



High-purity and high-concentration liquid fuels through CO₂ electroreduction

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Liquid fuels generated from the electrochemical CO₂ reduction reaction (CO₂RR) are of particular interest due to their high energy densities and ease of storage and distribution. Unfortunately, they are typically formed in low concentrations and mixed with impurities due to the current limitations of traditional CO₂ electrolyzers as well as CO₂RR catalysts. In this Perspective, we emphasize that while the declining renewable electricity price can greatly lower the formation cost of liquid fuels, the downstream purification process will add an extra layer of cost that greatly harms their economic feasibility for large-scale applications. Different strategies in reactor engineering and catalyst improvement are proposed to realize the direct and continuous generation of high-purity and high-concentration liquid fuels from CO₂RR electrolyzers, allowing this electrochemical route to become more competitive compared with the traditional chemical engineering industry in the future.

The continuously increasing concentration of carbon dioxide (CO₂) in the atmosphere raises serious concerns for global climate change^{1–3}. The aims of the Paris Agreement are to substantially reduce global greenhouse gas emissions and limit the global temperature increase in this century to no more than 1.5 °C over pre-industrial levels. Although ambitious goals for the reduction of carbon emissions were announced by international communities during the 2021 *Leaders Summit on Climate*⁴, there is still an urgent need for advanced technologies, including carbon capture, conversion and storage, to neutralize or even reduce the amount of CO₂ emitted. Thanks to the fast developments in renewable-grid technologies, we can now efficiently harvest green electricity from solar or wind energy and continuously lower its cost towards highly competitive levels. A representative example is the recently announced utility-scale solar 2025 cost target of only 3 cents/kWh⁵ by the US Department of Energy⁵. This continuously plunging cost of renewable electricity has significantly improved the market competitiveness and affordability of chemical feedstocks that can be produced via electrocatalytic processes such as the electrochemical CO₂RR^{6,7}.

Using the electrochemical CO₂RR to produce chemicals and fuels offers several advantages over traditional chemical engineering synthesis methods, which include operation under mild reaction conditions such as room temperature and ambient pressure, high energy conversion efficiencies, delocalized production and easy adaptability and scalability^{8,9}. Depending on the electrocatalyst used, a variety of chemicals and fuels can be obtained ranging from C₁ (for example, carbon monoxide (CO), formic acid (HCOOH), methane (CH₄) and methanol (CH₃OH)) to C₂ (for example, ethylene (C₂H₄), ethanol (CH₃CH₂OH) and acetic acid (CH₃COOH)) and even to C₃ (*n*-propanol (CH₃CH₂CH₂OH)) products (Fig. 1a)^{10,11}. Compared with gas-phase products, liquid fuels produced from the CO₂RR attract special interest due to their high energy density, their ease of transportation and storage, and their spontaneous separation from the input CO₂ stream¹². However, there are still substantial challenges that threaten the economic feasibility and large-scale application of producing liquid fuels via a CO₂RR approach^{9,10,13}. Most attention is currently being paid to catalyst development, as the catalytic selectivity and activity towards a target liquid fuel,

especially high-value C₂₊ liquids, are still not within industrially relevant ranges^{14–17}. Nevertheless, many other practical challenges need technological developments that are beyond the scope of the design of catalytic materials. Among them, issues regarding the purity and concentration of generated liquid fuels are prominent challenges that need to be solved. In traditional CO₂ electrolyzers, an aqueous electrolyte with soluble salts (such as KHCO₃, Na₂SO₄ or KOH) is used for two major functions (Fig. 1b): it ensures fast ion conduction between the cathode and anode for low ohmic drop, and it also collects the generated liquid products from the cathode under flow. As a result, the as-obtained liquid fuels are in a mixture with impurity ions, which prevents the fuels from being used directly. Therefore, additional downstream purification processes, such as reverse osmosis or electrodialysis, must be implemented to separate the liquid fuels from the ions (Fig. 1c)^{14,18,19}, which could dramatically increase the overall cost of CO₂RR-generated liquid fuels and further complicate their delocalized production. In addition, these CO₂RR-generated liquid fuels are typically heavily diluted in the electrolyte (usually present at less than 1 mol^{–1} concentrations), which even after the salt removal cannot fit into the existing global chemical commodity supply chains. The extra distillation step needed to obtain high-concentration liquid fuels will add another substantial layer of cost to the economics.

Here, in this Perspective, we would like to emphasize both the importance and the challenges of producing high-purity and high-concentration liquid fuels through CO₂ electroreduction, which are often overlooked in the CO₂RR field. Using previously reported techno-economic analysis models, we can point out that the extra costs associated with downstream purification and concentration will greatly harm the economic viability of the liquid products, suggesting the necessity of achieving high-purity and high-concentration liquid fuels directly from CO₂ electrolyzers. By briefly reviewing the recent progress of catalytic reactor design for addressing this impurity and low-concentration challenge, we propose different strategies as potential future research directions for further improvement of the product selectivity, activity, purity and concentration, helping to push the generation of liquid fuels via the CO₂RR closer to large-scale application in the future.

