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Carbon monoxide electroreduction as an emerging platform for carbon utilization

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The electrochemical conversion of carbon dioxide to value-added chemical products has been heavily explored as a promising strategy for carbon utilization. However, the direct synthesis of multi-carbon (C_{2+}) products suffers from undesired side reactions and relatively low selectivity. Electrochemically converting CO_2 to single-carbon products is much more effective and being commercially deployed. Recent studies have shown that CO can be electrochemically transformed further to C_{2+} at high reaction rates, high C_{2+} selectivity and inherently improved electrolyte stability, raising the prospect of a two-step pathway to transform CO_2. In this Perspective, the progress towards high-rate CO conversion is shown alongside mechanistic insights and device designs that can improve performance even further. A techno-economic analysis of the two-step conversion process and cradle-to-gate lifecycle assessment shows the economic feasibility and improved environmental impact of a high-volume commercial process generating acetic acid and ethylene compared to the current state of the art.

The potentially dire ecological effects stemming from anthropogenic climate change have accelerated the development in recent decades of alternative energy technologies that reduce net emission of CO_2 (refs. [1,2]). For example, significant progress in solar and wind electricity generation has recently resulted in market-competitive prices, reaching as low as US$0.02 kWh^{-1} in some areas[3,4]. Comprehensive solutions for addressing CO_2 emissions include decarbonization of the chemical production industry in addition to vastly reducing oil and natural gas use in the electricity generation and transportation sectors[5]. Technologies for CO_2 chemical conversion have emerged as attractive solutions because they can generate revenue from CO_2 feedstocks while reducing emissions and simultaneously reducing dependence on oil and natural gas for chemical and fuel productions.

Among them, electrochemical CO_2 reduction (CO_2R) is highly attractive, in which cheap, clean renewable electricity can be leveraged to synthesize valuable carbon-neutral products, where the electrolysis process couples readily with the intermittent nature of renewable electricity sources and operates near ambient conditions[6,7]. Depending on the electrocatalyst used, a variety of products can be produced including CO and formic acid, as well as C_{2+} products such as ethylene and alcohols. Production of single-carbon products is relatively simple to control, and high-rate CO_2R to CO is currently being developed for commercial applications[8–12]. As electricity prices decline, the production of C_{2+} products from CO_2R becomes more appealing due to their higher market potential[6,13]. To date, only copper-based catalysts have been shown to convert CO_2 into C_{2+} products with an appreciable selectivity; much work has been dedicated to their development and understanding[14,15]. However, further innovation is required to reduce the cathodic overpotential and to improve C_{2+} product selectivity[6,13].

CO is known as a key reaction intermediate on the pathway to C_{2+} compounds through CO_2R (ref. [14]) and studies of electrochemical CO reduction (COR) have shown vastly improved selectivity to C_{2+} and enhanced stability[15,16]. Recent progress demonstrating high-rate COR operation raises the tantalizing prospect of dividing the total conversion of CO_2 into discrete, optimized steps with CO as the intermediate feedstock[17–22]. Thus, the COR process has begun to receive renewed attention and shows significant promise, both for production of short-chain C_{2+} products—which has been widely studied—and for the newly identified ability to perform acylation reactions to produce a broader range of more complex compounds[23]. Industrially, carbon monoxide is derived from fossil resources such as methane and coal, and widely utilized for the production of critical compounds including methanol, acetic acid, phosgene and hydrocarbons[24]. The illustration in Fig. 1a shows the reach of COR using CO_2-derived CO as a platform technology with the ability to fulfil needs throughout the chemical production supply chain. From the perspective of early integration, it is easier to access markets where annual productions are low while production margins are high, pointing to acylation chemistries as the best short-term route. To maximize environmental impact, the carbon utilization technology must target higher-volume products, where significant innovation is still required to compete with established production methods (Supplementary Table 1).

This Perspective seeks to analyse and reconcile key impactful works on high-rate COR to multi-carbon products and paint a complete picture of the current technological status. We then present a brief techno-economic analysis (TEA) and cradle-to-gate lifecycle assessment (LCA) illustrating that production of high-volume acetic acid and ethylene through COR can be commercially competitive with further innovation and provide a roadmap towards achieving this goal.

Circumventing carbonate formation in direct alkaline CO_2R

Recently, several attempts to push production rates for C_{2+} products have been made through the use of a highly alkaline electrolyte (up to 10 M KOH) which dramatically reduces the overpotential for CO_2R (refs. [25–29]). A summary of these results in alkaline electrolytes is given Fig. 1b, which shows decent full-cell energetic efficiencies at appreciable reaction rates (Supplementary Table 2; assumes a 0.4 V anodic/cell overpotential except for when full cell voltage is reported). However, the use of alkaline conditions for CO_2R is fundamentally unsustainable due to the carbonate formation reactions

