vary, approximately 25%–50% of the total is for the membrane and catalysts, with the balance for structural components.^{2,3}

Water sources and water quality are important considerations when locating and operating a water electrolysis plant. Many sites that have abundant sources of solar or wind energy are in dry, arid en-

vironments or only have seawater available as a water source. Using seawater at coastal locations therefore presents an opportunity for access to both an abundant water source and inexpensive renewable electricity.⁴ Although the cost of water produced by large-scale seawater desalination plants can be relatively small compared with the overall operating expenses,¹ the development of dedicated desalination and deionization plants solely for water electrolysis requires large capital investments as well as continued operation and maintenance. The direct use of seawater for water electrolysis without deionization presents several challenges, with the primary obstacle being the competition between the oxygen evolution reaction and chloride ion oxidation. However, most research on direct use of seawater for electrolysis has focused on the development of selective catalysts with relatively less attention on the membranes and water quality.

Veroneau and Nocera⁵ proposed using a forward osmosis (FO) membrane adjacent to the water electrolyzer cell to draw desalinated water through the membrane from seawater. Using an electrolyte that was saltier than seawater enabled water transport into the cell by the osmotic pressure across the membrane (Figure 1A). This is not the first time that the use of a thin film composite FO or reverse osmosis (RO) membrane

has been proposed to continuously transport desalinated water directly into the electrolyte,⁶ but the experimental configuration using the FO membrane in their study was unique, and the results showed a proof of concept for this approach. However, there are chemical and structural challenges for the approach presented in their study.

FO and RO membranes are not completely selective, and therefore chloride ions will pass through the membrane and be oxidized at the anode, resulting in products that can damage electrolyzer components such as chlorine gas (lower pH) and hypochlorite (higher pH). Oxidation of chloride ions on some electrode materials at high current densities can also produce primarily more oxidized chlorate and perchlorate that would need to be removed from the seawater effluents. A concentration gradient across the FO membrane will also set up a reverse solute flux leading to losses of the phosphate buffer used in their study, or other possible electrolytes, into seawater.⁷ Losses of phosphate or other electrolytes could be relevant for both economic and environmental reasons.

The specific configuration shown in the Veroneau and Nocera study for integrating the FO membrane into the system requires further structural and operational considerations. The system depicted in their study (redrawn in Figure 1A) lacked a separator or membrane between the electrodes to prevent comingling of the H₂ and O₂ gases produced, which could create an explosive gas environment. Membraneless systems have been proposed based on forcing water through electrodes to avoid mixing the gases, but those designs incur large ohmic losses due to the spacing between

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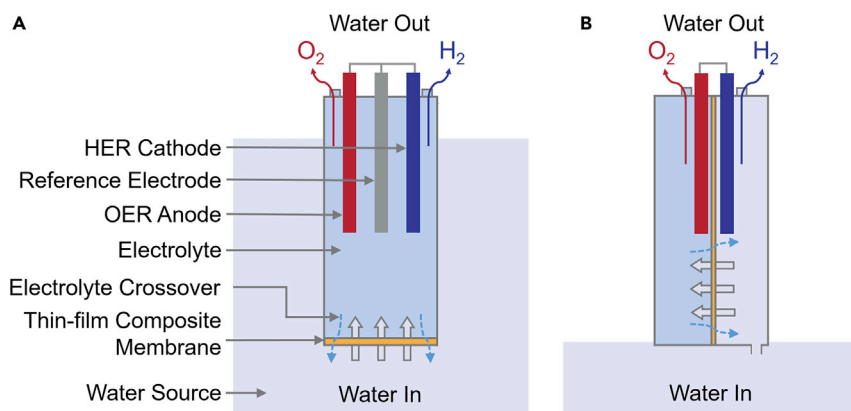


Figure 1. Schematic of the main components for two types of water electrolyzer cells that incorporate forward- or reverse-osmosis-type membranes

(A) The membrane is placed on the bottom of the cell and draws desalinated water into the electrolyte due to the higher osmotic pressure of the electrolyte. (Adapted from Veroneau and Nocera.¹)

(B) The membrane is placed between the two electrodes forming two separate chambers with the desalinated water drawn from the catholyte. (Adapted from Shi et al.³)

the electrodes that increase electrical power consumption and thus operational costs.³ The savings from avoiding full deionization of seawater in favor of FO-based membraneless designs therefore might not offset additional capital and operational expenses. The placement of the FO membrane as shown would also not be practical given that it would have a very small contact area with water because of the need to have closely spaced electrodes, although an external FO cell with a recirculating electrolyte could accomplish the same purpose of adding water into the electrolyte.

