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## Energy efficient ethanol concentration method for scalable CO<sub>2</sub> electrolysis

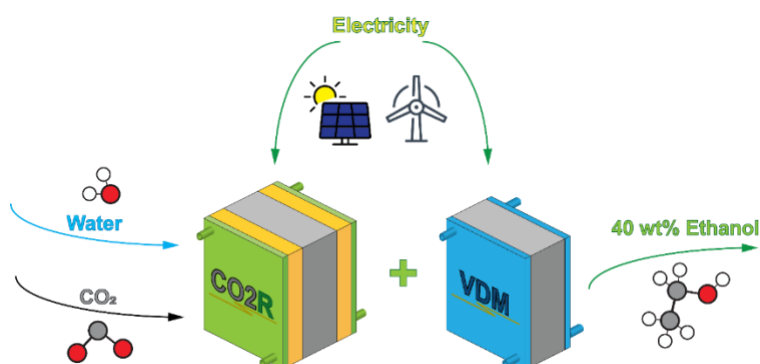
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### Abstract

Electrosynthesis of ethanol from carbon dioxide (CO<sub>2</sub>) is a promising route to generate a sustainable fuel and a convenient feedstock for chemical manufacturing. While excellent progress has been achieved in boosting the selectivity of CO<sub>2</sub> to ethanol, the subsequent ethanol separation remains a bottleneck, which prevents leveraging the laboratory results into large-scale systems. Here we report vacuum membrane distillation as a method that efficiently concentrates dilute ethanol streams produced by CO<sub>2</sub> electrolysis (CO<sub>2</sub>R), yielding up to ~40 wt.% ethanol in pure water. In our design considerations, we include previously underappreciated thermodynamic properties of the catholyte (salting-out effect) and propose strategies allowing a more precise estimation of energy inputs to the separation processes. Our work provides the basis for the detailed design of complex systems which integrate flow reactors and liquid separations and supports scaling of the systems considered so far as not optimized for industrial use.

### TOC



## Main Text

Electrochemical conversion of carbon dioxide (CO<sub>2</sub>R) is a promising alternative for bulk chemicals production from fossil fuels<sup>1,2</sup>. If the CO<sub>2</sub>R process uses biogenic carbon dioxide (CO<sub>2</sub>) and is powered by renewable energy, CO<sub>2</sub>R has the potential to yield indispensable chemical products with a minimum carbon footprint<sup>3</sup>. Among more than 15 compounds reported as potential products of CO<sub>2</sub>R<sup>4</sup>, ethanol is highly relevant to the chemical industry due to its use as a fuel additive<sup>5</sup> and as a convenient precursor to producing non-fossil fuels derived ethylene<sup>6</sup>. However, it is challenging to deploy CO<sub>2</sub>R to obtain ethanol streams of industrially relevant purity<sup>7</sup>, and this paper showcases an economically promising and technically feasible approach to yield streams of ethanol in pure water from CO<sub>2</sub>R.

In CO<sub>2</sub>R reaction, ethanol product is accumulated in the catholyte being continuously recirculated through the electrochemical reactor, both in high-current gas diffusion electrodes and H-cell cells (**Fig. 1a**). The chemical and physical properties of the catholyte (e.g., pH, viscosity) are crucial to the selective and efficient electrolysis of CO<sub>2</sub>, as the electrolyte layer adjacent to the CO<sub>2</sub>R catalyst belongs to the triple phase gas-solid-liquid boundary for the electrochemical reaction<sup>8</sup> (zoom in Fig. 1a). Thus, it is desirable to maintain a stable, controllable composition of the catholyte during CO<sub>2</sub>R experiments. High accumulation of any CO<sub>2</sub>R liquid product is not preferable, and it also triggers undesired crossover through the ion exchange membrane to the anode compartment, where ethanol is oxidized to acetic acid<sup>9</sup>. Thus, the ethanol concentration produced by CO<sub>2</sub>R is frequently below 4 wt.%<sup>10,11</sup>; reports targeting the production of higher ethanol concentration cite both increased crossover, limited stability, or Faradaic Efficiency (FE)<sup>12</sup>.