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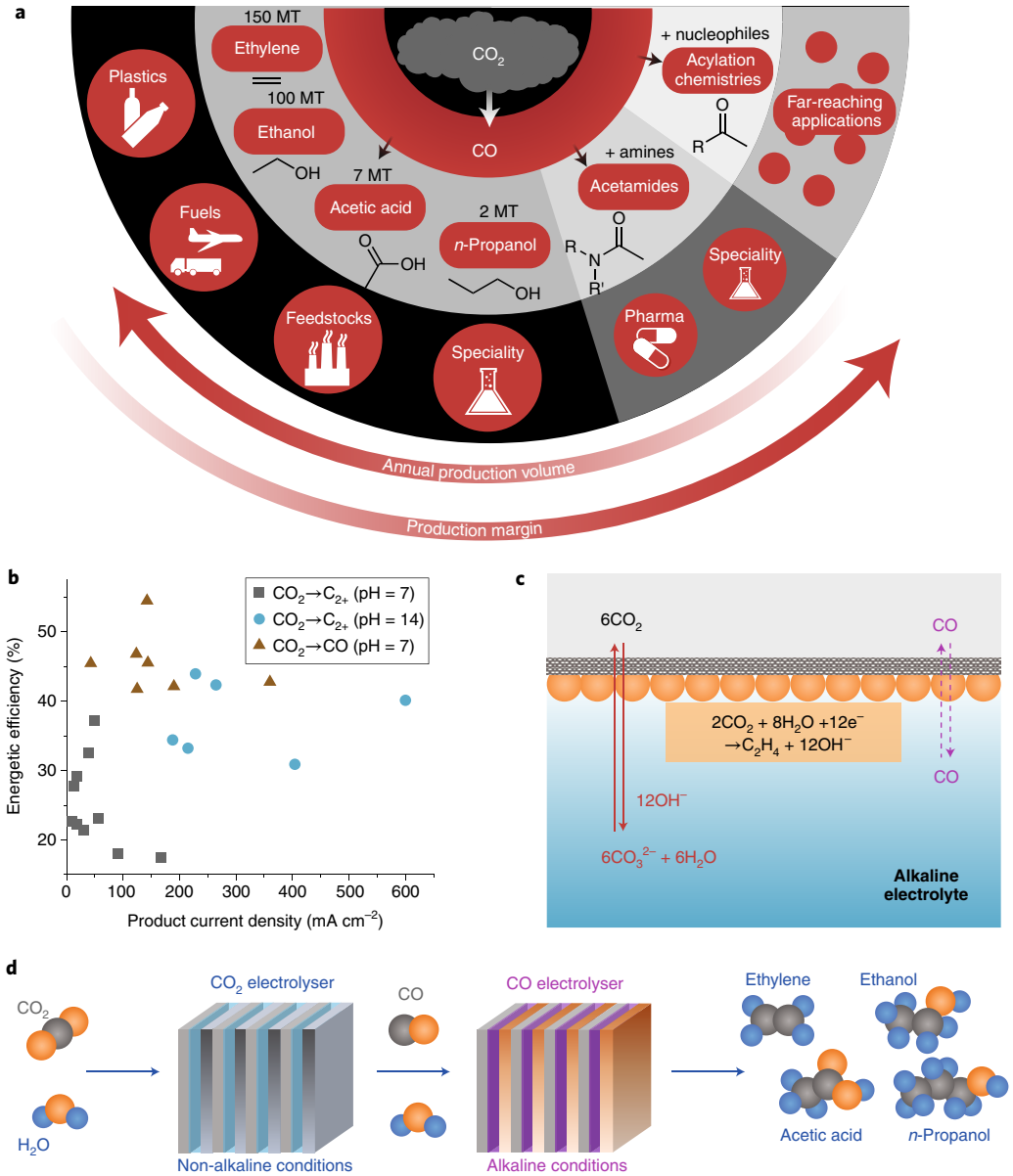

Fig. 1 | Overview of two-step CO_2R process and current state of direct CO_2R. a, Schematic overview of the core chemical products from two-step CO_2 conversion through COR, including products of co-reaction currently in varying stages of development. **b**, Recent state-of-the-art full-cell energy efficiencies and product current densities for CO_2 electrolysis to C_{2+} products or CO in various electrolytes (Supplementary Table 2, assumes a 0.4 V anodic/cell overpotential except for when full cell voltage is reported)[8–11,25–29,32–39]. **c**, Schematic illustrating the CO_2 consumption by OH^- to form CO_3^{2-}. **d**, Schematic of a two-step electrolysis process for CO_2 conversion to multi-carbon products using only CO_2 and H_2O as reactants.

that occur at the catalyst/CO_2 interface, which lead to the loss of both CO_2 and OH^-, as well as precipitation that degrades electrode performance (Fig. 1c)[11]. Using CO_2R to ethylene as an example, 2 mol CO_2 and 8 mol H_2O are consumed to produce 12 mol OH^- and 1 mol ethylene. This leads to the consumption of an additional 6 mol CO_2 to form 6 mol carbonate, resulting in the loss of 75% of the CO_2 reacted. The true consumption of CO_2 would be even higher due to free reaction with OH^- in the bulk electrolyte despite well-engineered electrodes. For this ethylene example, the cost of regeneration of CO_2 and KOH from the produced potassium carbonate would conservatively be ~US$300 per metric tonne of ethylene produced, which would have a significant impact on process economics and require product selling prices far above current market prices (Supplementary Note 1 and Supplementary Table 3). Therefore, CO_2R must be performed in non-alkaline conditions to minimize carbonate formation and prevent loss of electrolyte. While carbonate formation still occurs in neutral electrolytes utilizing anion exchange membranes, resulting in CO_2 shuttling to the anode[10,30], efforts are ongoing to address this using alternative configurations such as bipolar membranes[31].

In comparison with alkaline conditions, the demonstrated performance for CO_2R to C_{2+} products in non-alkaline electrolytes is significantly worse with both much lower reaction rates and low efficiencies, and these low-pH conditions tend to be better for making single-carbon products[32–39]. In contrast with CO_2R, COR is able to operate in highly alkaline electrolytes due to the inherent stability of CO (Fig. 1c), and high selectivity to C_{2+} products has been demonstrated with recent progress towards high reaction rates[17–22]. The rates of COR can match rapid production of CO through CO_2R, which has been studied extensively