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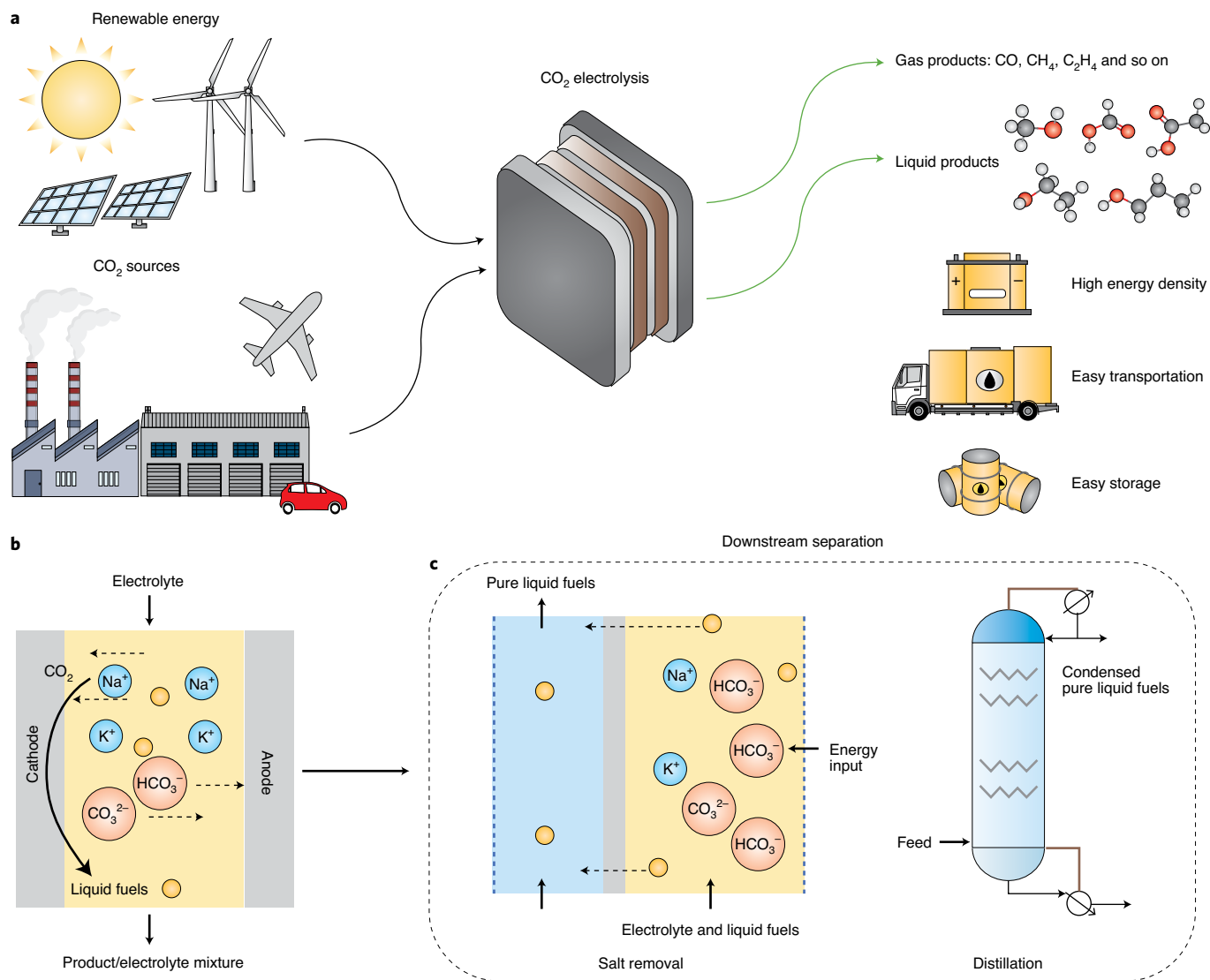


Fig. 1 | Overview of CO₂RR technology and downstream liquid product separation. **a**, Schematic illustration of sustainable chemical production via electrochemical CO₂ reduction. **b**, Traditional CO₂ electrolyzers use liquid electrolyte for ion conduction and liquid product collection and thus require a downstream separation process to recover the pure liquid fuels. **c**, Schematic of downstream separation processes including salt removal and distillation for high-purity and high-concentration liquid fuels. The yellow particles in **b** and **c** represent the desired liquid fuels.

Performance and production cost of CO₂RR-generated liquid fuels

To achieve high-purity and high-concentration liquid fuels from CO₂ reduction, the development of highly active and selective CO₂RR catalysts is a prerequisite^{14,18,20–28}. So far, around five types of liquid product can be generated with reasonable selectivity on different catalytic materials, including formic acid and methanol as C₁ liquids, acetic acid and ethanol as C₂ liquids, and *n*-propanol as a C₃ liquid. Each of these liquid fuels is formed through different reaction intermediates/pathways, which consequently require properly designed catalytic active sites and present different performance metrics (Fig. 2a,b). Therefore, the challenges in catalyst design for each target liquid fuel are completely different. In general, the deeper CO₂ is reduced, the higher the value and energy density the liquid product will have, but the lower the catalytic performance of the overall process could be, which is due to the involvement of more reaction steps and the existence of more possible competing pathways. As the simplest liquid product from the CO₂RR, with two electron-transfer steps, the generation of formic

acid involves a key intermediate of oxygen bonded *OCHO^{29,30} and can be highly selective (>85%) and active (>100 mA cm⁻²) on post-transition metals such as tin, lead and bismuth^{18,27,28}. More importantly, while there are side products such as hydrogen (H₂) or CO co-generated during the CO₂RR on these catalysts, formic acid is the only liquid product that they produce, suggesting an ultra-high relative purity in CO₂RR-generated liquid fuels. This excellent catalytic performance sets up a solid foundation to realize the direct production of high-purity and high-concentration formic acid. Although methanol is also a C₁ liquid, it does, however, involve six electron-transfer steps and its carbon is in the same deeply reduced state as ethanol and *n*-propanol, resulting in a much poorer catalytic performance compared with formic acid. So far, the state-of-art performance for CO₂RR-generated methanol in an aqueous electrolyte has been demonstrated on a molecular catalyst^{25,26}, delivering a maximal Faradaic efficiency (FE) of ~44% and a partial current density of ~10 mA cm⁻². Therefore, a notable improvement in the catalytic performance is a prerequisite for obtaining a high-purity and high-concentration methanol product. The situation becomes

