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Techno-Economic Assessment of Electrodialysis with Bipolar Membranes for Hydrogen Production

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The research for low-pollution fuels has shown that hydrogen can replace fossil fuels in different sectors such as transport, industry and energy production. As an alternative to water electrolysers, hydrogen can be produced from electro-membrane processes, which are generally used for desalination, energy recovery as well as for chemicals production. The technical feasibility of using such processes for the production of green hydrogen has already been demonstrated. Hydrogen-ElectroDialysis with Bipolar Membrane (H-EDBM), which couples hydrogen production with acid and base solutions generation, resulted particularly advantageous thanks to the higher current densities involved. The present work aims to conduct a thorough investigation of the H-EDBM process. A multi-scale model was modified to account for the electrode behaviour and used to simulate an industrial-scale H-EDBM unit working at 1000 A m^{-2}, for which the NaOH stream target was 1 M concentrated. To increase the hydrogen yield, additional electrodes were inserted between the stack repeating units of ion exchange and bipolar membranes (known as triplets). A techno-economic analysis was carried out by varying the number of electrodes added (i.e., without changing the NaOH production rate). Results appear to be very promising even in the case of a conservative economic scenario. The results show a levelized cost of NaOH of 0.26 € kg^{-1}_{NaOH} and a net present value of up to 60 M€ for a plant size of 50 m^3 h^{-1} of NaOH.

1. Introduction

The energy transition towards a more sustainable society is one of the most pressing challenges of recent years. It is driven by the urgent need of mitigating climate changes, reducing greenhouse gas emissions, and ensuring sustainable energy access for future generations. As the energy demand is increasing and fossil fuel reserves are destinated to run out shortly, there is an increasing focus on renewable energy sources and on low-pollution fuels (Nicoletti et al., 2015). Hydrogen is considered one of the most promising alternatives to fossil fuels in decarbonising sectors such as transport, industry, and power generation. Indeed, hydrogen has a high specific energy (three times more than gasoline), it can be used in a variety of applications, and, more important, its combustion does not produce greenhouse gases (Capurso et al., 2022). However, hydrogen is not present on Earth, representing an energy vector that must be produced sustainably to overcome the above-mentioned issues. Water electrolysis powered by renewable energy sources appears the most promising option to generate green hydrogen, but the current production cost is still high (i.e., 4-8 € kg^{-1}), limiting its widespread (Yue et al., 2021).

Recent studies have focused on promoting hydrogen formation in electro-membrane processes used for desalination, energy recovery from salinity gradients as well as acids and base streams production. These processes such as Electrodialysis (ED), Reverse Electrodialysis (RED) and Electrodialysis with bipolar membranes (EDBM) are usually adopted for the traditional water treatment industry, and, more recently, in the valorisation of wastewater streams via Zero or Minimal Liquid Discharge (ZLD or MLD) approaches, to reduce the impact of industrial plants (Cipolletta et al., 2021).

Moreover, these processes have been also suggested as a way to produce hydrogen, thanks to the presence of electrodes. For instance, Chen et al. (2017) studied the RED process and specifically, the conversion of a salinity gradient power into electricity and hydrogen, using titanium electrodes (coated with ruthenium and

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iridium) and hydrochloric acid and sodium hydroxide as catholyte and anolyte, respectively. Results demonstrated that the power density and hydrogen production rate both depend on the salt content of the feed solutions. Later, Pellegrino et al., (2023), experimentally tested the same technology for different configurations, such as ED, short-circuit RED and Assisted-RED. Although the process is feasible from a technical point of view, the hydrogen productivity is still low, due to the inherent low current densities of the system. Campisi et al. (2024) propose to insert additional shared electrodes between the repetitions of Ion Exchange Membranes (IEMs) within an ED unit to increase the active area of electrodes. As a consequence, the hydrogen yields increased and a Levelized Cost of Hydrogen of 3.4 € kg^{-1}_{H2} was obtained when considering favourable conditions. EDBM is an interesting electro-membrane process, which enables chemicals production, such as HCl and NaOH, starting from freshwater and the corresponding salt solution (i.e., NaCl), by applying an electrical potential to the external electrodes. The peculiarity of the process is the employment of Bipolar Membranes (BMs) for which the water dissociation is promoted. The H^+ and the OH^- migrate into the two adjacent compartments where HCl and NaOH are formed (i.e., the acid and base compartment, respectively). The acid and base compartments are separated from one side by the BM and from the other by the anion (AEM) and cation (CEM) exchange membranes, respectively, which encase the salt compartment. A repetition of BM, CEM and AEM and the compartments of acid, base and salt is called triplet. An EDBM unit is generally constituted by several repetitions of triplets placed between two electrodes.