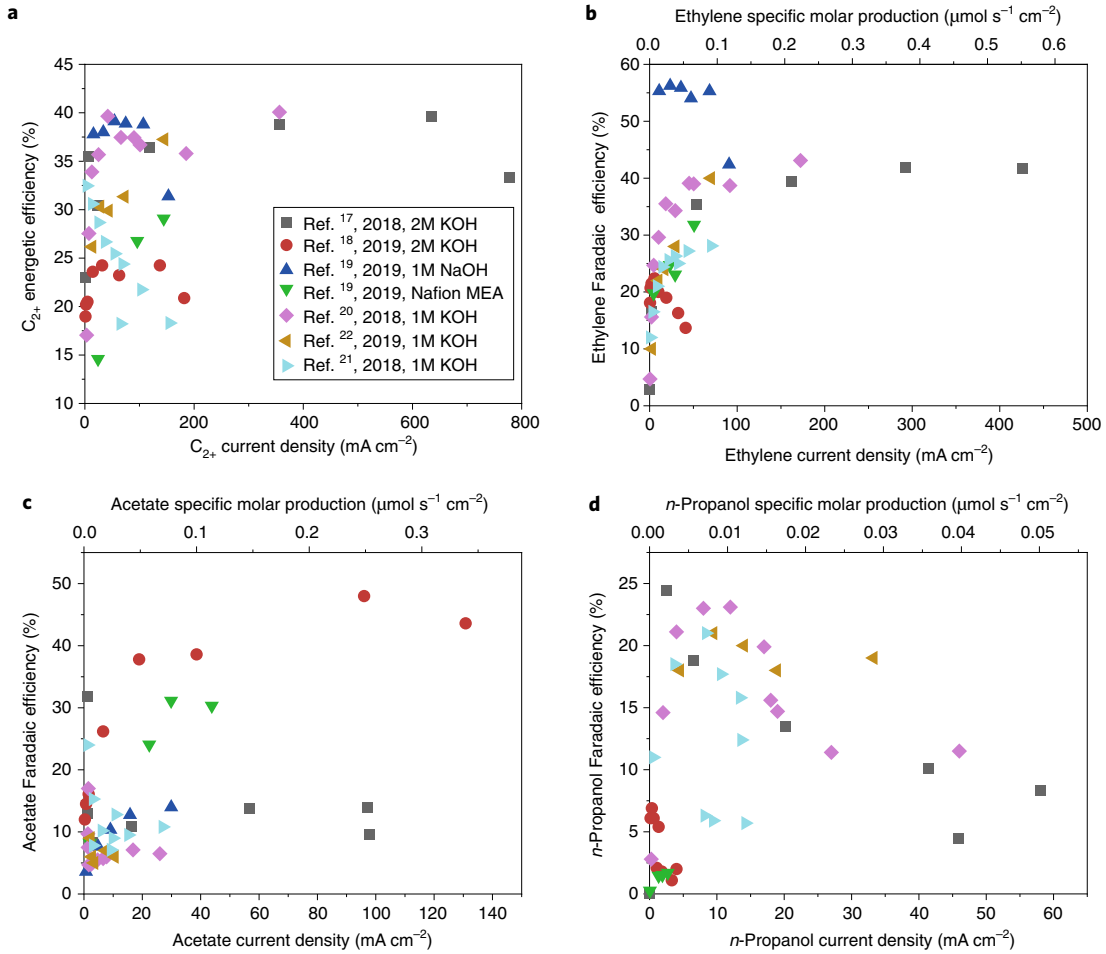

Fig. 2 | Performance of state-of-the-art COR cells with reported performance at high rates (>100 mA cm^{-2} total current density). Nanostructured Cu catalysts were used in all studies, with morphologies as detailed in their respective papers[17–22]. **a**, C_{2+} energetic efficiencies versus the C_{2+} partial current densities for each study (assumes 0.4V overpotential for anode). **b**–**d**, Faradaic efficiencies versus partial current densities from the same datasets for ethylene (**b**), acetate (**c**) and *n*-propanol (**d**).

in non-alkaline electrolytes[8–12]. Alternative methods of obtaining CO from CO_2 are already available commercially, such as a full-scale CO_2 to CO conversion device using solid oxide electrochemical cell technology currently produced and sold by Haldor Topsoe, which has a stated power requirement of ~7 kWh Nm^{-3} CO (45.4% total energetic efficiency)[40]. Therefore, an attractive pathway for C_{2+} production from CO_2 is a two-step process, whereby CO_2 is first converted to CO, and the resultant CO is converted to C_{2+} products through COR in alkaline electrolyte in a second reactor unit (Fig. 1d).

Reducing CO electrochemically at high rates

Although COR has been investigated since the pioneering work of Hori et al.[41], the focus was primarily on fundamental insights from batch studies and typically limited to current densities of only a few mA cm^{-2} (refs. [42–44]). Several recent articles have reviewed the state of COR at low current densities, which will not be duplicated in this Perspective[15,16]. The key practical issue in batch-type configurations is the extremely limited solubility of CO in aqueous electrolytes, which swiftly starves the electrocatalyst surface of reactant, driving up the overpotential and turning product selectivity towards CH_4. Increasing the reaction rate by circumventing this limitation has only been explored significantly within the past two years, and few studies to date have been performed in conditions capable of achieving high-rate C_{2+} production.

In order to summarize the current state of high-rate COR, we have plotted data from landmark studies in Fig. 2 where the total current density exceeds 100 mA cm^{-2} on a geometric basis without requiring excessive overpotentials[17–22]. While the electrochemical cell geometries differ among research groups and even within the same group, there are several key similarities: tests are conducted over some form of nanostructured Cu catalyst, catalysts are adapted into gas-diffusion electrode (GDE) assemblies where CO flows in a gas phase apart from any liquid catholyte, and a local high pH is maintained at the cathode. Individual advantages of each reactor design are discussed later in this Perspective.

The high-rate performances of COR are summarized in Fig. 2a, where an energetic efficiency of 40% has been achieved even at this early stage of development. As demonstrated by Jiao et al. the 40% energetic efficiency can be maintained at 600 mA cm^{-2} and decreases to 35% at approximately 800 mA cm^{-2}. This trend clearly suggests an urgent need to improve the overall cell energetic efficiency, which strongly affects the economics of this COR technology. More details are provided in the TEA section. Strategies to increase energetic efficiency of COR devices include searching for better electrocatalysts with lower overpotentials and higher selectivities, engineering electrochemical interfaces to minimize cell resistance, and optimizing cell operating conditions (for example, temperatures, pressures and pH conditions).

