

Producing Hydrogen and Fresh Water from Brackish Water Desalination via Electrodialysis

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Nowadays scientists and communities are particularly worried about climate change and the transition towards renewable energies is a matter of crucial importance. In this context, European Community is strongly promoting the production of green hydrogen, i.e. the electrolysis of water coupled with renewable electrical sources. In addition to the energy issue, United Nations have identified the lack of water as another big issue for modern society. Electrodialysis (ED) is an electro-membrane process able to desalinate a salty feed by the application of an external power supply. It takes advantage of the use of ionic exchange membranes which allow a controlled separation of ions from the salty feed to obtain freshwater and brine as outputs.

The present work tries to address the above issues by proposing the simultaneous production of fresh water and hydrogen with an integrated hydrogen-electrodialysis (HED) unit. The aim of the present work is that of assessing the economic feasibility of the process. To this purpose, a techno-economic model has been developed to predict the behaviour of the HED unit. The model is able to predict experimental data and should be regarded as a simple yet reliable tool to assess the process economic feasibility. Preliminary analyses suggest that the simultaneous production of hydrogen and fresh water may be profitable.

1. Introduction

The non-sustainable energy production with fossil fuels, the increase in energy demand caused by a growing world population and by the improved living standards are only a few of the main reasons for today energy crisis. In particular, there is an urgent need to stop the use of fossil fuels, as they are primarily responsible for the release of greenhouse gases, the main causes of global warming and atmospheric pollution.

Instead of fossil fuels, the focus must be on obtaining energy from green and zero-emission resources, in order to change the future of the world. Renewable sources are one of the ways for producing green energy and their intrinsic discontinuity can be overcome by the use of energy storage systems. In particular, hydrogen is the type of storage with the greatest future perspective. Actually, the hydrogen may be the key to a future green revolution, towards zero-emission energy production. For instance, European Union has identified hydrogen as the key driver to achieve CO₂ neutrality by 2050 (European Commission, 2022). Another main problem of today societies is the interactions and the nexus related to the energy crisis and security with food and potable water that requires the improvement of strategic and integrated policies between countries (de Amorim et al., 2018). Concerning the drinking water, the United Nations (UN) reports wide inequalities in access to water around the world due to inaccessibility or to the degradation of the water source, with a consequent fail in the fundamental human rights (UN Water 2021). For example, only 75% of people living on earth have access to safe drinking water: unsafe water is responsible for 6% of the world population's death (Ritchie and Roser, 2021). In this framework, electrodialysis is a technology capable of producing desalinated water from saline solutions. It is a widely consolidated technology in the literature for the production of water (Al-Amshawee et al., 2020). The core idea of the present work comes from the above considerations and it is to combine the production of hydrogen with the production of freshwater within one integrated technology called Hydrogen-Electrodialysis (HED).

Referring to the basic operation of the ED, it is a membrane technology composed of repetitive units named cell pairs. A cell pair consists of an anionic membrane (AEM) and a cationic membrane (CEM) between which there

are spacer-filled channels hosting the concentrated and diluted solution (Gurreri et al., 2021). In particular, the system is externally coupled to a power supply generating an electrical field at the electrodes placed at the end of the ED stack. Particularly, the electron flux in the external circuit is transformed into ionic fluxes, through the redox reactions occurring at the electrodes. Overall, the salty water feeding both channels (i.e. the concentrated and the diluted) is desalinated due to the migrative ionic fluxes at the cost of the adjacent solution that concentrates, thus producing a waste brine and fresh water at the outlet of the concentrated and the diluted channels, respectively. The technology is constituted by few components and auxiliaries, such as pumps, electrodes and polymeric membranes and its impact on the environment is negligible compared to the electric energy to be supplied to the unit (Vineyard et al., 2021). However, the latter impact can be significantly reduced by coupling the system with renewable sources. Regarding simultaneous hydrogen and water production, however, there are no examples in the literature except for the paper by Alshebli et al. (2023). In particular, they are the only ones that proposed this technology by coupling ED for the desalination of sodium sulphate (Na_2SO_4) solutions with hydrogen production. In this context, the present work proposes the coupling of ED for desalination of brackish waters with hydrogen production. The present work aims to assess the economic feasibility of the process, and consequently its pioneering application.