The possibility of simultaneously producing chemicals and hydrogen from a salt solution via EDBM (i.e., H-EDBM) was first proposed by Pellegrino et al. (2024). An experimental study on a laboratory scale was conducted with a stack 10 x 10 cm^2 and 5 triplets assembled, highlighting that significant high current densities (up to 1000 A m^{-2}) can be achieved with faradic efficiency of 98% and hydrogen productivity of 18.4 mol m^{-2} h^{-1}. Moreover, several stack configurations, which differed for the used end-membranes, were tested and economically compared, showing the benefit of using BMs as end-membranes.

Based on the successful demonstration of the feasibility of H-EDBM, the aim of the present work is to conduct a more in-depth technical and economic investigation of the process potentials. To this aim, a multi-scale model capable of comprehensively simulating the EDBM process was purposely modified to accounts for the behaviour of electrodes and validated with experimental data. In addition, appropriate economic equations were introduced to estimate the operative and capital costs of EDBM, as well as to identify the plant profitability and the production costs of the products.

2. Techno-economic model

2.1 The EDBM model and simulated unit

The EDBM model was published in the work of Virruso et al. (2024) and here adopted for the simulation of the H-EDBM process. The model has a multi-scale structure with distributed parameters along the main flow direction (i.e., axial). A total of six different sub models, properly collected, describe the whole behaviour of the process from the channel/membrane scale (the lowest scale) to the external hydraulic circuit level (the highest scale). The model takes into account also non-ideal phenomena such as concentration polarization, diffusive fluxes and parasitic currents.

A commercial EDBM unit, FT-ED-1600-3 from FuMA-Tech GmbH (Germany) was simulated, presenting an active membrane area of 34.5 x 45.4 cm^2, and a spacer thickness of 350 μm. The open-loop process configuration was adopted to conduct the simulation since it enables the continuous production of acid and base stream keeping high performance. The acid and base solutions are initialized at very low concentrations (i.e., 0.05 M), while the salty feed has a concentration of 1 M. gPROMS ModelBuilder® was adopted to implement the model and solve the relevant equations.

2.2 Economic model and main key performance indicators

The process model was coupled with an economic model which calculates capital and operative costs in accordance with the correlations employed by (Virruso et al., 2024). Contrary to what was previously done in the analyses for EDBM, an additional electrode cost of 300 € m^{-2} was considered among the capital costs, due to the requirement of specific electrodes for hydrogen production; this cost is calculated assuming half the cost of an electrolyzer (270 € kW^{-1}, IRENA, 2020). Furthermore, water costs were also taken into account, both for (i) freshwater (needed to produce the chemicals) and (ii) the stoichiometrically reacted water to make the hydrogen. The sum of the annualised capital and operative costs with the revenues defines the Net Present Value (NPV), which represents the cumulative cash flow value at the end of the plant lifetime (i.e., year *n*):

$$\mathrm{NPV} = \sum_{\mathrm{k=0}}^{\mathrm{n}} \frac{\mathrm{C_{H2}} \cdot \dot{\mathrm{Q}}_{\mathrm{H2}} + \mathrm{C_{O2}} \cdot \dot{\mathrm{Q}}_{\mathrm{O2}} + \mathrm{C}_{NaOH} \cdot \dot{\mathrm{Q}}_{NaOH} + \mathrm{C}_{HCl} \cdot \dot{\mathrm{Q}}_{HCl} - \mathrm{FCI} - \mathrm{Opex}}{(1+\mathrm{r})^{\mathrm{k}}} \quad (1)$$