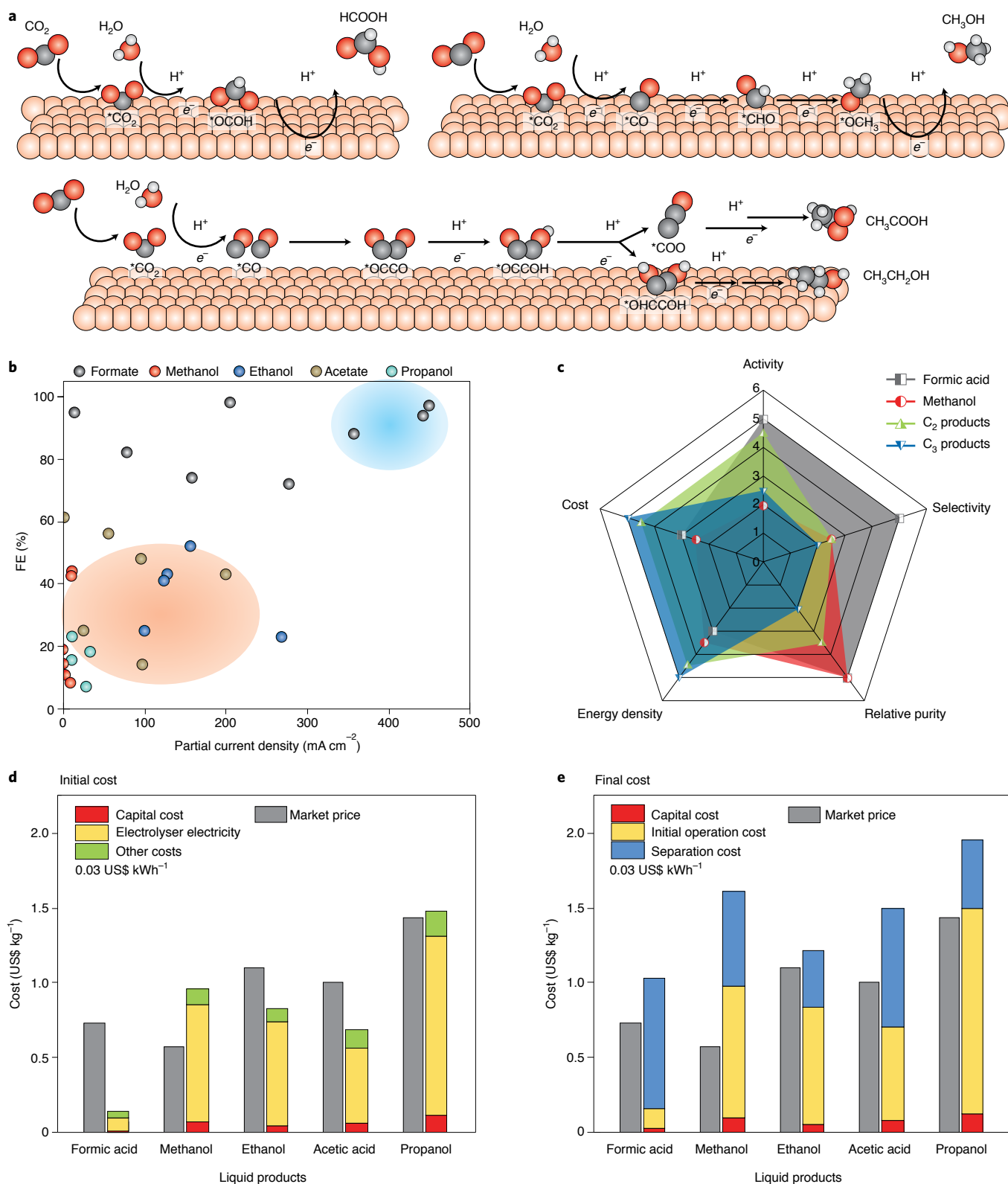


Fig. 2 | CO₂RR electrocatalysts for liquid fuels and technoeconomic considerations. **a**, CO₂RR pathways and key intermediates towards formic acid (top left), methanol (top right) and C₂₊ products (bottom). **b**, The state-of-the-art CO₂ reduction performance for C₁ and C₂₊ products in aqueous solutions. The blue-shaded region represents preferred catalytic performances in industrialization, while the orange-shaded region represents the state-of-the-art catalytic performances of higher-value CO₂RR liquid products. **c**, Radar chart summary of liquid-fuel activity, selectivity, relative purity, energy density and cost. **d**, The operation cost and apportioned capital cost of CO₂ reduction to liquid fuels without the consideration of a product-purification process³¹². **e**, The downstream salt removal and distillation process add an extra layer of cost for achieving high-purity and high-concentration liquid fuels that can fit into the market supply chain. A detailed set of criteria for the summary of CO₂RR electrocatalysts is available in Supplementary Note 1.

a little more complicated when it comes to C_{2+} liquids that have a higher monetary value and energy density than C_1 products. It is widely accepted that the formation of *CO and its subsequent dimerization is a crucial step in generating C_{2+} products during the CO_2RR ^{10,31,32}. At present, the only catalytic material known to be capable of catalysing this necessary C–C coupling step is copper due to its unique surface electronic structures^{31,32}. As shown in Fig. 2a (bottom), different C_2 products could share the same reaction intermediates before later following deviating pathways, which inevitably results in low relative purities of C_{2+} products compared with C_1 products (Fig. 2c)¹⁴. This co-generation of several liquid fuels dramatically increases the difficulty in obtaining a single high-purity liquid product, especially when they have quite similar liquid properties such as the boiling point^{15,33}. Therefore, designing suitable electronic properties for a copper-based catalyst to yield a desired single C_{2+} liquid product without sacrificing selectivity or activity will play a key role in achieving high-purity and high-concentration C_{2+} liquid fuels^{21,22}.