2. Methods and model

The water treated is brackish water (BW), with an inlet concentration of 5 g L^{-1} , and the purpose of the dilution is to reach a concentration target of 0.5 g L^{-1} . The stack is assumed $1 \text{ m} \times 1 \text{ m}$, assembled with 1000 cell pairs and able to treat a total flow rate of $98.1 \text{ m}^3 \text{ h}^{-1}$, with a velocity of 5 cm s^{-1} per channel.

However, a stack with only one cathode is unable to produce a significant amount of hydrogen. Industrial electrolyzers consist of a high repetition of cathodes and anodes to maximise hydrogen production. For this reason, the idea is to stack several electro dialysis units in a single vessel, starting always with the same total number of cell pairs (i.e. 1000) divided up for each electrode couple.

The proposed analysis defines an R-factor as the ratio between the number of cell pairs N_{cp} (fixed at 1000), and the number of electrodes minus one. In formula:

$$R = \frac{N_{cp}}{(N_{el} - 1)} \quad (1)$$

A schematic representation of the system and the corresponding R factor is shown in Figure 1.

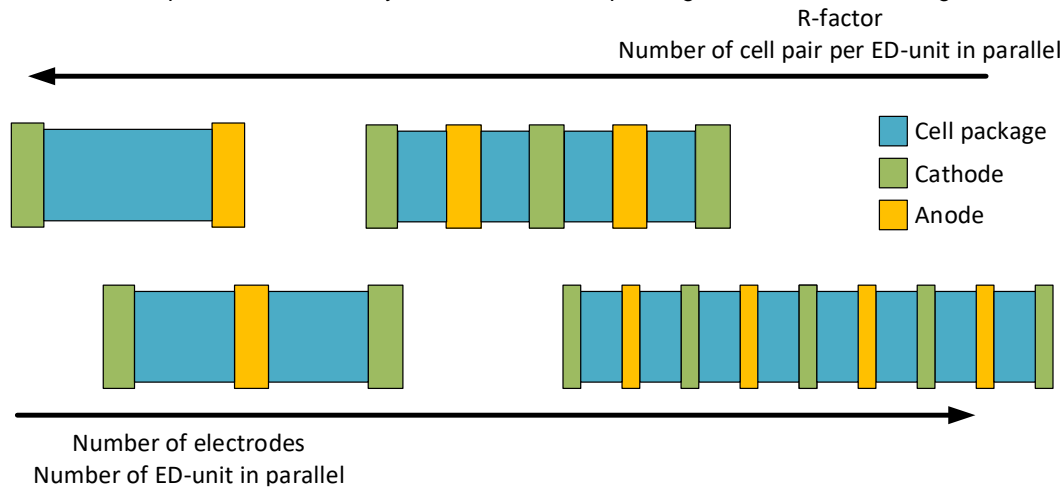


Figure 1: Schematic representation of parallel ED-units for hydrogen production along with the R-factor indication. The number of Electrodes inserted in the stack increases towards the right, with the consequent increase in the number of ED-units in parallel (R is decreasing). Conversely, moving from the right to the left, the lower the number of ED-units, the lower the number of electrodes and the higher the R-factor.

When R increases, the number of cathodes of the system and the number of ED-unit repetitions decreases, and consequently, the number of cell pairs per each ED-unit increases. Just to give an example, for R equal to 1000, one has 1000 cell pairs packed between a single cathode and anode as the first stack on the left-up of Figure 1. When R decreases, the number of electrodes inserted in the stack increases and the cell pairs are divided up in more ED-units working in parallel. The lower limit is R equal to 1, corresponding to a system composed of the repetition of 1000 ED-units, with 501 cathodes and 500 anodes constituted by 1 cell pair each.