While this does not impose hurdles in the lab-scale characterization of new CO<sub>2</sub>R catalysts, it is a significant bottleneck towards the large-scale process deployment<sup>13</sup>. Ethanol needs to be separated to allow for catholyte recycling, and separating a highly diluted stream requires an energy input exceeding ethanol's heat of combustion<sup>7</sup>. Techno-economic analyses (TEA) in CO<sub>2</sub>R field point out that electrocatalytic reactors must yield min. 10 wt. % ethanol to be considered scalable<sup>14,15</sup>. The concentration of ethanol leaving the CO<sub>2</sub>R reactor is critical to the energy cost of product purification<sup>7</sup>, because the separation of ethanol from a highly diluted mixture is associated with inevitable evaporation of a huge amount of water; this imposes a significant unnecessary energetic expense. The difficulties in reaching these goals made CO<sub>2</sub>-to-ethanol less frequently investigated in terms of process scalability<sup>16,17</sup>; thus, we sought to develop an energy efficient ethanol separation that allows to leverage the progress in CO<sub>2</sub>R field to yield scalable CO<sub>2</sub>-to-ethanol processes, and focused on solving the main bottleneck – the need to yield a higher ethanol concentration stream, that can be fed into the existing separation processes or directly used for further conversion.

We first sought to understand the thermodynamic behavior of liquids most frequently used as CO<sub>2</sub>R catholyte (e.g., potassium hydroxide solutions (KOH), in concentration between 1-7 M<sup>1,18</sup>). Due to the chemical absorption of CO<sub>2</sub> into KOH during CO<sub>2</sub>R, the catholyte turns into a mixture of KOH and salts: potassium bicarbonate (KHCO<sub>3</sub>) and carbonate (K<sub>2</sub>CO<sub>3</sub>). While TEAs in CO<sub>2</sub>R area typically quantify the energy input into ethanol separation for the ethanol-pure water system, from a thermodynamic standpoint, the separation of ethanol from catholyte solution significantly differs due to the salting-out effect<sup>19,20</sup>. The effect is extremely well studied in the field of separation and thermodynamics<sup>20</sup>, and is frequently used to intensify distillation operation<sup>21</sup>. However, the authors are not aware of any consideration of this effect

in separation of CO<sub>2</sub> electroreduction products and focus here on including this effect in CO<sub>2</sub>R relevant applications. When the electrolyte is added to water, electrolyte's solvation decreases water and ethanol miscibility by reducing hydrogen bonding between water and ethanol. To quantify the importance of salting-out in separation of ethanol from CO<sub>2</sub>R catholytes, we performed a series of headspace gas chromatography experiments. We measured the amount of ethanol in the gas phase over solutions of 3 wt. % ethanol in different liquids: pure DI water, KOH in water, carbonate salts in water (**Fig. S1 a-b and Table S2**), deploying every time the same, controlled conditions. We were not able to quantify the ethanol concentration in the gas phase for the 7 M KHCO<sub>3</sub> solution due to immediate crystallization upon addition of ethanol<sup>22</sup>, however, for KOH and K<sub>2</sub>CO<sub>3</sub> solution samples, the effect of salting-out is surprisingly high - the concentration of ethanol in the vapor phase above 7M KOH is six times higher than above water, suggesting that vapor-liquid equilibrium driven approach (distillation) can yield an efficient separation method.

Seeking to perform the separation of ethanol in an energy-efficient manner, we considered a number of membrane separation methods<sup>23</sup>, among which pervaporation is a well-known method for ethanol removal<sup>24</sup>. Pervaporation is a two-step process (1) permeation through the permeable membrane by the permeate (ethanol), and (2) subsequent evaporation of ethanol into the vapor phase. Therefore, this approach does not benefit from the salting out effect we observed. Due to solution-diffusion mechanisms inside the membrane, at the point of its evaporation ethanol is already separated from the salt solution, thus cannot use this additional driving force. Furthermore, the membranes used for permeation applications, such as Polydimethylsiloxane (PDMS) are less resistant to the high pH and therefore not applicable for our separation (7M KOH has a pH > 14).