where C is the specific product price in € kg^{-1}, $\dot{Q}$ is the mass flow rate in kg y^{-1}, r is the discount factor, FCI is the Fixed Capital Investment and the Opex are all the operative expenditure of the plant.
A special case of the NPV is obtained when it assumes a value of zero, which corresponds to the condition for which all revenues equal all expenses at the end of the n years of the plant lifetime. By rearranging Eq.1, it is easy to isolate the production cost of base and hydrogen, which in the case of NPV=0 define the Levelized Cost of Base (LCOB) (for NaOH) and of Hydrogen (LCOH), defined by Eq.2 and Eq.3, respectively. This condition corresponds to the minimum price that must be given to a product to cover all production costs, or, in other words, corresponds to the production cost for that product. Clearly, it will be necessary to price the other products (HCl, O_2 and H_2 in the case of LCOB or vice versa) to calculate the respective levelized cost, since multiple goods are involved.

$$\mathrm{LCOB} = \frac{\sum_{k=0}^{n} \frac{\mathrm{FCI} + \mathrm{Opex} - \mathrm{C_{O2}} \cdot \dot{Q}_{O2} - \mathrm{C_{H2}} \cdot \dot{Q}_{H2} - \mathrm{C_{HCl}} \cdot \dot{Q}_{HCl}}{(1+r)^k}}{\sum_{k=0}^{n} \frac{\dot{Q}_{NaOH}}{(1+r)^k}} \quad (2)$$

$$\mathrm{LCOH} = \frac{\sum_{k=0}^{n} \frac{\mathrm{FCI} + \mathrm{Opex} - \mathrm{C_{O2}} \cdot \dot{Q}_{O2} - \mathrm{C_{NaOH}} \cdot \dot{Q}_{NaOH} - \mathrm{C_{HCl}} \cdot \dot{Q}_{HCl}}{(1+r)^k}}{\sum_{k=0}^{n} \frac{\dot{Q}_{H2}}{(1+r)^k}} \quad (3)$$

All the economic parameters and prices assumed in the techno-economic analysis are collected in Table 1.

3. Results and discussion

Generally, an EDBM unit consists of a large number of triplets installed between the electrodes, but this number does not exceed 50 triplets due to process performance decreases, mainly related to parasitic currents. For this reason, the following analysis considered a stack with a maximum number of installed triplets equal to 20, which has shown promising performance (Virruso et al., 2023). To increase the process capacity, several stack units were considered in parallel to reach a total number of triplets in the plant equal to 100 in all the investigated configurations.

Table 1: Economic parameters and prices used in the economic analysis

Parameter	Value	[-]	Parameter	Value	[-]
BM cost	580	€ m^{-2}_{BPM}	*Water cost*	1	€ m^{-3}_{w}
IEMs cost	114	€ m^{-2}_{IEM}	*Electricity cost*	0.075	€ kWh^{-1}
Spacer cost	25	€ m^{-2}_{IEM}	*HCl price*	0.01	€ kg^{-1}_{HCl}
Electrode cost	300	€ $m^{-2}_{Electrodes}$	*O_2 price*	0.1	€ kg^{-1}_{O2}
Casing cost $\%_{CellPack}$[1]	50	%	*Plant lifetime **n***	20	y
Peripheral $\%_{STACK}$[2]	120	%	*Membranes lifetime t_m*	7	y
Maintenance $\%_{FCI}$[3]	10	%	*Electrodes lifetime t_{el}*	7	y
*Salvage value **S***	10	%	*Discount rate **r***	3	%
Load factor L_p	0.91	-			

[1] Percentage of the CellPack calculated as the cost of all the triplets, i.e., the sum of the spacers, IEMs and BPs membranes
[2] Percentage of the STACK calculated as the sum of the CellPack, Electrodes and Casing costs
[3] Percentage of the FCI defined as the sum of the STACK and Peripheral costs