2.1 Techno-economic model

The techno-economical model has been implemented on Excel VBA. The adopted technical model of the ED technology is widely discussed in Campione et al. (2019). It solves the mass balances and the electrical equations (each one relevant to a branch of the equivalent electrical circuit). The stack constituted of membranes and spacer-filled channels are represented as ohmic resistances. The concentration difference produced in the ED unit at the membrane interphases corresponds to a chemical potential difference to be exceeded to desalinate the brackish water.

The electrodes, the electrode solution and the additional end membrane (used for separating the cell package by the electrode) constitute the blank resistance. It is typically constant and negligible for industrial scale ED systems. This is not the case in HED where the blank resistance is not constant, due to the different reactions at the electrodes, nor negligible as a large number of electrodes is considered (i.e. R close to 1). Even though specific equations exist for modelling the electrodes phenomena (e.g., Butler-Volmer equation), in this preliminary work the electrode voltage drop is assumed constant to a fixed value of 1.7 V, a value included between typical alkaline electrolyser voltage (IRENA, 2021).

As far as economic aspects are concerned, the feature of the system and the output values of the technical model are used as input for estimating the capital expenditure and the operative costs. The Fixed Capital Investment (FCI, €) takes into account the direct costs (equipment) and the labour costs for construction (estimated as 10 % of the equipment costs). Conversely, the yearly manufacturing expenditures (Opex, € year⁻¹) take into account the day-to-day expenditures such as chemicals, electricity etc. and other costs evaluated as the 4 % of the FCI (Giacalone et al., 2019). Some of the parameters used for the economic analysis are reported in Table 1.

Table 1 Input parameters

Economic parameter	Value	Units
Plant lifetime n	20	year
Discount rate r	3	%
Salvage value S	10% of FCI	€
Working hour	8000	$\text{h} \cdot \text{year}^{-1}$
Membrane lifetime t_m	7	year
Electrode cost $C_{\text{ELECTRODE}}$	300	$\text{€} \cdot \text{m}_{\text{el}}^{-2}$
Electricity cost $C_{\text{ELECTRICITY}}$	0.07	$\text{€} \cdot \text{kWh}^{-1}$
Water price C_w	variable	$\text{€} \cdot \text{m}_w^{-3}$
Hydrogen price C_{H_2}	variable	$\text{€} \cdot \text{kg}_{\text{H}_2}^{-1}$
Oxygen price C_{O_2}	0.1	$\text{€} \cdot \text{kg}_{\text{O}_2}^{-1}$
Stack length L	1	m
Stack width b	1	m
Spacers width δ	300	μm
Number of cell pairs N_{CP}	1000	-
Inlet velocity of the feed v	5	$\text{cm} \cdot \text{s}^{-1}$
Active area of membrane and electrode	1	m^2

The project lifetime n is assumed equal to 20 years, a conservative value due to the novelty of the technology compared to the 40 years of the existing plant (e.g. electro dialysis reversal (EDR) plant situ in Pantelleria, Italy, and operated since 1975 to 2014). The discount rate r and the salvage value have been considered equal to 3 % and the 10 % of FCI, respectively. Furthermore, a straight-line method has been used for the depreciation and the FCI is entirely made at the start of year 0. It is also the year of starting operation of the plant. Finally, a cash flow diagram has been elaborated for the estimation of the main economic outputs as the sum of all the expenditures and all the revenues. At the end of its lifetime, the value registered by the cash flow is known as Net Present Value (NPV) and its value indicates how much remunerable the plant is. The NPV is defined as the sum of all the discounted cash flows. In formula:

$$\text{NPV} = \sum_{k=0}^n \frac{C_{\text{H}_2} \cdot \dot{Q}_{\text{H}_2} + C_{\text{O}_2} \cdot \dot{Q}_{\text{O}_2} + C_w \cdot \dot{V}_w - \text{FCI} - \text{Opex}}{(1+r)^k} \quad (2)$$

where C is the product price, \dot{Q} is the mass flow rate in kg year^{-1} , \dot{V} is the volumetric flow rate in $\text{m}^3 \text{year}^{-1}$ and the subscript H_2 , O_2 and w refers respectively to hydrogen, oxygen and water.