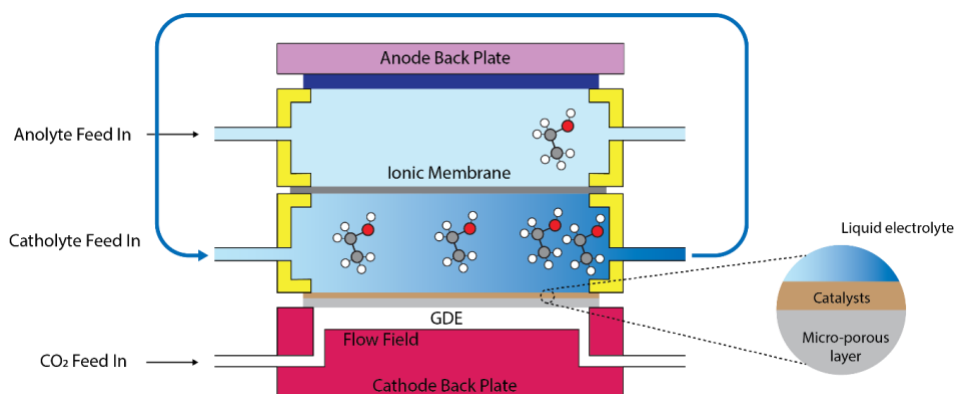
Given the described material, transport, and thermodynamic considerations, we turned to another membrane separation technology – membrane distillation<sup>25,26</sup>, which increases the separation efficiency by providing an extended mass transfer area through a porous membrane structure. Materials used for membrane distillation are more chemically resistant (because the membrane does not need to allow for permeation) and thus can perform well in the highly alkaline CO<sub>2</sub> electroreduction environment. Considering the design constraints of the entire CO<sub>2</sub>R-based chemical plant, we proposed to drive membrane distillation by vacuum instead of thermal heat to avoid the need to cool down the catholyte after the separation step before recycling it back to the CO<sub>2</sub>R reactor operating under room temperature. Additionally, the use of a vacuum reduces that start and shutdown times, as there is no need to heat the catholyte, making the system more convenient to operate under the availability of low-cost, surplus renewable energy. We sought to enhance the mass transfer area using porous, hydrophobic Polytetrafluoroethylene (PTFE) and Polyvinylidene fluoride (PVDF) membranes which discriminate water in the neighborhood of the membrane and are compatible with pH ~14. Furthermore, as PVDF is also oleophilic, it further supports the concentration of ethanol close to the evaporation interface.

We deployed vacuum membrane distillation (VMD) for the first time to separate ethanol from highly alkaline solutions used in the CO<sub>2</sub>R field and performed a series of characterization experiments using a stainless-steel membrane contactor, vacuum pump, and control system embedded in a laboratory rotary evaporator and high-performance liquid chromatography (HPLC) for ethanol quantification (**Fig 1b, S2, and SI Experimental procedure**). We deployed membranes with different pore sizes and investigated the separation performance under a range of ethanol concentrations which can be obtained from CO<sub>2</sub> electrolysis (0.5 – 3 wt.% in

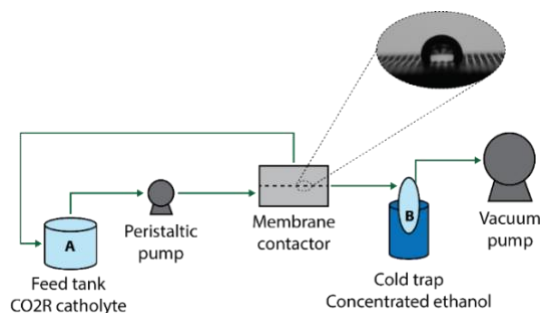
3.5 M KOH, **Table S3**). Across all studied conditions, the use of VMD allowed to substantially concentrate dilute ethanol in one step of separation and obtain ethanol in pure water of concentration up to 39.5 wt.%, with PVDF membrane yielding higher ethanol concentration as it is more oleophilic (**Fig. 1c**). Concentrated ethanol stream can be used e.g., the direct conversion of ethanol to ethylene oxide<sup>27</sup>, or other chemicals through conversion to ethylene<sup>28</sup>. We anticipate that this efficient separation is possible mostly due to the pronounced salting-out effect. Comparing against VMD ethanol – pure water separation, we were able to almost double the concentration of separated ethanol (25 wt.% vs. 13% reported deploying similar conditions and 0.2  $\mu\text{m}$  PTFE membrane for separation of 2 wt.% ethanol from water<sup>29</sup>). Thus, operating under salting-out conditions clearly improved the separation, and VMD was demonstrated to be feasible for the specific separation process. For a broader database of results for VMD for ethanol–pure water system, we recommend consulting the work of Cinelli *et al.*<sup>26</sup>