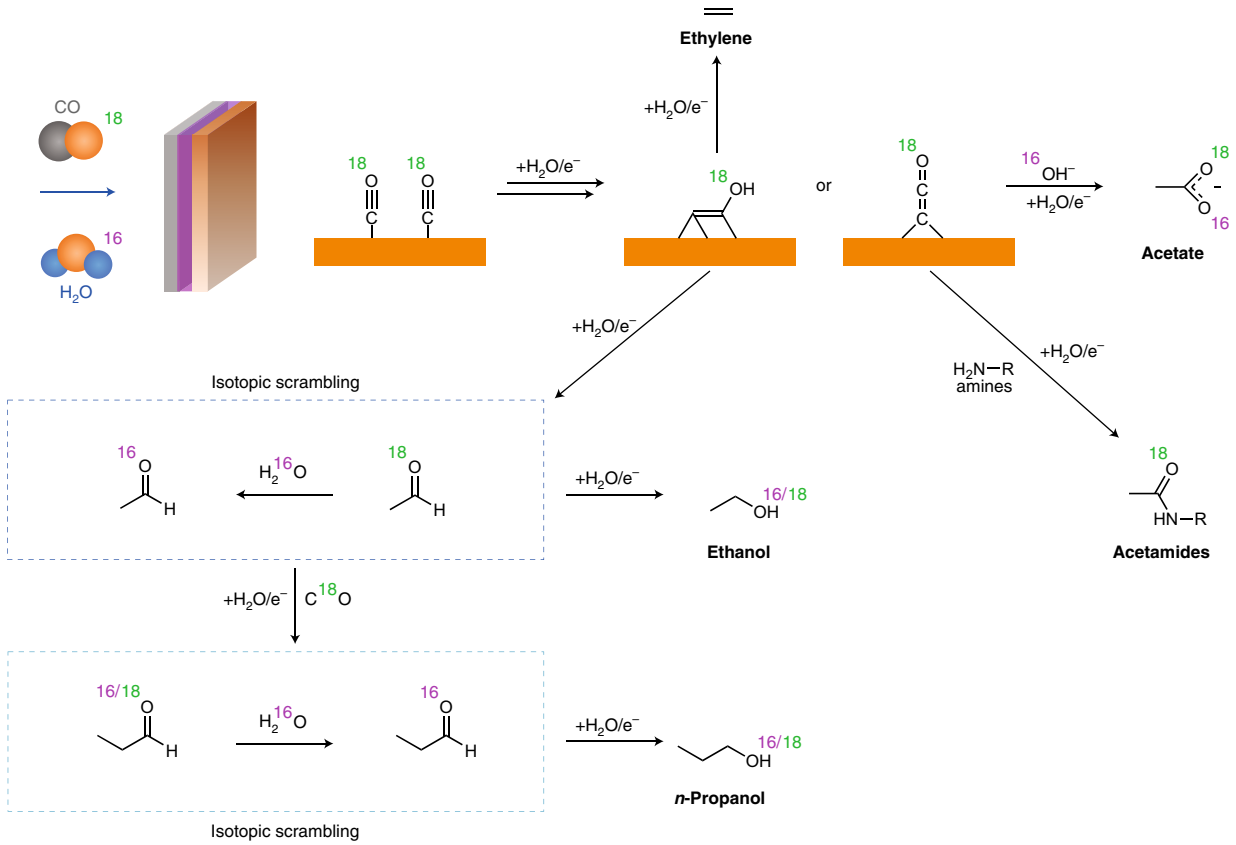

Fig. 3 | Mechanism of COR. A proposed mechanism explaining the incorporation of electrolyte oxygen into oxygenate products based on results of $C^{18}O$ reduction in unlabelled H_2O by Jiao et al.[17,23].

Figure 2b,c aids in answering the most critical question in COR research to date: which product(s) is the most desired target(s)? Ethylene production has been achieved at both high rates and high Faradaic efficiency (FE), though work remains to achieve both simultaneously. Acetate (OAc^-) can be produced at reasonably high rates as well and while maintaining FE above 45%. Catalyst structure and GDE configuration appear to be the primary means to tune activity between these two products, through further study is required to achieve consistency. A much higher OAc^- selectivity was obtained in COR compared to CO_2R. The economic opportunity of acetic acid production through COR will be discussed at the end of this Perspective. The promise of effective *n*-propanol synthesis has been proposed as a reason to investigate COR, but an unfortunate trend is apparent in Fig. 2d: the highest FEs occur at very low molar production rates (partial currents), and quickly tail off to single digits before reaching 50 mA cm^{-2}. A significant breakthrough would be required to achieve practical performance but given the higher market value it remains a worthy goal.

Note that ethanol is not a primary focus here as TEA results suggest that ethanol produced through the electrolysis route is not likely to be cost-competitive to subsidized corn ethanol[13], although interestingly the state of research follows ethylene trends more closely than *n*-propanol (Supplementary Fig. 1). As shown in the next section, this is likely because ethylene and ethanol share the same initial pathway and further protonation is easier than CO addition.

Elucidating the COR reaction mechanism

The production of OAc^- with an appreciable selectivity at high current densities has only recently been demonstrated for COR in highly alkaline environments, since OAc^- is not typically a major CO_2R product on copper electrodes. As a result, theoretical investigations of CO_2R on Cu electrodes have typically neglected calculating the mechanistic pathway towards OAc^- (refs. [45,46]). A recent computational study of CO_2R mechanism on Cu surfaces by Bell and Head-Gordon proposed that OAc^- could be formed through direct electrochemical reduction as part of a pathway towards ethylene, and suggested isotopic labelling experiments using $C^{18}O$ could be a potential method to verify the reaction pathways towards OAc^- (ref. [47]). Jiao et al. performed $C^{18}O$ reduction in a flow cell[17], and the majority of the acetate product was partially labelled, indicating incorporation of oxygen from the electrolyte into the product. Interestingly, ~80% of ethanol and ~90% of *n*-propanol were unlabelled, and acetaldehyde was entirely unlabelled. Coincidentally, Ager et al. performed a similar isotopic labelling experiment using $C^{16}O$ with $H_2{}^{18}O$ in a batch cell configuration, and observed similar fractions electrolyte oxygen incorporation across all products[48].

The mechanistic explanation of these isotopic labelling studies is shown in Fig. 3. Previous full solvent calculations for COR on Cu(100) at neutral pH found that adsorbed carbon monoxide initially dimerizes and is protonated to form *(OH)C=COH, which can then be further protonated to *C=COH (refs. [46,48]). Ethylene and alcohol formation then proceeds through parallel pathways through further reduction of *C=COH. More recently, additional calculations at high pH found that *(OH)C=COH can also dehydrate to form a surface ketene *C=C=O (ref. [49]). These calculations, along with the strong experimentally observed dependence of OAc^- formation with pH (OH^- concentration), suggest that OAc^- forms through direct OH^- attack of a ketene intermediate[17,18,42]. This is consistent with the observation of partially labelled OAc^- product in the isotopic labelling studies. Additionally, it has recently been discovered that a ketene or ketene-like intermediate appears to be a key driving force behind acylation of nucleophilic co-reactants[23].