Levelized costs are parameters of interest in economic analyses. A levelized costs is the price at which a product should be sold in order to have a NPV equal to zero at the end of project lifetime (i.e. n years in the present case). In the present work we consider two main products being Hydrogen and freshwater: as a consequence, two different levelized costs can be defined: levelized cost of water (LCOW) and levelized cost of hydrogen (LCOH) defined as in eq. (3) and eq. (4):

$$\text{LCOW} = \frac{\sum_{k=0}^n \frac{\text{FCI} + \text{Opex} - C_{\text{O}_2} \cdot \dot{Q}_{\text{O}_2} - C_{\text{H}_2} \cdot \dot{Q}_{\text{H}_2}}{(1+r)^k}}{\sum_{k=0}^n \frac{\dot{V}_w}{(1+r)^k}} \quad (3)$$

$$\text{LCOH} = \frac{\sum_{k=0}^n \frac{\text{FCI} + \text{Opex} - C_{\text{O}_2} \cdot \dot{Q}_{\text{O}_2} - C_w \cdot \dot{V}_w}{(1+r)^k}}{\sum_{k=0}^n \frac{\dot{Q}_{\text{H}_2}}{(1+r)^k}} \quad (4)$$

Clearly, in order to evaluate the LCOW is necessary to fix the price of the other products (i.e. hydrogen and oxygen) since more than one product is present in the plant. Similarly, the price of water and oxygen are to be fixed to calculate the LCOH.

3. Technical and cost analysis

ED and electrolyzers are energy-demanding processes, the first requires energy for promoting the migrative flux of ions, whilst the second is for enabling the redox reactions. In ED, in order to achieve the concentration target of 0.5 g L^{-1} at the outlet of the $1 \text{ m} \times 1 \text{ m}$ stack, it is necessary to have a determinate current flowing in the system equal to 92 A . This constraint does not apply to electrolyzers which can reach current densities of $0.2 - 0.8 \text{ A cm}^{-2}$ (Chatenet et al., 2022). The HED technology is a combination of the two processes and involves a higher energy requirement (compared to the single technology), necessary for the hydrogen and oxygen evolution reactions (requiring an additional 1.7 V of voltage) and for the freshwater production. Figure 2 plots the trends of the voltage and power for the three different technologies versus the R-factor. The equivalent electrolyser is assumed to operate at the same current of the HED/ED stack and is constituted of 1000 cells, thus, there is no dependence of voltage and power on the R factor. The ED system corresponds to the case $R=1000$, i.e. the unit constituted by two electrodes and one single cell package of 1000 cell pairs. In the case of HED the system is constituted by several cell packages separated by electrodes, each cell package is a stand-alone ED-unit, and the voltage required by each ED-unit is represented in Figure 2a. When R is equal to 1, the voltage required by a single ED-unit of HED system is 2.7 V , greater than an equivalent single-cell of an electrolyser because comprehensive of desalination and hydrogen production voltage. Greater the R, larger the voltage required by the single ED-unit, that becomes the same of the ED stack for $R=1000$ and requiring almost 500 V . An opposite trend is shown in Figure 2b, where the total power required by the HED system is plotted. As R increases, the difference between the ED and HED power becomes smaller and smaller so that the two curves overlap for R higher than 100. However, there is also a consequent reduction in the hydrogen production.