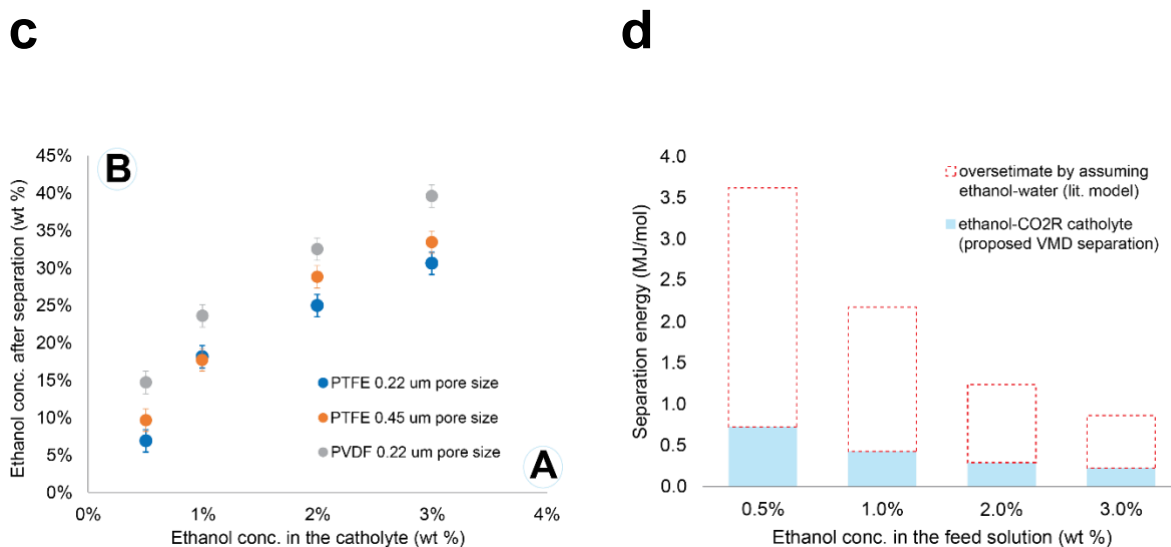
Translating our results into the assessment of the energy input necessary for ethanol separation (**SI, Process Model**), we demonstrated that the use of VMD allows recovering dilute ethanol (0.5 – 3 wt. %) at a minimum energy expense (0.2 – 0.7 MJ/mol), comparable or lower than ethanol heat of combustion (1.4 MJ/mol<sup>7</sup>) (**Fig 1d**). The energy requirement for separation is significantly lower than suggested by ethanol-water separation models currently adopted in CO<sub>2</sub>R TEAs (dashed line in Fig 1d). These findings highlight that any TEA analysis should account for the salting-out effect and consider how the presence of salts affects the vapor-liquid equilibrium (VLE) for the considered catholyte. Reported here gas space chromatography experiments are a facile way of quantifying the VLE for ethanol–catholyte systems.

**a**



**b**





**Fig.1. Integration of ethanol separation by Vacuum Membrane Distillation (VMD) into CO<sub>2</sub>R:** a) cross-section of a gas-diffusion electrode-based reactor, most commonly used for CO<sub>2</sub> electrolysis experiments under a high, industrially relevant current density; b) experimental setup used for the VMD experiments; details of the procedure and the equipment used are given in the SI, Experimental methods and Table S2, indexes A and B refer to the measurements plotted in 1. c.; Note that the picture of the droplet on the membrane surface was taken prior to the experiment and does not aim to visualize the separation process in-operando, c) results of VMD runs performed for the separation of ethanol from 3.5 M KOH catholyte using PTFE membranes of different pore sizes, under 25°C, 20-25 mbar pressure, d) energy requirement for the separation of ethanol from catholyte solution, 3.5 M KOH, is drastically lower than ethanol heat of combustion, pointing out that VMD can be a feasible, energy-efficient separation of ethanol from very dilute solutions. The literature model<sup>7</sup> accounts for a 100% efficient VLE separation at an equilibrium stage. The final CO<sub>2</sub>R product concentrations correspond to the values in Fig. 1c.