While it is likely that the performance metrics of CO_2 -to-liquid-fuel catalysts will keep improving in the near future, they may still not be sufficient to make this electrochemical process highly competitive with traditional chemical engineering industries. This economic feasibility can be clearly shown by feeding the current state-of-the-art CO_2RR performances into previously reported techno-economic analysis and product-separation analysis models (Supplementary Fig. 1)^{9,12,34}. An initial production-cost analysis takes three main components into consideration: the electricity input, the raw materials' input, which includes CO_2 and water consumption (Supplementary Fig. 2), and other associated costs such as maintenance, pressure-swing adsorption and so on (Supplementary Note 1). On the basis of the US Department of Energy's recently announced utility-scale solar 2025 cost target⁵, we estimated a cost of renewable electricity of 3 cents kWh^{-1} . Without considering the downstream separation processes, the production cost with the apportioned capital cost of formic acid is much lower than the current market price (Fig. 2d). For alcohols such as methanol and propanol, since each molecule requires a greater electron input and their FE values are typically lower, their electricity cost dominates the production cost, and the overall cost is slightly higher than their current market price. This situation could be notably improved in the future with enhanced catalytic performances.

Whereas the generated CO_2RR liquid fuels except for methanol and *n*-propanol are profitable in terms of their initial production cost, the generated liquid fuels from traditional CO_2 electrolyzers cannot be treated as the final commercial products to be fitted into the current market supply chain due to their low concentrations as well as their low purity. Therefore, taking into consideration the downstream product-separation process needed for obtaining commercial-grade liquid fuels, another layer of cost will be added and the story could be completely changed. There are two steps potentially involved in the liquid-fuel purification process. For non-anionic liquid products such as alcohols, a one-step distillation process could directly separate the liquid-fuel molecule from the water and ions in the liquid electrolyte to achieve high purity and high concentration. For anionic liquid products such as formic acid and acetic acid, since they are in the form of ions in the liquid electrolyte, to remove these solutes an impurity-ion separation and acidification process (such as reverse osmosis or electrodialysis) will be needed to obtain a low-concentration pure liquid-fuel solution before a distillation process can even be applied^{35,36}. For a consistent comparison, we used the distillation cost model reported in the same study as the techno-economic analysis model, for all liquid-fuel products¹². Please note that an extra ionic separation cost, obtained from a previous report^{35,36}, was included for formic acid and acetic acid due to their deionized status in water. As shown in Fig. 2e, due to the substantial cost contribution from the product-purification

processes, the final cost of all liquid products in their high-purity and high-concentration form becomes higher than the current market price, making this CO_2RR -to-liquid-fuel route not yet economically viable. This analysis clearly suggests the urgency not only of catalyst improvement but also novel catalytic reactor engineering to enable the direct generation of high-purity and high-concentration liquid fuels without the need for cost-intensive downstream purification processes.

Opportunities and challenges of reactor design for high-purity liquid fuels

To address this liquid-fuel impurity challenge, we need to decouple the two main functions—the ion conduction and the liquid product collection—performed by a traditional liquid electrolyte in CO_2 electrolyzers. One recent promising strategy has been to replace the liquid electrolyte with a thin layer of porous solid electrolyte (PSE) between the cathode and anode^{14,18,19,37}. As shown in Fig. 3, in the solid-electrolyte reactor design, the catalyst-coated gas diffusion layer (GDL) electrodes on the cathode and anode are in close contact with an anion exchange membrane (AEM) and a cation exchange membrane (CEM), respectively. The cathodic side is continuously supplied with a CO_2 stream for the CO_2RR , and the anodic side is supplied with a circulating acidic solution or deionized water for water oxidation. In the middle chamber, a PSE layer is placed between the AEM and CEM to facilitate ion transport with minimized ohmic losses and to allow for a deionized water stream to collect the liquid-fuel molecules generated, therefore successfully decoupling the ion-conduction and product-collection functions. The solid electrolyte can be made of ion-conducting polymers or inorganic ion conductors, and can conduct either cations or anions or both. During the CO_2RR , electrochemically generated ions/molecules such as $HCOO^-$ (formate) or CH_3COO^- (acetate) move across the AEM towards the middle PSE layer, and can be driven by both an electric field (E) and gradient diffusion¹⁴. Meanwhile, protons generated from water oxidation on the anode move across the CEM into the middle chamber to compensate the charge. The target molecules (such as $HCOOH$) are thus formed within the middle layer via ionic recombination and are later efficiently carried out via the deionized water stream through this porous layer.