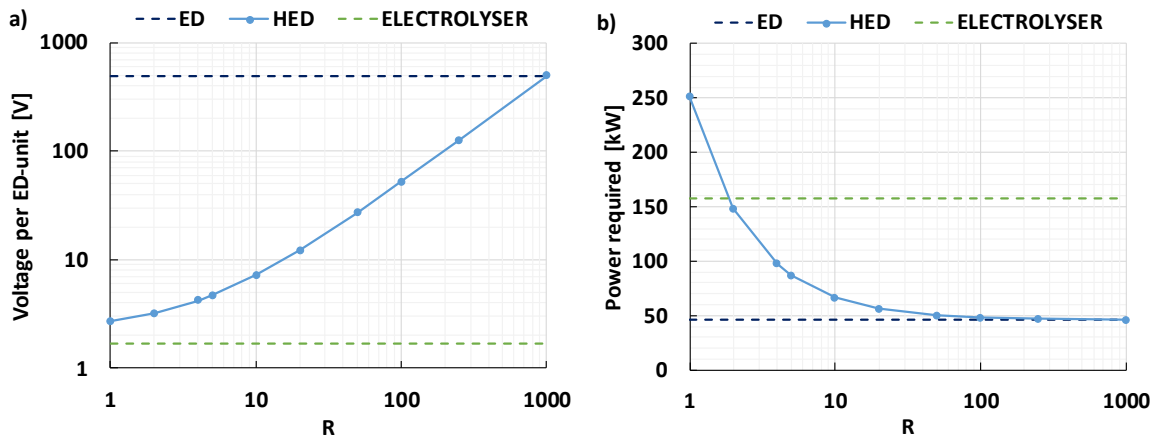


Figure 2: Required voltage (a) and power (b) as a function of the R-factor for the ED, HED and Electrolyser systems.

The two HED-ED power curves tend to overlap for higher R values because as R increases, desalination requires the greatest energy contribution, making the hydrogen production energy negligible. The largest potential loss is due to the electrodes when R equals to 1 because there is a high amount of hydrogen produced. As the cell package increases in cell pairs (i.e. R increases), hydrogen production decreases and practically when R becomes higher than 50, overall hydrogen production is so low that it becomes a negligible dissipative effect for the system.

Figure 3a shows the trends of LCOW and LCOH as a function of R. The dashed curves refer to the ED and electrolyser systems: also in this case, the LCOH for the electrolyser is constant because it is independent of the R factor. The continuous curves are related to the HED technology: the levelized costs are calculated by fixing the other product selling price equal to zero (e.g., the LCOW is calculated considering $0 \text{ € kg}^{-1}_{\text{H}_2}$ as selling price for hydrogen). As far as the trends of LCOW are concerned, these follow the trends shown by the power in Figure 2b. From the perspective of water production, the addition of many electrodes requires higher energy costs and higher capital expenditure, which means that if hydrogen is not priced, water must be sold at a value of $0.49 \text{ € m}^{-3}_{\text{w}}$ for $R=1$. As R increases, its cost value asymptotically approaches $0.1 \text{ € m}^{-3}_{\text{w}}$, which corresponds to the cost value of a typical unit consisting of a single cell package enclosed by two electrodes, i.e., the case of a standard ED stack ($R=1000$). Conversely, LCOH exhibits a minimum for R equal to 1, but the progressive decrease in the cathodes' number (corresponding to an increase of R) leads to decrease in the hydrogen production and the LCOH drastically rises. However, the LCOH is about $11.9 \text{ € per kg}_{\text{H}_2}$ for the case of $R=1$, no selling price for water is considered and all the expenses of the system are held by hydrogen production.

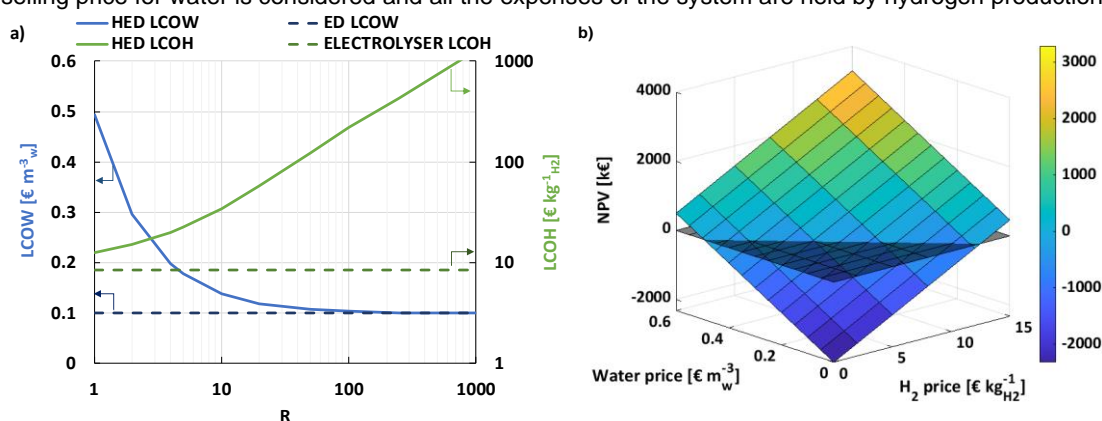


Figure 3: a) Trend of the LCOW and LCOH versus the R-factor. b) NPV versus selling prices of water and hydrogen for $R=1$: the horizontal grey surface highlights the plane where NPV is zero.