Given the excellent capability of the PVDF membrane to separate even a very dilute ethanol stream, we sought to deliver a proof of concept of a combined CO<sub>2</sub> electroreduction in a flow reactor and a subsequent VMD. We used a previously reported method for a copper GDE cathode preparation<sup>30</sup> (experimental details in SI, Electrochemical experiments) and ran an electrochemical experiment under a current of 500 mA/cm<sup>2</sup>. At the beginning of the experiment, ethylene and carbon monoxide were synthesized with the highest selectivity, and FE for ethanol was around 11%. After 20 mins, the FE towards gaseous carbon-containing products dropped significantly, with hydrogen being the main product obtained in the gas phase; selectivity towards ethanol was unaffected. We subsequently collected the catholyte to run a VMD of the electrosynthesized ethanol in a batch mode. The catholyte was re-used after the separation, and while the selectivity towards ethylene continued to drop over time (similarly to the previous reports using the same catalyst<sup>31</sup>), the selectivity to ethanol remained stable, encouraging to envision ethanol electrosynthesis on a timescale relevant for practical applications.

In addition to the electrochemical stability, the membrane separation must be stable and allow for a long-term operation. It has been observed that the porous membrane materials used as catalysts for CO<sub>2</sub>R drastically lose their hydrophobic properties over time, and we thus sought to understand if the membrane used for separations would be prone to a similar degradation. After running six hours of an uninterrupted VMD separation, we noted no change to the hydrophobic properties of the membrane, measured by the wetting angle (Fig 2b), suggesting that our combined process could be realized on a much longer timescale.