Whereas recent studies by our group and other groups^{14,18,37–40} have demonstrated this solid-electrolyte reactor design to be highly effective in producing high-purity liquid-fuel solutions, such as over 30 wt% pure formic acid solution¹⁹, challenges still persist in different components of the reactor that will retard its large-scale application in the future (Fig. 3). Typically, the performance of the CO_2RR catalysts is estimated first in a flow-cell reactor under neutral ($KHCO_3$) or alkaline (KOH) conditions. Previous density functional theory calculations and experimental studies have suggested that the interfacial pH can influence the product distribution considerably^{41–43}. For example, C_{2+} products are favoured over C_1 products at high pH values on copper catalysts^{44,45}, hence strong alkaline solutions have sometimes been used to promote C_{2+} FE values in flow-cell reactors^{24,46}. When the same types of catalyst were tested in the solid-electrolyte reactor, they could perform differently in the CO_2RR since the local pH environment may not be as high as in an alkaline electrolyte^{47,48}. Another difference in the chemical environment of a solid-electrolyte reactor is the lack of cations. It has been observed in previous studies that alkali metal cations (Na^+ , K^+ and so on) can significantly improve the CO_2RR performance via introducing a local electric field^{49–52}. Consequently, the cation promotion observed in flow cells cannot be directly translated into solid-electrolyte reactors.

In addition to the catalyst translation, another big challenge is the permeability and stability of the ion-exchange membranes^{29,53}. As mentioned above, on the cathodic side, the generated anionic products can diffuse through the AEM into the solid-electrolyte

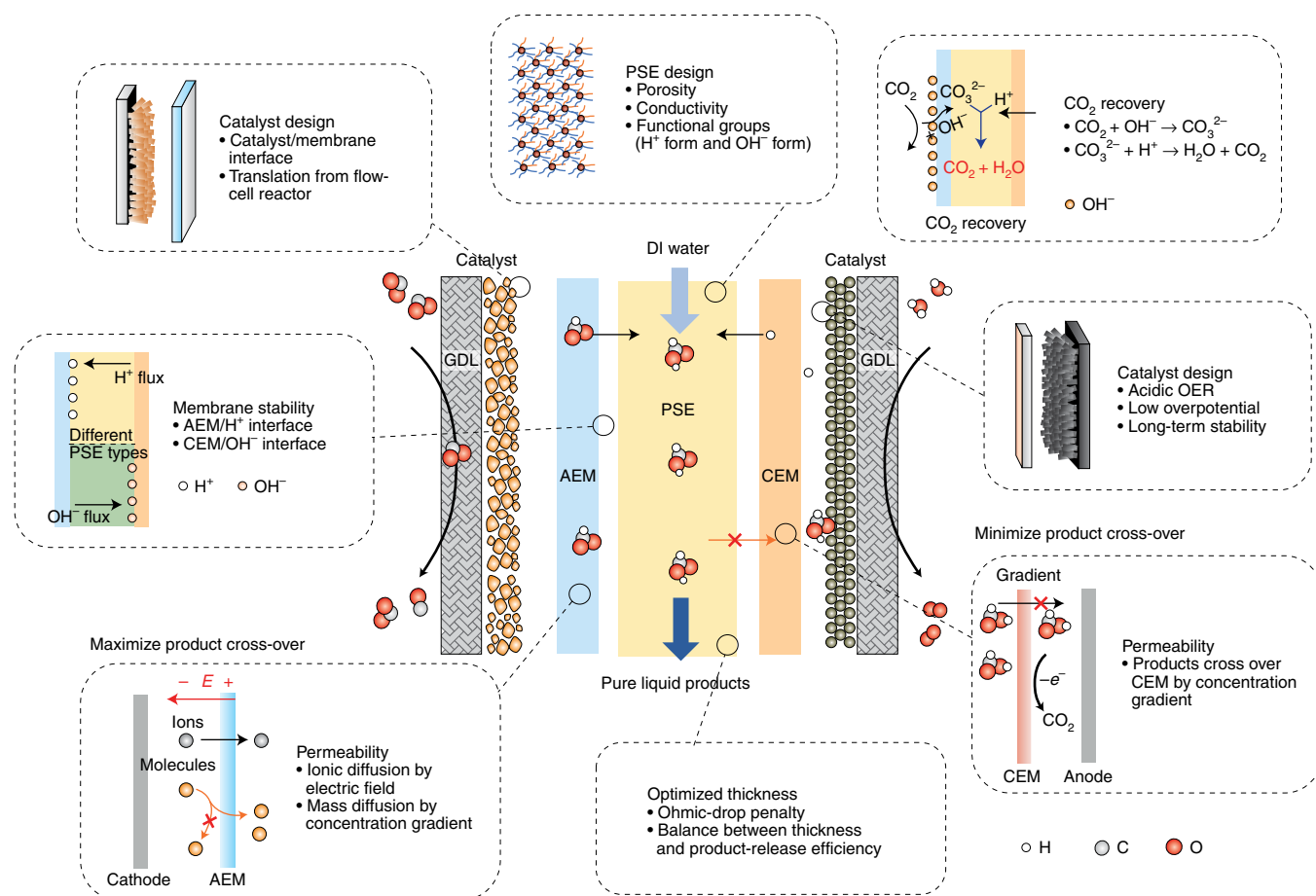


Fig. 3 | Solid-electrolyte reactors. Schematic representation of a CO_2RR electrolyser with a PSE. As shown in the main cell schematic, from left to right, the components of an electrolyser: GDL, cathodic catalyst, AEM, PSE (or solid-electrolyte layer), CEM, anodic catalyst and GDL. The cathodic side is continuously supplied with a CO_2 stream for the CO_2RR , and the anodic side is supplied with a circulating acidic solution or deionized water for water oxidation. Electrochemically generated ions/molecules such as HCOO^- move across the AEM towards the middle PSE layer, and protons generated from water oxidation on the anode move across the CEM into the middle chamber to compensate the charge. The target molecules (such as HCOOH) are thus formed within the middle layer via ionic recombination, before being efficiently carried out via the deionized water stream that flows through this porous layer. For future improvements, an analysis of each component in a solid-electrolyte reactor is given around the electrolyser schematic. DI water, deionized water.