Considering the scenario where hydrogen production is the maximum (i.e. $R=1$), Figure 3b plots the NPV for the case in which different prices for water and hydrogen are considered. Clearly, the larger the selling prices, the larger the NPV. However, as shown by the grey horizontal plane (e.g., the NPV plane equal to zero), there is a part of the graph where the NPV is always negative, and no earning occurs. Water price is the most affecting price in the technology, a small increase causes a consistent variation in the NPV, this is due to the huge amount of fresh water produced, corresponding to almost 45 m^3 of fresh water per hour. Hydrogen average cost typically ranges between 4.24 to $10.89 \text{ € kg}^{-1}_{\text{H}_2}$ (Parkinson et al., 2019) depending on the kind of renewable electrical sources, meanwhile the cost of water production with ED is estimated to be almost $0.38 \text{ € m}^{-3}_{\text{w}}$ for a salinity feed of 5 g L^{-1} (Generous et al., 2021). Even if the LCOH found for the HED technology is of $11.9 \text{ € kg}^{-1}_{\text{H}_2}$, this value could be reduced increasing the cost of water. The economic analysis clearly indicates that it is necessary to increase the hydrogen productivity (about 1.73 mol h^{-1} per m^2 of electrode surface). This low value is due to the fixed current that has to be applied in the system for the desalination purpose: as a consequence, a higher feed concentration would yield an increase in the current density, i.e., in the hydrogen productivity. Accordingly, the reduction of the LCOW and LCOH would be targetable for the examined system.

4. Conclusions

Turning into eco-friendly policies can reduce or even solve the dramatic problem of global warming. The development of technologies able to produce hydrogen is strongly promoted by European countries and the United Nations. Furthermore, the need for fresh water is another topic of Agenda 21. This work focused on the economic feasibility of a unit able to produce simultaneously hydrogen and fresh water from brackish water. The proposed technology is an electrodialysis unit where the redox reactions are aimed at producing H_2 and O_2

evolutions. Although the idea is technically feasible, the low hydrogen productivity due to a single cathode affects the system. For these reasons, a several repetition of units of electrodialysis, divided up the initial cell package and sharing the electrodes with the adjacent units, is suggested to increase the amount of hydrogen produced. The technical analysis carried out shows that the hydrogen production clearly affects the energetic demand of the process when several electrodes are inserted in the ED stack. Conversely, when the number of electrodes added to the stack is lower, the contribution of hydrogen production becomes a negligible dissipative term. As a consequence, when the maximum number of electrodes is assembled, the LCOH is the minimum and is equal to 11.9 € kg⁻¹H₂ (without considering a selling price for desalinated water). As expected, when the number of electrodes decreases, the LCOH drastically increases. LCOW (considering no selling price for hydrogen) increases to a value of 0.47 € m⁻³_w when the system is equipped with several electrodes, due to the large capital cost of the additional electrodes and the relevant significant energy demand. Although the price of hydrogen could reach lower values when the water is also sold, a limit of this system is the small current density fixed by the target concentration of the outlet fresh water. With this respect, operating the system with higher feed concentration (e.g. seawater) would require higher currents thus leading to higher hydrogen productivity and possibly to lower levelized costs. However, this has to be proven and will be matter of a future work.