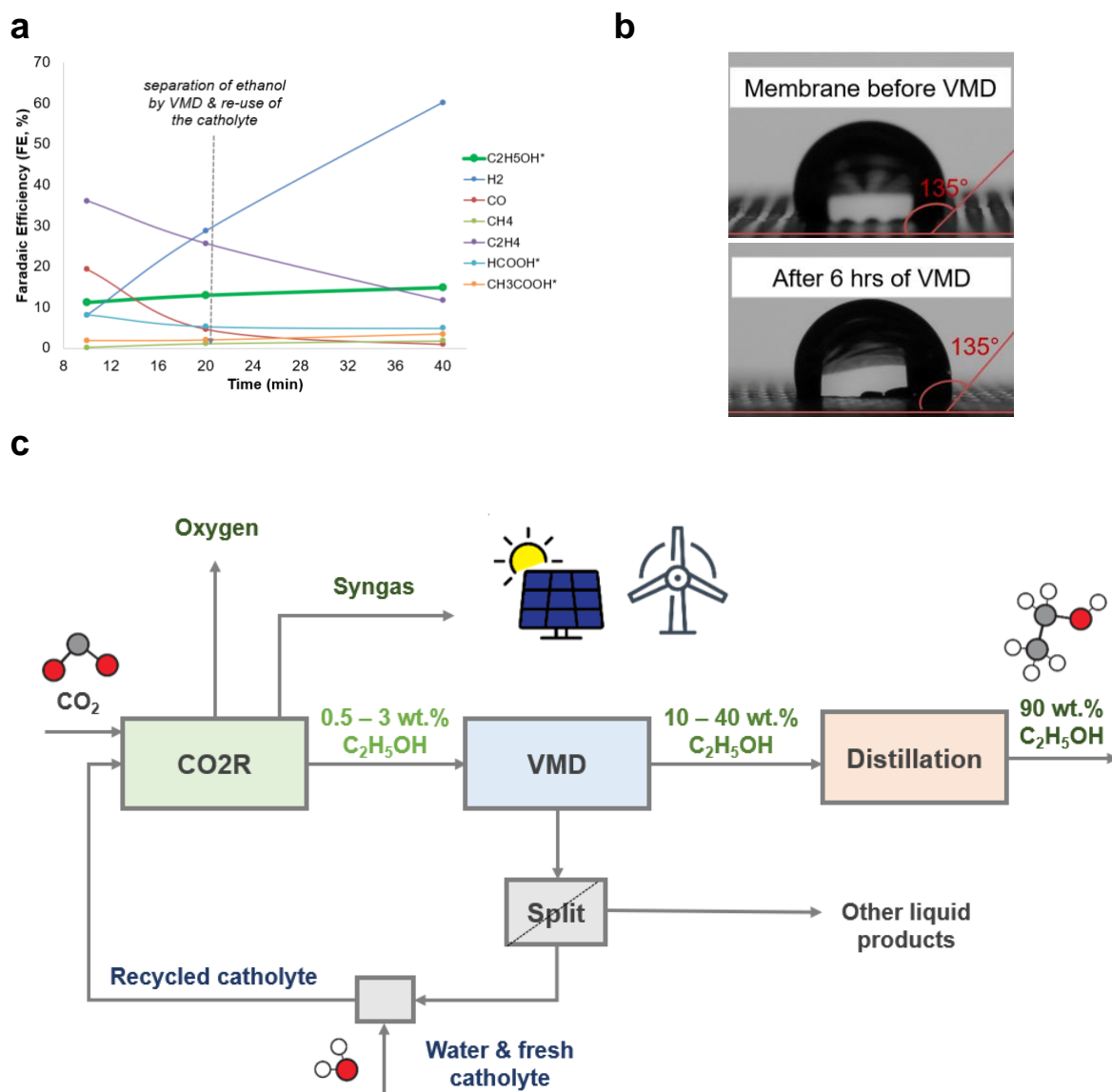


Fig. 2. Proof of concept a) Faradaic Efficiency for the electrochemical CO<sub>2</sub> electroreduction combined with VMD; CO<sub>2</sub>R was performed under 500 mA/cm<sup>2</sup>, 3.5 M KOH, b) unchanged wetting angle of the VMD membrane before and after six hours long VMD under 20 mbar, c) scheme of the conceptualized process for ethanol electro-synthesis from CO<sub>2</sub>. Split refers to a mass-flow controller-based system, where a minor part of the stream is directed to waste disposal; this strategy can be deployed if the waste component can be significantly concentrated in the recycled stream and only a minor amount (mass-basis) of the component

needs to be separated in a single pass. For the industrial use of split streams, see the use of Argon split in oxygen-based ethylene oxide production process<sup>32</sup>.

The small size of the electrochemical reactor used in this study (1 cm<sup>2</sup> of cathode area) made it challenging to achieve the minimum target for an energy-efficient separation (0.5 wt.% ethanol), however meeting this goal would be feasible using larger CO<sub>2</sub>R reactors or by running electrolysis in a facility designed for overnight experiments, allowing for >24 hours of uninterrupted CO<sub>2</sub>R. Both strategies have been successfully reported in the literature for CO<sub>2</sub>R copper catalyst systems<sup>10,12,18</sup>. Notably, most of the literature reports on ethanol synthesis deploy a batch mode, where the catholyte is continuously recirculated; thus, ethanol concentration can increase. Coupling this mode with the VMD separation does not allow to operate the electroreduction unit continuously, imposing a hurdle towards the large-scale application of CO<sub>2</sub>R.

To address this limitation, we conceptually propose a two-step operation mode that allows achieving the level of ethanol concentration that supports energy-efficient separation without jeopardizing other functionalities of the reactor (Fig. 2c). In mode A, which is activated upon the start-up of the system, the VMD separation stage is not active, and the catholyte is continuously recirculated to allow for the accumulation of ethanol up to min. 0.5 wt.%, leveraging from the cited above experimental reports.

Subsequently, mode B is activated, where the catholyte stream continuously passes through the VMD section, and ethanol is recovered. The amount of ethanol separated in the VMD unit can be adjusted as a function of the membrane surface (for that purpose, the corresponding flux of ethanol through the membrane needs to be measured at industrially relevant mass transfer conditions). In the integrated process, the VMD unit is sized to remove only the ethanol produced in a single pass. Notably, as the VMD unit does not remove all ethanol accumulated in the catholyte stream and as a result, the separation happens at a favorable higher concentration of ethanol. Before recycling the catholyte to the CO<sub>2</sub>R, other products, such as formate and acetate, can be removed by a simple purge. Because the initial catholyte recycling (mode A) allows achieving a higher concentration of formate and acetate, disposing of a small fraction of the catholyte stream removes the amount of formate and acetate generated in a single pass through the reactor, and the build-up is mitigated. The stream of ethanol concentrated by VMD to 10% is subsequently concentrated to 90% using state-of-the-art distillation.