The EDBM can be operated at a current density being one order of magnitude larger compared to other electro-membrane processes, thus allowing a higher hydrogen production, as the latter is directly proportional to the current. For this reason, the current density chosen in the present work is the maximum obtained in the work of Pellegrino et al. (2024), i.e., 1000 A m^{-2}, and a faradic efficiency of 100 % was assumed (according to experimental data), which leads to 18.6 mol m^{-2} h^{-1} of produced hydrogen. In order to increase the process productivity, also an increase of the electrode active area would be beneficial, however, the geometry of the EDBM is fixed by the manufacturers due to technical limitations.
On the other hand, Industrial electrolyzers provide to assemble multiple anodes and cathodes in order to increase the capacity. Consequently, the insertion of additional shared electrodes between the triplets is here proposed as a strategy to increase hydrogen productivity, while keeping a constant chemicals production. In this way, it is possible to imagine an EDBM stack with a single pair of electrodes separated by 20 triplets, or 5

shared electrode stacks with 4 triplets each, up to the limiting case of 20 stacks whose electrodes are spaced by a single triplet. Clearly, in each cell package between two electrodes a bipolar end-membrane is necessary to ensure a proper functioning of the unit.

3.1 Technical analysis

The specific energy consumption for the production of hydrogen (HSEC) and for NaOH (BSEC) versus the number of triplets (N_{tr}) assembled per stack is shown in Figure 1a, while the corresponding mass flow rates are shown in Figure 1b. The squares refer to the two extreme cases: (i) alkaline electrolyzer (in orange) and (ii) EDBM stack with 20 triplets (in blue). The alkaline electrolyzer is assumed to work under the same operating conditions of the EDBM unit, thus, the same geometries and the same current density.
For such an electrolyzer, an HSEC of 59.7 kWh kg^{-1}_{H2} is calculated (assuming an overall potential drop of 2.23 V per cell, in which 1.23 V is due to the thermodynamic potential, 0.93 V is due to the electrodes overvoltage and 0.07 V due to the ohmic losses). The linear trend of the HSEC is shown on a logarithmic axis for ease of reading. As it can be seen, the HSEC increases as the number of triplets rises, in accordance with the concomitant reduction of the quantity of H_2 produced (Figure 1b). The difference between the one-triplet HSEC and the electrolyzer case (N_{tr}=0) (equal to 103.7 kWh kg^{-1}_{H2}) is due to the chemical production expenditure of the EDBM process.

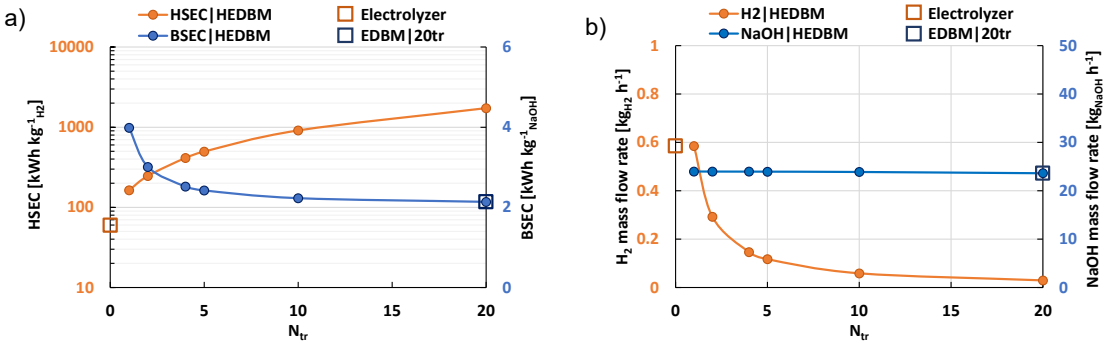

Figure 1 a) Trend of the specific energy consumption for the production of hydrogen (HSEC) and NaOH (BSEC); b) Mass flow rate of hydrogen and NaOH versus the number of triplets N_{tr} assembled between two consecutive electrodes. The empty squares represent the two-limit cases of an alkaline electrolyzer (orange) and the EDBM stack assembled with 20 triplets (blue).