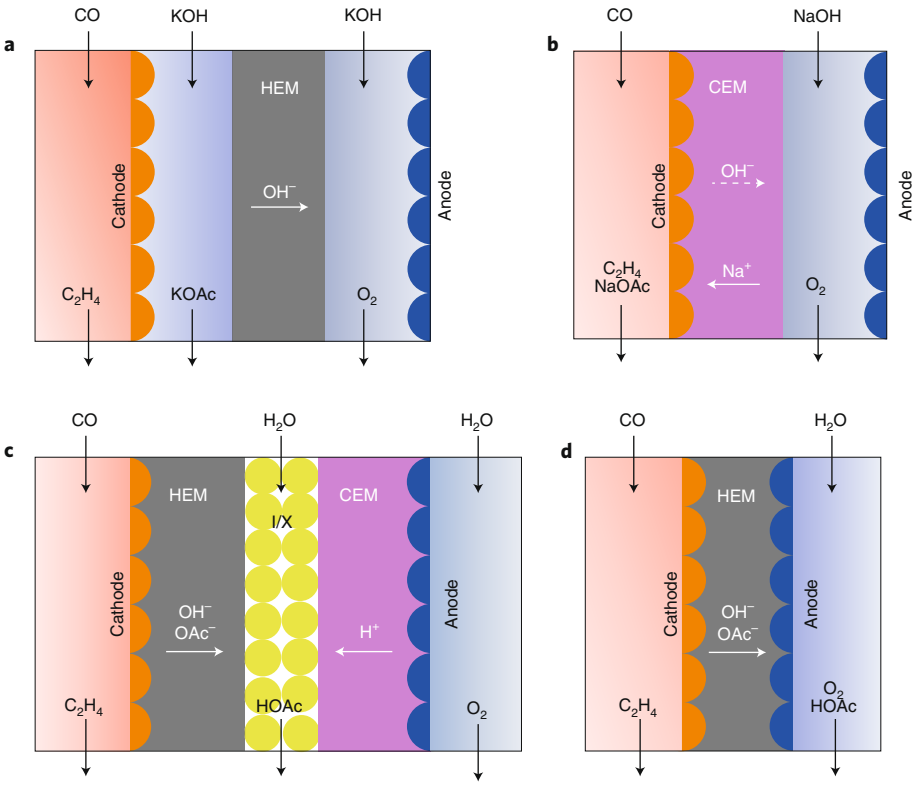

Fig. 4 | Current and proposed COR electrolyser designs. a–d, Vapour-fed CO electrolyser design schematics including typical three-compartment alkaline flow cell (**a**), cation-exchange membrane with alkaline anode (**b**), dual-membrane with central ion-exchange compartment for acetic acid production (**c**) and complete membrane-electrode assembly design for acetic acid production (**d**).

That study used $C^{18}O$ in unlabelled H_2O with NH_3 as the co-reactant resulting in labelled acetamide (CH_3CONH_2), which is consistent with a nucleophilic attack on labelled ketene. Previous studies also suggested a potential route for OAc^- formation through Cannizarro-type disproportionation of acetaldehyde catalysed by highly alkaline conditions[50,51]. While this would also lead to partially labelled OAc^-, the molar production of OAc^- observed experimentally often greatly exceeds that of ethanol, indicating Cannizarro disproportionation is not a dominant pathway[17,18].

The incorporation of electrolyte oxygen into other oxygenate products is likely due to the isotopic scrambling of acetaldehyde prior to further reduction to ethanol or propionaldehyde, leading to *n*-propanol[17,52]. The formation of alcohols through aldehyde intermediates was previously suggested by Stephens and Chorkendorff[44]. Clark and Bell showed that acetaldehyde and propionaldehyde are present in high abundance near the catalyst surface, indicating that these aldehydes are free species prior to further reduction to ethanol and *n*-propanol[53]. While Ager and Goddard calculated a mechanistic pathway to ethanol and *n*-propanol containing electrolyte oxygen involving water attack of a *C=CH intermediate, the energetic barrier is less favourable than the non-electrolyte containing pathway[48]. By contrast, the hydration of these aldehydes in highly basic conditions is energetically favourable[52]. Therefore, acetaldehyde and propionaldehyde likely undergo oxygen exchange prior to further reduction to alcohols. Combining differential electrochemical mass spectrometry (DEMS) and isotopic labelling studies could provide additional insights into the acetaldehyde scrambling mechanism.

Designing practical CO electrolysers

The use of a vapour-phase flow cell has enabled COR (and CO_2R) at industrially relevant current densities[54,55]. A three-compartment electrolyser design pioneered by the Kenis group is illustrated in Fig. 4a[56]. This reactor architecture enables the examination of catalyst activity in the absence of mass transport limitations, however there are several issues regarding its practicality at an industrial scale. The use of flowing liquid electrolytes with a thickness of >1,000 μm imparts a significant ohmic resistance in the cell. For example, 3 mm of 1 M KOH has a voltage drop (*IR* drop) of ~800 mV at a current density of 500 mA cm^{-2}. Moreover, the liquid product concentrations exiting the electrolyser in these studies are on the order of 1 mM (ref. [17]). While these issues can be remedied by decreasing the liquid electrolyte layer thickness, this will increase liquid product crossover to the anode. For ethylene production, high product concentrations (that is, high CO single pass conversion) could be achieved using this configuration, and in the absence of liquid products the catholyte could be eliminated with a membrane electrode assembly.