Besides ethanol synthesis, the gaseous outlet of the reactor consists of several valuable products, such as hydrogen, carbon monoxide, and ethylene, as well as unreacted carbon dioxide. Detailed insights into the separation of gaseous CO<sub>2</sub>R products have been reported before<sup>33</sup>; however, since the technology described here is designed for ethanol production, the gas separations are not embedded, and the gaseous stream is planned to be sold as syngas<sup>14,34</sup>. On the anode side, oxygen is being produced, together with a minor amount of CO<sub>2</sub>, which is degassed as a result of the crossover of carbonate and bicarbonate ions through the anion exchange membrane and their oxidation on the anode. While we do not account for the possibility of selling the oxygen with a minor amount of CO<sub>2</sub>, we do account for CO<sub>2</sub> loss in our mass efficiency calculations (a complete mass balance for all streams is given in the Supplementary Information, Process Model section).



Looking towards a potential large-scale application of the system, we sought to evaluate the economic viability of the proposed CO<sub>2</sub> electrolysis – VMD system (Table 1 summarizes all cost factors and assumptions). Leveraging from the developments in PEM electrolyzers in hydrogen production, the investment cost associated with CO<sub>2</sub>R is highly uncertain, as it will be strongly affected by market growth. For hydrogen PEM hydrogen electrolyzers, the future cost varies between 200 – 600 \$/kW, depending mainly on the yearly demand<sup>35</sup>. Thus our TEA focuses solely on assessing the operational costs related to the electrosynthesis of ethanol from CO<sub>2</sub> and is therefore, not sensitive to the achieved current density. To justify further insights into the reactor investment costs, green ethanol needs to be produced at a cost lower than the current benchmark. Consequently, we focused on identifying the performance metrics that need to be achieved.

Table 1. Summary of the cost indicators and assumptions for the techno-economic analysis. Note that this analysis accounts only for the operational costs of ethanol electrosynthesis due to significant uncertainties related to the capital costs.

Parameter	Value
<i>System inputs</i>	
CO <sub>2</sub> (assumed 40% utilization)	25 \$/tonne (benchmark for CO <sub>2</sub> from bioethanol process <sup>36</sup> )
Electricity	0.02 – 0.045 \$/kWh <sup>37</sup>
Water	0.001 \$/L <sup>38</sup>
<i>System outputs</i>	
Ethanol	1.84 \$/kg <sup>36</sup>
Syngas	0.1 \$/kg <sup>14,34</sup>
Oxygen (with a minor amount of CO <sub>2</sub> )	0 \$/kg (assumed not to be sold)
<i>System characteristics</i>	
Faradaic efficiency	15 – 60% to ethanol (main by-product: hydrogen)
Ethanol concentration after CO <sub>2</sub> R	0.5 wt. %
Ethanol concentration after VMD	10 wt. %
Full cell voltage	2 – 3 V (assumption for optimized cells)
Catholyte	3.5 M KOH

Deploying a recent protocol for the assessment of emerging technologies for CO<sub>2</sub> electrolysis<sup>39</sup>, we evaluated the operational costs for ethanol synthesis using described above system under two scenarios: our experimentally demonstrated FE towards ethanol (15%) and a higher FE, representative for other reports focusing on ethanol catalyst optimization (60%)<sup>11,13,40</sup>. Looking across the lower range of renewable electricity prices reported by the International Energy Agency<sup>37</sup>, even a low FE to ethanol could yield an economically viable process, provided the CO<sub>2</sub>R unit operates under the full cell voltage in the range of 2 V (corresponding to a very high energy efficiency). However, increasing the FE towards ethanol is highly desirable as it widens the window of economic viability and compensates for the lower energy efficiency or higher renewable energy costs. Therefore, the initial investment into CO<sub>2</sub>R to ethanol process would strongly benefit from the availability of highly selective catalysts, and presented here separation approach will support leveraging early-stage laboratory findings into scalable systems. We encourage the readers to use the referred TEA

tool<sup>39</sup> to generate similar assessments for the regional prices of renewable energy and CO<sub>2</sub> feedstock.