When 20 triplets are considered, the lowest hydrogen productivity is obtained, equal to 0.029 kg_{H2} h^{-1}, which consistently causes the HSEC to increase dramatically. This occurs because the electrode surface area available for hydrogen production (i.e., cathode surface) is quite reduced, since 20 triplets are installed between a couple of electrodes and the total number of triplets in the plant is maintained constant. On the other hand, increasing the number of cathodes (i.e., decreasing the N_{tr}) would drastically rises up the hydrogen productivity to almost 21 times the reference EDBM|20tr case. Conversely, as mentioned above, the base production remains unchanged as the number of electrodes assembled changes, maintaining an average production of 23.9 kg_{NaOH} h^{-1}. The no-perfectly horizontal trend of the NaOH mass flow rate is explained by the fact that the current efficiency of the EDBM decreases as the number of triplets increases, due to the increase in dissipation due to parasitic currents, falling from 98% to 96.6%.
In contrast to hydrogen, BSEC decreases with the number of triplets, as the energy expended is mainly due to the migration of ions for the production of chemicals, meanwhile, the electrodic voltage losses cannot be considered negligible for low N_{tr}. These voltage drops at the electrodes are about 3 V, which take into account (i) the thermodynamic potential of 0.4 V (since the unit works with an acidic solution at cathodes and an alkaline one at the anodes), (ii) the electrodes overvoltage of 0.75 V and (iii) the ohmic losses, mainly related to the bubble presence, that weight for 1.85 V since the system is not optimized. To this voltage loss, a further 1.87 V must be added due to the ohmic resistance and to the water dissociation energy attributable to the end-membrane (i.e., the BM).

3.2 Economic analysis

A very preliminary analysis was done on the calculated Levelized Cost values. In Figure 2, the trends of LCOH and LCOB are reported as the number of triplets varies. As it can be observed, an equivalent alkaline electrolyzer has an LCOH of 4.13 € kg^{-1}_{H2}, while this value rises to 15 kg^{-1}_{H2} when there is 1 triplet per stack. Further increasing the number of installed triplets, the LCOH rises significantly, reaching a value of 186 € kg^{-1}_{H2}

at 20 triplets. This can be explained by considering that as N_{tr} increases, the production of hydrogen decreases and its production cost becomes dramatically higher. Furthermore, the plot was obtained by assuming a zero selling price of the other main product, therefore the LCOH also takes into account the costs related to the production of the other chemicals.
The LCOB is less affected by the number of triplets, indeed it goes from 0.26 to 0.41 € kg^{-1}_{NaOH}, with a 60 % increase compared to its reference cost. What should be noted is that, even if the cost of hydrogen is at least one order of magnitude higher compared to the base cost, the production (mass flow rate) of the base stream is 2 orders of magnitude higher than hydrogen. This evidence strengthens the need of using a high number of electrodes to increase the production of hydrogen, similar to a large hydrogen production industry, for which up to 1000 cells can be used for a single electrolyzer.

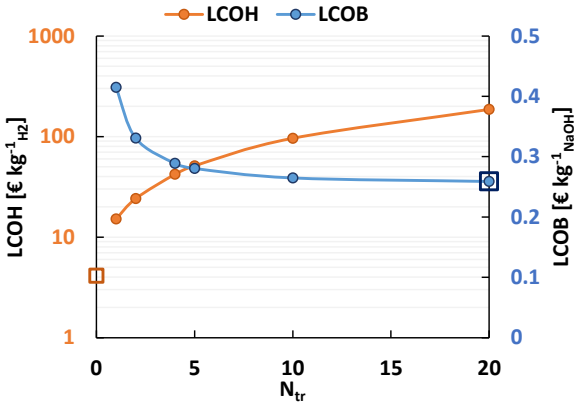

Figure 2 Trend of the LCOH and LCOB versus the number of triplets N_{tr}. The other main product (NaOH for the hydrogen, and hydrogen for the NaOH) is not sold. The empty squares represent the two-limit case of an alkaline electrolyzer (orange) and the EDBM stack assembled with 20 triplets (blue).