layer, driven by the electric field during electrolysis. However, there is another type of diffusion through the membrane, which is driven by the concentration gradient. Generated molecules like ethanol and *n*-propanol are not negatively charged but can still diffuse across the AEM due to their high concentrations at the catalyst/AEM interface. Although most of the generated alcohols will remain in the liquid phase (dissolved in the AEM and the deionized water stream of the middle chamber), there will still be a portion of alcohols that remain on the cathodic side and which will be carried out by the CO_2 stream, reducing the product-collection efficiency. Therefore, a high permeability for the AEM is needed to produce pure liquid fuels, especially for these alcohol products, which can be achieved by tuning the material properties of the membrane. Potential research could be focused on surface and structure modification to increase the porosity of the membrane, for example, using hollow polymer structures⁵³. By contrast, on the anodic side, we should minimize the liquid product crossover through the CEM, which can be oxidized back to CO_2 by the anodic catalyst under a positive potential. Future studies could benefit from previous work in direct methanol fuel cells where the liquid-fuel crossover needs to be greatly suppressed. In addition, the operational pH range of ion-exchange membranes should be widely extended for high chemical stability under the reaction conditions. This is because in a solid-electrolyte

reactor, the membrane and solid electrolyte can have distinct pH environments. Using proton-conducting solid electrolytes as an example, under the operating conditions there will be a high proton flux at the interface between the AEM and the solid electrolyte, which could destabilize the polymer structure or functional groups in the AEM as it is usually used under basic conditions.

Although the solid-electrolyte approach avoids subsequent energy- and cost-intensive product-separation processes, this extra layer between the cathode and anode introduces additional ohmic resistance that could reduce the reactor's energy efficiency. This can be considered as the energy penalty that we must pay to separate the liquid fuels from the electrolyte. Compared with the traditional zero-gap membrane electrode assembly (MEA) reactor that has a typical cell resistance of $\sim 0.5 \text{ ohm cm}^2$ (refs. ^{50,54}), the solid-electrolyte reactor presents a resistance of $\sim 3.5 \text{ ohm cm}^2$ using a solid-electrolyte layer thickness of about 25 mm under steady-state operating conditions. This resistance could be dramatically reduced in the future by engineering ultra-thin solid-electrolyte layers^{14,19}. Whereas the cell voltage and efficiency may not be notably different under small-current operation, it could be hundreds of millivolts higher when using larger currents, thereby lowering the energy conversion efficiency in converting CO_2 molecules to liquid fuels. Substantial joule heating may occur during long-term operation, which could

decrease the lifespan of membranes and catalysts. Several strategies could be adopted in the future to resolve this issue of ohmic drop, including reducing the thickness of the middle layer, increasing the solid-electrolyte ion conductivity and improving the contact interface between the solid-electrolyte layer and the membranes. Although we understand that the ohmic drop could be linearly reduced with a thinner solid-electrolyte layer, it cannot be thinner than a certain range as we will need to strike a balance between the ohmic-drop and product-release processes. When the solid-electrolyte layer is too thin, pressurization of the microfluidic channels occurs, leading to potential problems with leakage, membrane breakoff and the product-release efficiency. Therefore, finding the optimized thickness of this middle layer can help us to deliver the best cell operation performances. Moreover, optimization of the thickness can also be accompanied by tuning the material properties of the solid electrolyte^{55,56}. Porosity is needed in the solid-electrolyte layer to enable efficient crossflow of water or gas for the product collection. Tunable porosity is desirable for optimizing both the ion conduction and the product recovery. By tuning the size of the solid-electrolyte particles/domains, we can balance the porosity and ion conductivity of this PSE layer: smaller particles improve ion hopping between the particles, and larger ones increase the pore size for a more efficient flow of the water or gas stream. Meanwhile, different substrate materials functionalized with ion-conducting groups can also be used in a solid-electrolyte design. For example, silica or carbon particles, which are commercially available in large quantities and with tunable sizes ranging from nanometre to millimetre sizes, can be used as the substrate material to be assembled with H⁺ or OH⁻ ion-conducting functional groups. Systematic tuning will need to be done to optimize the solid-electrolyte layer for better catalytic performances.

In addition, the catalytic activity and stability of the oxygen evolution reaction (OER) on the anodic side play a central role during the commercialization process of CO₂RR-generated liquid fuels^{57–60}. Different from an AEM assembly reactor where the OER catalyst is operated under alkaline conditions, OER in this solid-electrolyte reactor needs to be operated at an acidic pH so that the proton is the only cation that moves across the CEM into the solid-electrolyte layer for the production of high-purity liquid fuels. In practical operation, the long-term stability of the OER catalyst is even more important than its activity, but the only reliable catalyst under acidic OER conditions so far is IrO₂ (refs. ^{58,61}). There is an urgent need to explore highly stable and low-cost catalysts to replace IrO₂ for practical acidic OER processes.

Last but not least, the PSE reactor design could provide a feasible and effective method to prevent interaction between cathode-generated carbonate and the anode, which has been emphasized in recent literature reports^{50,62,63}. During CO₂RR electrolysis, large numbers of hydroxide ions (OH⁻) are generated at the cathode/electrolyte interface, which will react rapidly with the input CO₂ stream to form carbonate (CO₃²⁻) or bicarbonate (HCO₃⁻) ions. These formed bicarbonate/carbonate ions will go across the AEM to the anodic side to form CO₂ again and is mixed with O₂ gas, resulting in a substantial carbon loss for the overall carbon efficiency. By applying a PSE buffer layer between the cathode and anode, these locally generated carbonate ions will be driven by the electric field to cross over the AEM and then be recombined with protons (that have crossed from the anode) to form CO₂ gas again, which can be easily recaptured by continuously flushing the PSE layer with deionized water. Future studies can be performed to improve the carbon efficiency when using solid-electrolyte reactors.

