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

Bruce E. Logan*, Le Shi, and Ruggero Rossi Department of Civil & Environmental Engineering, Penn State University, University Park, PA, 16802, USA.

*Corresponding author. Email: blogan@psu.edu

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 *PNAS* suggests an electrolyzer that produces desalinated water from abundant seawater using forward osmosis.

Hydrogen gas production currently contributes to over 2% of global CO₂ emissions as it is mostly produced from fossil fuels.² 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 splitting pure water, 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.² 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% to 50% of the total is for the membrane and catalysts, with the balance for structural components.^{4, 5}

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 environments 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.⁶ While the cost of water produced by large-scale seawater desalination plants can be relatively small compared to the overall operating expenses² the development of dedicated desalination and deionization plants solely for water electrolysis plants 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 Nocera¹ 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,³ 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 the electrodes that increase electrical power consumption and thus operational costs.⁵ 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 as it would have a very small area due to 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 Nocera¹ 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 as 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**).³ This approach replaces relatively expensive ion exchange membranes (~\$1000 USD/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 Nocera¹, 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,⁶ 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 may 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, due to 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.



Fig. 1. Schematic of the main components for two types of water electrolyzer cells that incorporate active layer forward or reverse osmosis type membranes. (A) The membrane placed on the bottom of the cell and draws desalinated water into the combined 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)

ACKNOWLEDGMENTS

The authors acknowledge funding from the National Science Foundation grant CBET-2027552, and by USAID and NAS through Subaward 2000010557. Any opinions, findings, conclusions, or recommendations expressed in this article are those of the authors alone, and do not necessarily reflect the views of USAID or NAS.

- 1. Veroneau, S.S. and Nocera, D.G. (2021). Continuous electrochemical water splitting from natural water sources via forward osmosis. Proc. Nat. Academy Sci. 118, e2024855118.
- 2. Birol, F. (2019). The future of hydrogen: seizing today's opportunities. https://www.iea.org/reports/the-future-of-hydrogen_
- 3. Shi, L., Rossi, R., Son, M., Hall, D.M., Hickner, M.A., Gorski, C.A., and Logan, B.E. (2020). Using reverse osmosis membranes to control ion transport during water electrolysis. Energy Env. Sci. 13, 3138-3148.
- Mayyas, A.T., Ruth, M.F., Pivovar, B.S., Bender, G., and Wipke, K.B. (2019). Manufacturing cost analysis for proton exchange membrane water electrolyzers. National Renewable Energy Lab. (NREL), Golden, CO (United States). <u>https://www.osti.gov/servlets/purl/1557965</u>.
- 5. Esposito, D.V. (2017). Membraneless electrolyzers for low-cost hydrogen production in a renewable energy future. Joule. 1, 651-658.
- 6. Dresp, S., Dionigi, F., Klingenhof, M., and Strasser, P. (2019). Direct electrolytic splitting of seawater: Opportunities and challenges. ACS Energy Lett. 4, 933-942.
- 7. Phillip, W.A., Yong, J.S., and Elimelech, M. (2010). Reverse draw solute permeation in forward osmosis: Modeling and experiments. Environ. Sci. Technol. 44, 5170-5176.
- 8. Radjenovic, J. and Sedlak, D.L. (2015). Challenges and opportunities for electrochemical processes as next-generation technologies for the treatment of contaminated water. Environ. Sci. Technol. 49, 11292-11302.
- 9. Logan, B.E., Wu, J., and Unz, R.F. (2001). Biological perchlorate reduction in high-salinity solutions. Water Res. 35, 3034-3038.