References

- Al-Amshawee, S., Yunus, M.Y.B.M., Azoddein, A.A.M., Hassell, D.G., Dakhil, I.H., Hasan, H.A., 2020. Electrodialysis desalination for water and wastewater: A review. *Chemical Engineering Journal* 380, 122231. doi.org/10.1016/j.cej.2019.122231
- Alshebli, R.F., Yuzer, B., Bicer, Y., 2023. Experimental investigation of simultaneous hydrogen production and desalination via electrodialysis process. *International Journal of Hydrogen Energy* S0360319922058207. doi.org/10.1016/j.ijhydene.2022.12.104
- Campione, A., Cipollina, A., Bogle, I.D.L., Gurreri, L., Tamburini, A., Tedesco, M., Micale, G., 2019. A hierarchical model for novel schemes of electrodialysis desalination. *Desalination* 465, 79–93. doi.org/10.1016/j.desal.2019.04.020
- Chatenet, M., Pollet, B.G., Dekel, D.R., Dionigi, F., Deseure, J., Millet, P., Braatz, R.D., Bazant, M.Z., Eikerling, M., Staffell, I., Balcombe, P., Shao-Horn, Y., Schäfer, H., 2022. Water electrolysis: from textbook knowledge to the latest scientific strategies and industrial developments. *Chem. Soc. Rev.* 51, 4583–4762. doi.org/10.1039/D0CS01079K
- de Amorim, W.S., Valduga, I.B., Ribeiro, J.M.P., Williamson, V.G., Krauser, G.E., Magtoto, M.K., de Andrade Guerra, J.B.S.O., 2018. The nexus between water, energy, and food in the context of the global risks: An analysis of the interactions between food, water, and energy security. *Environmental Impact Assessment Review* 72, 1–11. doi.org/10.1016/j.eiar.2018.05.002
- European Commission, Directorate-General for Energy, Breitschopf, B., Zheng, L., Plaisir, M., Bard, J., Schröer, R., Kawale, D., Koornneef, J., Melese, Y., Schaaphok, M., Gorenstein Dedecca, J., Bene, C., Cerny, O., Gérard, F., 2022. The role of renewable H₂ import & storage to scale up the EU deployment of renewable H₂: report. Publications Office of the European Union. doi.org/10.2833/727785
- Generous, M.M., Qasem, N.A.A., Akbar, U.A., Zubair, S.M., 2021. Techno-economic assessment of electrodialysis and reverse osmosis desalination plants. *Separation and Purification Technology* 272, 118875. doi.org/10.1016/j.seppur.2021.118875
- Giacalone, F., Papapetrou, M., Kosmadakis, G., Tamburini, A., Micale, G., Cipollina, A., 2019. Application of reverse electrodialysis to site-specific types of saline solutions: A techno-economic assessment. *Energy* 181, 532–547. doi.org/10.1016/j.energy.2019.05.161
- Gurreri, L., Filingeri, A., Ciofalo, M., Cipollina, A., Tedesco, M., Tamburini, A., Micale, G., 2021. Electrodialysis with asymmetrically profiled membranes: Influence of profiles geometry on desalination performance and limiting current phenomena. *Desalination* 506, 115001. doi.org/10.1016/j.desal.2021.115001
- IRENA, 2021. Making the breakthrough: Green hydrogen policies and technology costs. International Renewable Energy Agency.
- Parkinson, B., Balcombe, P., Speirs, J.F., Hawkes, A.D., Hellgardt, K., 2019. Levelized cost of CO₂ mitigation from hydrogen production routes. *Energy Environ. Sci.* 12, 19–40. https://doi.org/10.1039/C8EE02079E
- Ritchie, H., Roser, M., 2021. Clean Water and Sanitation. *Our World in Data*. < https://ourworldindata.org/clean-water-sanitation > accessed 10.07.2023.
- UN Water (Ed.), 2021. Valuing water, The United Nations world water development report. UNESCO, Paris, < https://www.unwater.org/publications/un-world-water-development-report-2021 > accessed 10.07.2023.
- Vineyard, D., Hicks, A., Karthikeyan, K.G., Davidson, C., Barak, P., 2021. Life cycle assessment of electrodialysis for sidestream nitrogen recovery in municipal wastewater treatment. *Cleaner Environmental Systems* 2, 100026. doi.org/10.1016/j.cesys.2021.100026