The production of concentrated liquid products is more challenging and requires an alternative flow cell architecture, because the circulation of electrolyte for the configuration in Fig. 4a will result in liquid products segregating across both the catholyte and anolyte. Recently, Kanan and colleagues demonstrated a COR electrolyser design capable of producing a concentrated (1 M) sodium acetate (NaOAc) stream[19]. The electrolyser consisted of a vapour-fed (3 atm CO) Cu-Nafion membrane electrode assembly (MEA) cathode and a NaOH anolyte with a freestanding Ti anode (Fig. 4b). The slow flux of water towards the cathode enables the formation of a concentrated NaOAc product stream. Additionally, a high CO single-pass conversion of ~70% was achieved, which is much higher than typical CO_2 conversions in CO_2R in alkaline, which are limited to <25% due to CO_2 consumption to form carbonates as discussed earlier[57]. However, in both configurations shown in Fig. 4a,b, the use of basic catholyte leads to the formation of OAc^- (salt) rather than acetic acid, a more valuable industrial chemical. The conversion of OAc^- salt to acetic acid will require an energy-intensive acidification process.

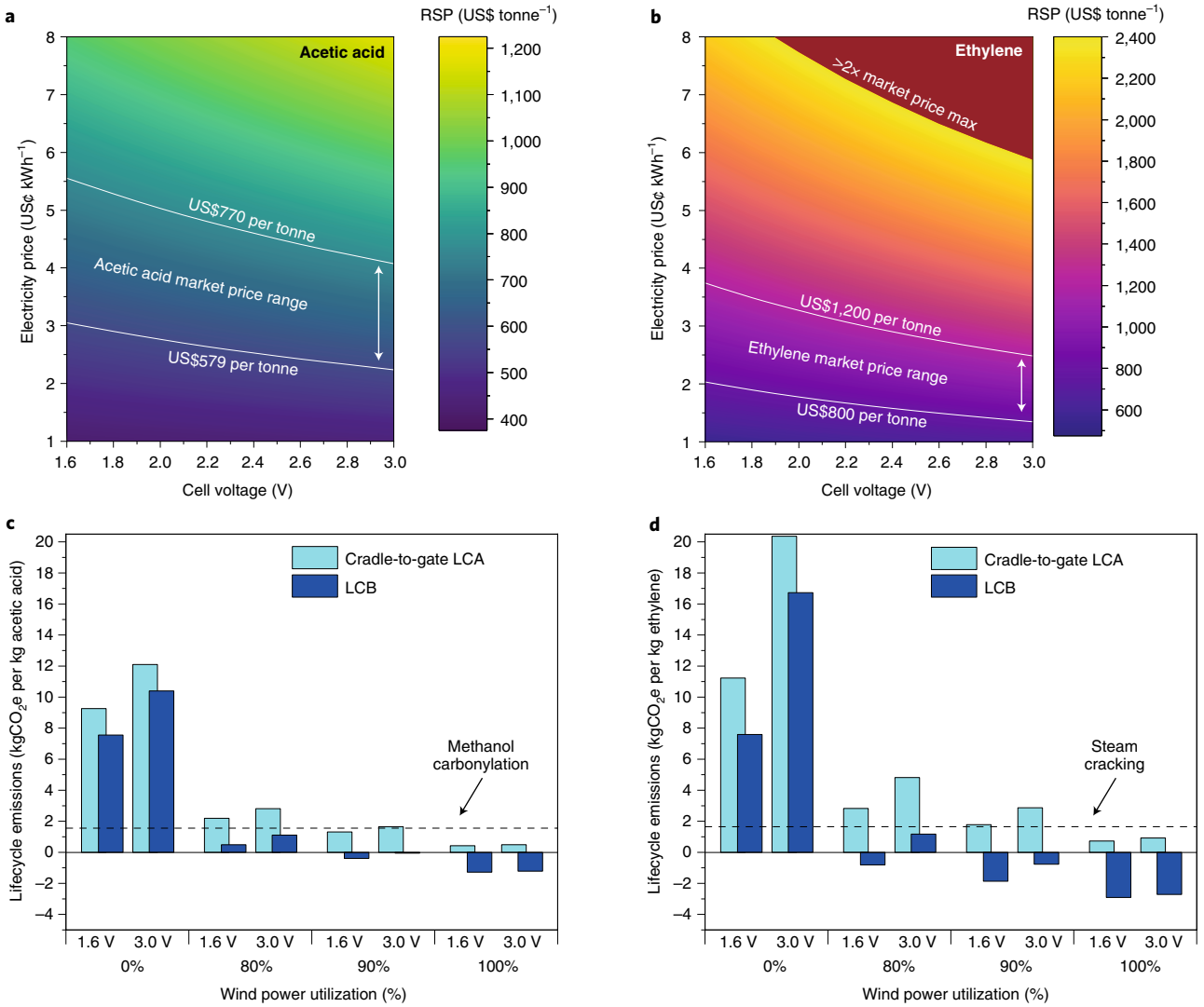

Fig. 5 | TEA and LCA for complete CO_2 conversion with COR. a,**b**, TEA for a COR device producing acetic acid (**a**) or ethylene (**b**) in a complete two-step conversion from CO_2 feedstock, showing the dependence of the required sale price (RSP) of each product (end-of-life NPV = US$0 with 20% rate of return) on the electricity price and cell voltage. The solid white contours show the approximate range of current market prices. The dark red area in **b** denotes RSP greater than double the maximum of the market price range. **c**,**d**, Cradle-to-gate CO_2 emissions from LCA and the local carbon balance (LCB) for two-step CO_2 utilization through COR producing acetic acid (**c**) or ethylene (**d**). Emissions are calculated using IPCC 100-year global warming potentials for all contributing gases. Results are presented as a function of total cell voltage (both CO_2R and COR) and percentage of onshore wind power electricity instead of the current US grid mix. Both models include upstream emissions from energy sources and material processing. Total emissions for established production of acetic acid from methanol carbonylation and ethylene from steam cracking are indicated by dashed lines.