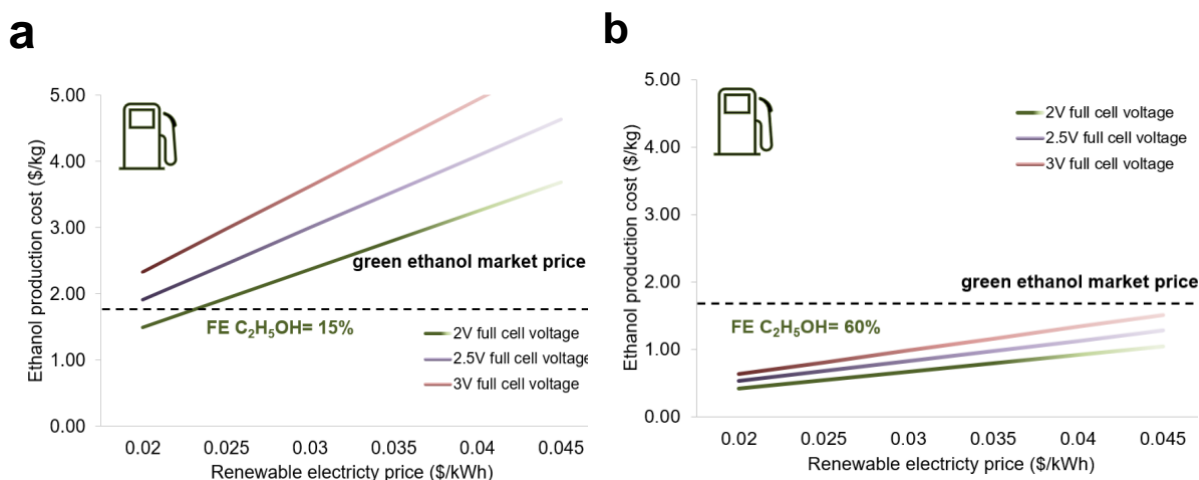


Fig.3. Techno-economic analysis for the ethanol electrosynthesis process: a) operational cost for ethanol FE 15%, b) operational cost for ethanol FE 60%. The main by-product is, in both cases, hydrogen, and the model does not account for catholyte losses. Details in SI, Process modeling, and techno-economic analysis section and Table S1).

Described above conceptual proof-of-concept and the TEA assume achieving 0.5 wt.% of ethanol (after CO<sub>2</sub>R, prior to VMD). Deploying VMD at 3 wt.% would allow achieving a much higher purity of the ethanol stream leaving the electrolyzer, further reducing described costs. However, the higher concentration will result in higher migration of ethanol through the AEM and associated product loss. Thus, it becomes critical to identify the optimum concentration from both separation and crossover perspective, and the availability of detailed mathematical models for the latter would allow for more precise insights into the problem. It is also important to note that during the CO<sub>2</sub>R experiment, the catholyte will convert into a mixture of (bi)carbonates (due to the chemical absorption of CO<sub>2</sub>), which is anticipated to make the separation even more efficient. Figure S1 shows that the vapor above K<sub>2</sub>CO<sub>3</sub> consists of a higher amount of ethanol than the vapor about KOH (for the same concentration of K<sup>+</sup>). Thus, the separation of ethanol will be further facilitated over time, and the detailed dynamic process models will need to account for the shift in vapor-liquid equilibrium.

Furthermore, though not identified in our experiments, copper catalyst can also yield other volatile products such as acetone or propanol, and based on the principle of VMD, these products would be recovered together with ethanol. Ensuring selectivity between ethanol and other volatile products will be critical for successfully integrating the proposed separation method.

We encourage the electrolysis community to consider embedding membrane separators in their systems, both experimentally and within the modeling studies. The latter will strongly benefit from a more detailed consideration of the thermodynamic properties of the catholyte, which based on our results, have a drastic effect on the output of the electrolysis-based

chemical plant. This inspires further research into the separation of other liquid products (e.g., acetate), as well as opens countless opportunities for CO<sub>2</sub>R process optimization – we showcase that the choice of catholyte and its concentration is also essential from the standpoint of the subsequent separation.

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