The system proposed by Veroneau and Nocera⁵ could be modified to contain an ion exchange membrane or separator between the electrodes to maintain separation of the gases produced. Water electrolyzers either have proton exchange membranes (PEMs), more generally classified as cation exchange membranes (CEMs) in the presence of other cations for applications with an acidic electrolyte, or ion-neutral separators or anion exchange membranes (AEMs) with an alkaline electrolyte to avoid gas transport between the chambers. The ion exchange

membranes have an additional advantage of enabling H₂ gas to be produced at higher pressures, which can offset expensive H₂ gas compression costs. Porous or very thin separators are less desirable because they limit pressures that can be built up between the chambers.

An alternative to ion exchange membranes or porous separators is to use a thin film composite membrane (e.g., RO or FO) placed between the electrodes that is sufficiently permeable to protons (or hydroxide ions) for balancing charge (Figure 1B).⁶ This approach replaces relatively expensive ion exchange membranes (~\$1,000/m²) with a much less expensive thin film composite membrane (< \$10/m²). An RO-based design maintains separation of the gases and enables pressure to be built up between the electrolyte chambers to concentrate the H₂ gas. Anolyte salts are contained by the RO membrane, as in the FO design of Veroneau and Nocera,⁵ and seawater is used as a catholyte. Desalinated water is refreshed into the anolyte either by its saltier composition acting as a draw solution for water in the catholyte, or through adjusting relative pressures between the chambers to obtain pressurized water

flow into the anolyte. This design also has salt ion crossover challenges due to chloride ion transport into the anolyte through the RO membrane, and salt ions that should be retained in the anolyte can leak into the seawater catholyte. Solutions are needed to minimize the crossover of unwanted ions in both of the RO- and FO-based membrane systems in Figure 1. Possible solutions include anode catalysts with very low activities with chloride ions,⁴ or catalysts with selective chloride oxidation to chlorate and perchlorate at high current densities that would not damage electrolyzer components.⁸ Chlorate and perchlorate could be removed through biological reduction in separate systems.⁹

Hydrogen production from water splitting is essential for developing a carbon neutral energy infrastructure, and it might be the next greatest technology challenge in terms of reducing capital costs, following the amazing success in reducing the costs of photovoltaic panels for electricity generation. Being able to directly use seawater in a compact water electrolyzer could greatly simplify water purification operations and reduce ancillary component costs and are therefore important considerations in advancing water electrolyzer technologies. Still greater challenges remain in addressing the ion selectivity of the membranes, catalyst needs, costs of structural components and optimization of the architecture. Hydrogen gas, because of its importance in fertilizer production, as well its planned uses for large transport vehicles, will need to be produced more economically and by processes that use only carbon-neutral energy sources.

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Turning up the heat on photocatalytic ammonia production

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Cheap, scalable, and efficient solar energy conversion technology is a promising alternative to the existing ammonia production industry. In the inaugural issue of *Chem Catalysis*, Zheng and co-workers address this by reporting the efficient production of ammonia from nitrogen by using a nature-inspired iron-molybdenum disulfide photocatalyst at elevated temperatures.

Ammonia production via the Haber Bosch process is one of the largest chemical industries (by volume) in the world.¹ The majority of this ammonia is used in the agriculture industry in fertilizers for food in order to feed the ever-growing global population.² Since its implementation in the early 1900's, the process has grown in scale to now account for 1%–2% of the annual global energy consumption.² Ammonia production is currently centralized due to the high energy demands, which results in additional monetary and energy costs from delivery to the areas of consumption. The transformation that converts nitrogen gas and hydrogen gas takes place in reactors containing iron-based hetero-

geneous catalysts (with additional metal additives as promoters) at high temperatures and pressures. These energy-intensive conditions are necessary to overcome the high activation barrier needed to break the strong $N\equiv N$ triple bond. The net reaction, however, is exothermic and thus becomes more unfavorable at elevated temperatures. Some ongoing research efforts aim to uncover catalyst systems that are more active than the commercial iron-based materials (such as $Co_3Mo_3N^3$) that might allow these processes to occur at lower temperatures, thus lowering the overall energy demand.

Generation of the necessary hydrogen gas for ammonia production is also

problematic. Steam reforming of methane in natural gas is commonly used to produce hydrogen for the Haber-Bosch process, which is energy intensive in itself and also produces vast quantities of carbon dioxide. In fact, the ammonia production industry accounts for 1.2% of the global carbon dioxide emissions.⁴ These collective issues point to the need for alternative technology that relies on a different source of energy other than fossil fuels in order to support the growing demand for ammonia.

Fortunately, there is a massive nuclear fusion reactor 93 million miles above our heads that has provided the planet with nearly all its energy since before humans were around. Solar energy conversion technology could be implemented at many different points in the overall ammonia production process (Figure 1).¹ For instance, photovoltaic (solar-to-electricity) technology combined with electrocatalytic water splitting could be used to supplement the hydrogen needed for the Haber-Bosch process.

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