The direct electrochemical reduction of CO to acetic acid could be achieved using a dual-membrane electrolyser shown in Fig. 4c. A similar design was employed by Dioxide Materials to produce concentrated formic acid from CO_2R (ref. [58]). At the cathode, CO is vapour fed to an OH^- exchange membrane (HEM) MEA, where OAc^- will diffuse to a centre chamber containing an ion-exchange resin (I/X). On the anode, a cation-exchange membrane enables proton transfer to the centre compartment, leading to the acidification of the OAc^- product. One limitation of this design may be crossover of the resultant acetic acid to the anode, creating two product streams. However, acetic acid is a terminal product in ethanol oxidation and may not appreciably oxidize on common OER catalysts[59]. Therefore, as a further alternative, a selective OER catalyst and robust HEM would enable the use of a full MEA configuration where both the anode and cathode catalysts are deposited on the HEM, minimizing ohmic losses (Fig. 4d). Concentrated acetic acid could then be produced by acetate diffusion to a pure H_2O stream and preferential electrolysis of OH^-/H_2O over OAc^- at the anode, while acetate production is maintained by a high local cathodic pH at high current densities. Furthermore, this design would require a high acetic acid selectivity, since the additional voltage penalty due to the anode/cathode pH polarity will decrease the energetic efficiency of by-products (ethylene, alcohols) relative to production in a fully alkaline electrolyser.

Techno-economic aspects of COR

To illustrate the market potential of high-volume chemical production from a two-step process beginning with captured CO_2, we have conducted a TEA for both acetic acid and ethylene targeted production. A useful metric to assess viability is to calculate the required sale price (RSP) at which the end-of-life net present value (NPV) of a full-scale plant producing 100 metric tonnes per day would be exactly US$0. The results are given in Fig. 5, which shows the RSPs as a function of electricity price and the total cell potential.

The analysis in Fig. 5a,b is adapted from our previous TEA of direct CO_2R (ref. [13]), which has been extended to include COR and acetic acid (Supplementary Note 2). At a reasonable total operating voltage of 2 V (cathodic overpotential of 0.651 V for acetic acid and 0.541 V for ethylene, assuming an additional 0.4 V for the total impact of both anodic and membrane overpotentials), the RSP of acetic acid becomes competitive at electricity prices below 5.0 US¢ kWh^{-1} and undercuts the range below 2.7 US¢ kWh^{-1}. Ethylene production under the same conditions enters the market price range at electricity prices below 3.3 US¢ kWh^{-1} and falls below the range at 1.8 US¢ kWh^{-1}. The US national average electricity price for 2018 was 6.9 US¢ kWh^{-1} and as low as 4.6 US¢ kWh^{-1}, indicating that acetic acid may be immediately profitable without substantial further technical improvements to the core electrochemical devices, though short-term ethylene production would require plant construction in regions with ample lower-cost electricity. An important note is that this analysis neglects any future policy-driven incentives for carbon utilization, which would make this two-step process profitable much sooner without waiting for fair market electricity prices to drop. The practical cell voltage for mature devices is not yet clear but is unlikely to exceed 2.5 V; this minimizes both incidental production of CH_4 which occurs at large cathodic overpotentials (maintaining ethylene as the sole hydrocarbon product) and cooling requirements for handling accumulation of low-grade heat.

The heavier dependence of ethylene RSP on electricity prices is unsurprising given that COR to ethylene is an $8e^-$ process compared to $4e^-$ for acetic acid (starting from CO), but this dependence also leads to a much faster decrease in ethylene RSP as the electricity price drops below the 3 US¢ kWh^{-1} target under both operating scenarios. Co-production of both ethylene and acetic acid together balances the costs and leads to a much wider range of profitable scenarios. Producing a mixture such as this is likely to occur based on the current state of research on Cu catalysts; discovery of newer, more selective catalysts could improve the prospects for high profitability. Additionally, acetic acid production directly in alkaline electrolytes would be in the form of OAc^- balanced by the alkaline cation and requiring some form of cyclical ion exchange to generate the end products. This motivates efforts to operate the COR cell at closer to neutral conditions, which would minimize this separation cost, making this a high-value development target going forward.

A critical result of this analysis is that it points to a wide range of practical scenarios for implementing high-rate COR as a commercial two-step process from CO_2, indicating that this technology should no longer be thought of as simply a way to probe the CO_2R mechanism and should instead be developed as its own process. As has already been shown earlier in this Perspective, OAc^- and acetic acid production is most effective at high current densities and where the cell design maximizes CO availability at the interface, and the pH close to the electrode is much higher at these same high rates. These practical characteristics parallel those used to justify calls for study of CO_2R at high rates[55], and along with the promise of commercial practicality we strongly suggest that COR development efforts shift towards cell designs that allow for high-rate, flow-type operation.

Cradle-to-gate lifecycle assessment

The primary motivation of CO_2 utilization is to reduce total lifecycle emissions of greenhouse gases by switching to new chemical production technologies that can harness emissions from other sectors. It is critical that these new technologies have lower emissions footprints than existing technologies, which requires a comprehensive inventory for fair comparison. To model emissions appropriately for COR as a production method for both acetic acid and ethylene, we have conducted a complete LCA for the cradle-to-gate CO_2 equivalent emissions (in $kgCO_2e$) of the two-step conversion through sequential CO_2R and COR from CO_2. The total emissions have been assessed as a function of overall cell potential of both the CO_2R and COR devices and the percentage of renewable onshore wind power utilized instead of the current electric grid mix. The LCA totals include contributions of electricity to drive the electrolyser, distillation or PSA powered by electricity, and upstream emissions leading to the CO_2 source. The overall results are shown in Fig. 5c,d.

In this analysis, each unit operation was modelled as a separate process in the openLCA software package using Intergovernmental Panel on Climate Change (IPCC) 100-year global warming potential impact methods (version 1.9.0, https://openlca.org). Mass and energy inventories for CO_2R and COR follow the model employed in the TEA section. The US National Renewable Energy Laboratory (NREL) lifecycle inventory database was used as the primary data source for upstream emissions and basis for state-of-the-art methanol carbonylation to acetic acid and steam cracking to ethylene[60]. As connectivity within this database often involves processes with multiple product outputs, physical allocation has been employed to limit the final product systems to a single product output (scaled to 1 kg of acetic acid or ethylene). Supplementary power grid emissions data was added from a separate IPCC lifecycle accounting[61], reflecting more recent worldwide electricity generation trends and including albedo effects.