Figure 3 shows the NPV trend for different hydrogen prices (in the range 4-8 € kg^{-1}_{H2}) when the base is sold at a plausible price of 0.4 € kg^{-1}_{NaOH} (Zhang et al., 2017). In the case of 20 triplets, considered as a reference for a common EDBM unit, and assuming that the hydrogen is not sold leads to an NPV values of about 350 k€. The black curve shows precisely the case in which no revenue is obtained from hydrogen regardless of the number of triplets. The decrease in the N_{tr} leads to a reduction in the NPV, low down to -38 k€, due to the high voltage drop that occurs at the electrodes. On the contrary, when hydrogen is sold, as expected, the higher the selling price, the larger the obtained profit. As shown, as long as N_{tr} remains above 5, there is only a slight dependence of NPV on hydrogen sales. This is primarily due to its limited productivity, for which the main source of revenue remains NaOH. While reducing N_{tr} between 1 and 4 leads to an increase in the NPV for a hydrogen selling price higher than 6. Considering a price of 6 € kg^{-1}_{H2}, the addition of shared electrodes to increase hydrogen production does not improve the profit, since the NPV is lower than that at 20 triplets, although the almost constant trend. An NPV of 520 k€ can be achieved if the hydrogen is sold at 8 € kg^{-1}_{H2}.

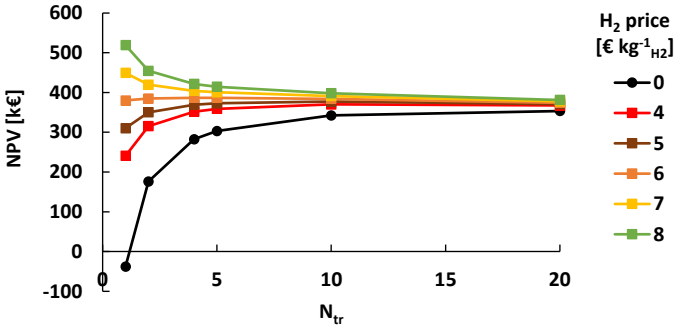

Figure 3 Net Present Value (NPV) versus the number of triplets for the selling price of 0.4 € kg^{-1}_{NaOH}, parametrised to different prices of hydrogen.

The obtained NPV is relatively small, but it should be considered that the EDBM units, just like electrolysers, are modular; hence, to increase the size, it is possible to increase the number of units in parallel. As a consequence, the Levelized Costs would remain more or less constant, but the NPV would result larger. For example, in this work, a system that produces a flow rate of 21 kg h^{-1} of NaOH (about 0.5 m^3 h^{-1}) was considered, which is a pilot size. Therefore, if a flow rate of 50 m^3 h^{-1} is used, the corresponding NPV would become about

60 million euros in the case of 1 triplet per stack and selling the hydrogen at 8 € kg^{-1}_{H2}. Furthermore, it must also be considered that the system would be affected by a beneficial scale effect, reducing the specific capital costs, which positively influences the economics of the entire process. Finally, it should be considered that the economic analysis was carried out adopting the current commercial costs of the membranes, thus, much larger profits are expected in the near future thanks to the widespread of the EDBM process.

4. Conclusions

This work analysed the H-EDBM from both technical and economic points of view, adopting a fully validated model which has been modified to consider the electrode behaviour, responsible for the hydrogen production. The addition of shared electrodes between triplets was proposed to increase production, making the technology more attractive to the market. An increase in HSEC occurs with the N_{tr} per stack, while the opposite trend was found for the BSEC. An equivalent electrolyser would consume 104 kWh kg^{-1}_{H2} less than the limit case of 1 triplet, where this surplus is mainly due to the desalination of the salty stream and the chemical formation. The model was also coupled with economic correlations to study and assess the feasibility of such a process. The identified LCOH results still high (~15 € kg^{-1}_{H2}), since the base is not sold. If a selling price for the NaOH of 0.4 € kg^{-1}_{NaOH} is considered, the NPV would reach around 350 k€ for the reference case of 20 triplets. This value could be further increased up to 520 k€ if additional electrodes are inserted in the system and the H_2 is sold at 8 € kg^{-1}_{H2}. Furthermore, the NPV could rise up to 60 M€ for an industrial scale plant, thanks to the modularity of the H-EDBM system. The techno-economic analysis was performed under conservative economic conditions, and in a futuristic perspective, a reduction of the capital expenditure would significantly reduce the costs and further increase the profitability of the plant.

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