Towards highly concentrated liquid fuels

While the solid-electrolyte reactor design can help to deliver high-purity liquid-fuel solutions by avoiding the use of traditional liquid electrolytes, the direct generation of highly concentrated pure liquid fuels is still challenging and may require alternative reactor

architectures. A simple approach to concentrating the final product is to directly decrease the deionized water flow rate through the solid-electrolyte layer while maintaining the CO₂ reaction rate. However, if the water flow rate drops to a threshold value this could greatly decrease the product selectivity due to the following reasons. First, with increased liquid product concentrations inside the middle solid-electrolyte layer, the thermodynamic equilibrium will shift towards the reactants, dramatically increasing the reverse reaction rate of CO₂ reduction and thus harming the product-generation performance. Second, the high liquid product concentration will accelerate the crossover rate of the liquid fuel into the anodic side where it will be oxidized, resulting in a low apparent product selectivity. Third, for carboxylic acid products such as formic acid and acetic acid, their high concentration will result in a low pH within the solid-electrolyte layer and could degrade the performance of the AEM and the catalyst during long-term operation. Therefore, how to increase the liquid-fuel concentration while not sacrificing the reactor performance remains an open challenge.

As a preliminary trial to address this low-concentration issue, our group used a humidified inert carrier gas flow, instead of a deionized water flow to collect high-purity and highly concentrated (up to 100 wt%) formic acid¹⁸. The central idea here is to maximally bring out the generated liquid product to reduce the concentration in the middle chamber, while not diluting the product concentration. Using a gas flow to flush our liquid fuels in their vapour phase, and followed by an easy cold condensation process, we can again separate the liquid product from the carrier gas and thus collect the liquid product at a high concentration. This product concentration can be properly controlled by tuning the water vapour pressure in the carrier as well as the gas flow rate. The lower the amount of water vapour carried in, the higher the liquid-fuel concentration that can be obtained since a smaller amount of water will be condensed in the cold trap. Demonstrated as an extreme case, we achieved 100 wt% pure formic acid by flowing dry nitrogen gas without water vapour in it¹⁸. However, a major challenge here is the poor stability of the solid electrolyte and ion-exchange membranes under low-water conditions. Therefore, significant improvements are still needed to meet the practical application standards (Fig. 4a). First, the product-release efficiency can be further improved by tuning the porosity and structure of the solid-electrolyte materials as well as the cell operation conditions. A highly porous solid-electrolyte layer could improve the ion conduction but may hinder the product vapour-release process due to distorted escape pathways. Based on the boiling point of the target product, the cell operation temperature can be finely tuned to maximize the evaporation of liquid fuel while suppressing the water vapour for a high product concentration. Second, to maintain a sufficient water level within the solid-electrolyte layer for good stability while not diluting the generated pure liquid fuels, solid-electrolyte materials can be engineered to increase the binding with water molecules while decreasing the binding with the target liquid-fuel molecules. Third, the temperature of the cold trap can be finely tuned to further separate the water and liquid-fuel vapours for high-concentration products. Fourth, future studies could also be focused on developing new types of ion-exchange membranes and solid electrolytes that can be reliably operated under low-water conditions.

This carrier gas flow–cold trap condensation strategy could also be used in other types of CO₂ electrolyser for different target liquid fuels (Fig. 4b,c). Different from anionic products, which are negatively charged ions and are driven by the electric field to move across the AEM into the solid-electrolyte layer, the generated alcohols are neutral molecules and can only be driven across the AEM by the concentration gradient. Therefore, taking advantage of this inefficient liquid-fuel crossover, we could collect highly concentrated alcohols from the cathodic side in an MEA reactor instead of using the solid-electrolyte design. In this case, AEMs with different types