While it is common to label CO_2 utilization technologies carbon-negative by simply treating captured CO_2 as a negative emission, the ideal method in evaluating new technologies is a complete cradle-to-gate LCA where all upstream emissions are considered and CO_2 is an internal product stream between the direct emission source and the point of capture (labelled cradle-to-gate LCA in Fig. 5c,d). This method allows for direct comparison with fossil-derived product systems by considering identical system boundaries. In this case, we consider a best-case scenario where CO_2 is derived from natural gas processing, which produces a nearly pure CO_2 output stream with effectively no energy cost for capture (0.0391 kg CO_2 per scm natural gas). Upstream capture emissions in this case are allocated as 0.232 $kgCO_2e$ per kg acetic acid and 0.496 $kgCO_2e$ per kg ethylene in terms of the final contribution to downstream products, which are then net positive. The use of nearly pure CO_2 is critical because contaminants such as SO_x can have detrimental effects to catalytic performance, especially on copper[62]. Investigation of other impurities such as NO_x and O_2 on COR performance is still needed.

If the CO_2 feedstock was instead treated as a negative emission in the system balance, then the 1.47 $kgCO_2e$ per kg acetic acid and 3.14 $kgCO_2e$ per kg ethylene used as feedstock could simply be deducted from the combined electrolyser and separation emissions. We refer to this as the local carbon balance (LCB) and also report results for this method in Fig. 5c,d. This form of carbon accounting neglects following the complete lifecycle of CO_2 from the point of emission from a fossil or non-fossil source, but the argument may be made that direct-air carbon capture treats CO_2 as a natural resource agnostic of the actual source. Such values may be used to cross-compare with other studies that ignore total lifecycle emissions for CO_2 inputs or count mid-stream consumption as a negative emission.

The direct comparison in Fig. 5c,d ultimately reveals that renewable energy utilization above 90% allows both acetic acid and ethylene two-step production to emit less than competing technologies in the complete LCA, and rapidly scales to less than 1 $kgCO_2e$ per kg product for even the least-efficient ethylene production scenario at near 100% wind power. In the LCB, negative emissions begin around 80% wind power utilization and likewise continue to improve with more renewable power in the mix. Consequently, short-term implementation of this two-step electrolysis should be co-located with renewable electricity generation, where the low start-up times also raise the prospect of using chemical production as a load balancing mechanism. Using cheap energy in bursts may be practical when the current density can pass a certain threshold (Supplementary Fig. 2) and focusing improvements on increasing

current density has the added effect of reducing overall capital costs for the electrolyser. However, further investigation of catalyst stability under highly variable current load is needed.

Outlook

While development of COR is limited compared to decades of CO_2R studies, the trends observed thus far indicate this is an emerging platform with great promise for effective high-value C_{2+} production with the prospect of reducing overall greenhouse gas emissions. We would like to emphasize the following key points of the emerging COR technology:

COR is more effective for sustained C_{2+} production than direct CO_2R. The core issue of alkaline electrolyte degradation by free reaction with CO_2 is eliminated by switching to CO as the reactant. This is currently a significant hurdle for direct CO_2R to C_{2+}, which has only been effectively demonstrated in alkaline electrolytes. It should be noted that contemporary TEAs of this direct CO_2R omit electrolyte regeneration by assuming neutral or acidic pH conditions but with performance metrics that are optimistic even for alkaline conditions; in the absence of a breakthrough the actual costs will be inherently more expensive (hundreds of US dollars per metric tonne of product). By contrast, CO_2R to CO shows great promise and both the flow-type devices and solid oxide electrochemical cells are scaling towards greater commercial availability. Therefore, we recommend a shift to focus on two-step conversion of CO_2 to C_{2+} with COR as a core component. While a two-step CO_2 conversion process incurs some additional capital costs, the impact on the per-mass production cost is negligible compared with electricity costs and performance improvements.

COR device development has a clear roadmap. As shown by aggregating all the landmark high-rate COR data to date, ethylene and acetate/acetic acid are the two products that can be generated with both high molar production and high FE. Tuning between one or the other appears to be a function of Cu catalyst structure and GDE configuration, and both should remain as the primary development targets. As local pH conditions at the cathode increase dramatically at high rates compared to the bulk electrolyte, it is critical that studies employ flow-type configurations capable of high COR rates to ensure that the correct performance characteristics are captured. These high-rate conditions are also of greater interest to the industrial community, where electrolysis cells are an attractive option for harnessing short bursts of cheap electricity even where energy costs are too high for sustained production. This recommendation extends to development of other critical device components required to improve energy efficiency, including new selective membranes with low area specific resistance and minimal product crossover. If studies are conducted at low rates for fundamental study of new materials, it would be of great value to the community to also report high-rate data showing that the activity remains under more practical operation conditions. Taking the further step of using MEA-based designs free of aqueous electrolytes will further improve the achievable energetic efficiency due to reduced overpotential from the electrolyte.

COR opens a broader range of C_{2+} products through co-electrolysis. While the base COR reaction adds acetate/acetic acid to the mix of C_{2+} compounds compared to direct CO_2R, the newly identified ability to perform acylation through co-reaction with nucleophilic feedstocks provides a pathway to speciality chemicals. Specifically, $CH_3CO–$ attaches to each active functional group, always increasing the final molecular mass of the product of interest. The available data clearly demonstrate amine-to-amide conversion, and the mechanism of acylation through in situ ketene generation likely extends to many more types of nucleophilic functional groups. This capability is not only interesting on a fundamental level, but creates yet another opportunity unique to COR. A significant challenge for commercialization of direct CO_2R to C_{2+} has been the need to immediately scale into massive markets with tight margins and fierce competition, particularly for production of ethylene and ethanol. Producing speciality chemicals through COR is an attractive strategy for reaching the market much sooner, as volumes tend to be achievable for smaller companies. Application areas are diverse and are highly dependent on the library of compounds able to be synthesized through COR, which remains to be thoroughly explored with further research. Replacing OER on the anode with an alternative co-reaction that takes place at a lower potential will further improve overall device economics and reduce power requirements, thereby expanding the promise of this system[63].

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Author contributions

M.J. and G.S.H. contributed equally to this work. M.J., G.S.H. and F.J. performed data analysis and wrote the manuscript. F.J. supervised the whole project.

Competing interests

G.S.H. and F.J. are co-founders of Lectrolyst, a company developing devices for electrocatalytic conversion including carbon monoxide reduction.

Additional information

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