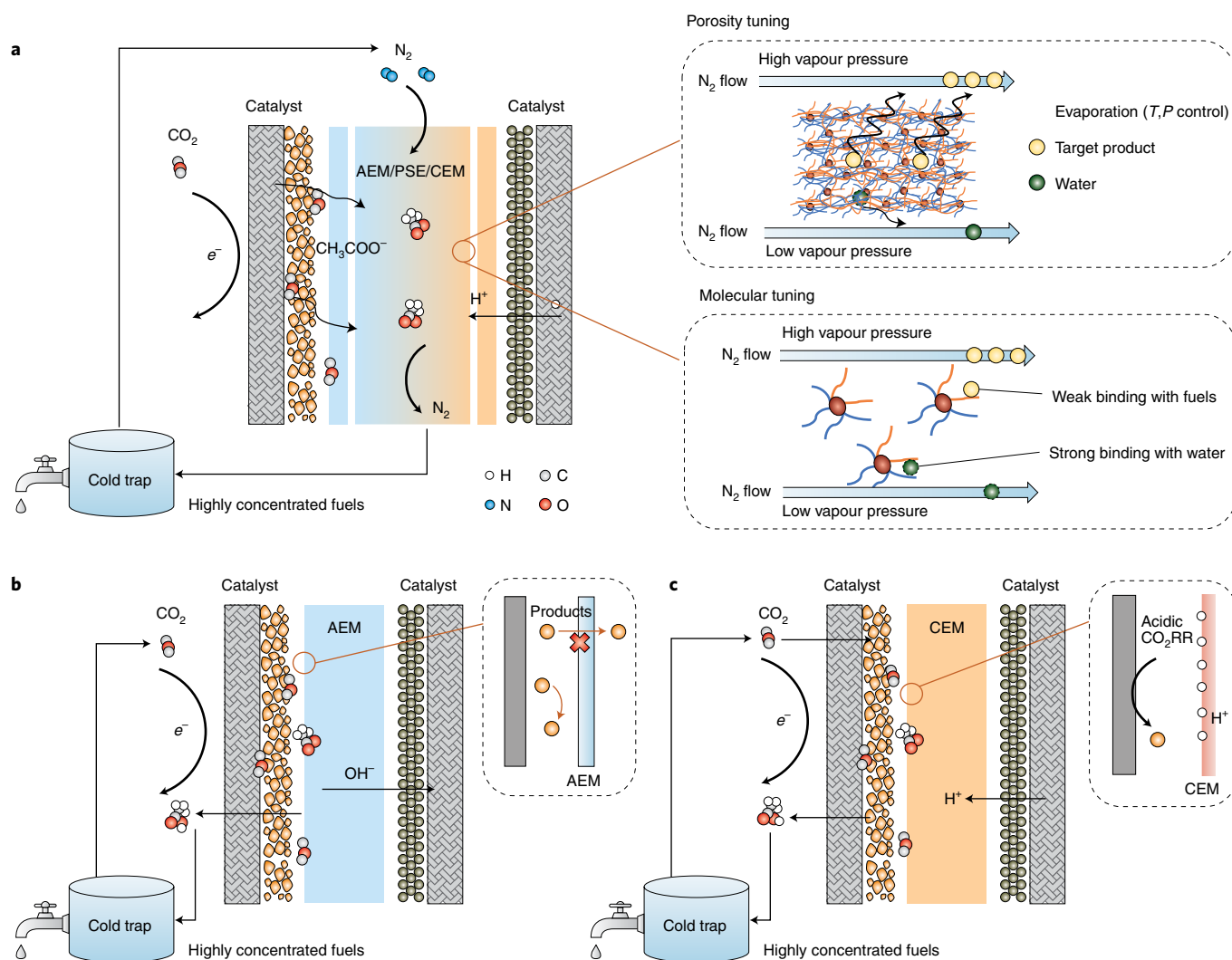


Fig. 4 | CO₂ electrolyser designs for high-purity and high-concentration liquid fuels. **a**, Schematic illustration showing inert gas flow in a solid-electrolyte cell to bring out liquid-fuel vapours for highly concentrated products. Tuning of the solid-electrolyte porosity, as well as the polymer binding with water versus the liquid-fuel molecule, could be used to maximize the vapour pressure of liquid fuels. **b**, Schematic of the AEM assembly cell for the production of concentrated liquid fuels, where the AEM does not allow the crossover of generated liquid fuels. Therefore, the generated liquid-fuel vapour could be carried out by the CO₂ stream to achieve high concentration and high purity. **c**, Schematic of the CEM assembly cell that requires a high catalytic CO₂RR performance in an acidic environment. The generated liquid product can be carried out by the CO₂ stream in its vapour phase and then cold-condensed into high-purity and high-concentration liquid fuels.

of polymer backbone could be designed to minimize the alcohol crossover towards the anodic side, allowing greater accumulation of the product at the catalyst/AEM interface to be carried out by the CO₂ stream in its vapour phase. Operating at an elevated temperature could be implemented to facilitate evaporation of the liquid fuel. The gas flow of the CO₂ stream can also be tuned to maximize the product-release efficiency. High-concentration anionic products could also be obtained using this MEA design with a CEM instead of an AEM to provide protons. However, the concentrated proton flux at the catalyst/membrane interface could promote the competing hydrogen evolution reaction. How to design high-efficiency CO₂RR catalysts that operate under acidic conditions is still an open challenge in this field. One strategy that has been demonstrated by Kanan and colleagues is to use sodium hydroxide solution on the anodic side to allow Na⁺, instead of H⁺, to cross the CEM to compensate the charge, although the final product will therefore be sodium acetate instead of acetic acid⁶⁴. Recently, Huang et al.⁶³ successfully utilized the K⁺ cation effect to achieve high-performance

CO₂ electrolysis in a strong acid, which also provides insight into the importance of acidic electrochemical CO₂ conversion.

Summary and future outlook

In summary, technoeconomic analysis of CO₂ reduction to liquid fuels delivers an important message that the electrolyte mixture and low-concentration issue in traditional electrolyzers, which is often overlooked in the CO₂RR field, could be one of the biggest barriers during the commercialization process. One promising but challenging direction is to design novel catalytic reactors, such as solid-electrolyte reactors, that can produce high-purity and high-concentration liquid fuels directly without the need for downstream product-separation processes. While most of the current research has been focused on developing high-performance CO₂RR catalysts, with exciting progress made over the past decade, more efforts need to be devoted to the other components of CO₂RR electrolyser design, including GDLs, membranes, solid electrolytes, interfaces, and so on, to ultimately deliver the goal of commercial-grade

liquid-fuel products. Future progress in reactor engineering for the reduction of CO₂ to pure liquid fuels will also greatly benefit other areas of electrosynthesis, such as the reduction of oxygen to hydrogen peroxide and the reduction of nitrogen to ammonia, to realize the direct generation of pure liquid products, pushing these electrochemical applications to the next level of development.

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Author contributions

H.W. supervised the project. P.Z. summarized the data. P.Z. and H.W. co-wrote the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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