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Carbon-efficient carbon dioxide electrolysers

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The electroreduction of CO_2 (CO_2R) is the conversion of CO_2 to renewable fuels and feedstocks, a promising technology that could support the transition from fossil to renewable sources in the chemical industry. Today the viability of CO_2R technology is limited by carbonate formation via the reaction of reactant CO_2 with hydroxides and the energy cost incurred to regenerate the reactant. In this Review, we analyse the literature on four emerging high single pass CO_2 conversion approaches: CO_2 regeneration from carbonate, CO_2R in acidic media, cascade CO_2R-COR and CO_2R direct from a capture liquid. We analyse each system, describe the challenges associated with each pathway and outline future research directions towards the goal of ensuring that CO_2R is viable and thus scalable.

The petrochemicals sector enables the production of fuels, plastics, fertilizers, detergents, digital devices and clothing ubiquitous in modern society[1,2]. The industry is a major energy user, with usage matching that of the steel and cement industries combined[3]. The dependence of the chemical sector on fossil fuels for process energy and feedstocks poses an important global challenge: the chemical sector makes up 18% of today's industrial CO_2 emissions[3]. The sector is on course to emit 200 million tons of CO_2 equivalent by 2050[4]. Cost-effective, low-carbon routes to manufacture chemical feedstocks and fuels are needed to mitigate environmental impacts.

Employing waste CO_2 as a feedstock to produce multicarbon (C_{2+}) products would offer a route to carbon-neutral chemical production[5]. Electrochemical CO_2 reduction (CO_2R) converts CO_2, water and low-carbon electricity into chemicals and fuels[6] (Fig. 1a). This process can be tuned to target products that are currently manufactured using emissions-intensive thermochemical processes at the million-ton scale, such as ethylene, ethanol and n-propanol[7,8]. By converting electrical energy into dispatchable fuels, CO_2R also offers a means of renewable energy storage[9–12]. The feedstock CO_2 could be captured from the atmosphere[13], waste emissions[14,15] or biological processes[16,17]. Through these routes CO_2R helps close the carbon cycle[18].

The feasibility of CO_2R requires stable operation at industrially relevant current density and energy efficiency (EE)[19,20]: current densities above $100\,mA\,cm^{-2}$ with EEs exceeding 50% (refs. [21–23]). The electrolyser configuration greatly influences the reaction rate, EE and stability of CO_2R[24]. Today, CO_2R is performed in three electrolyser configurations: H-cell[25,26], flow cell[27–31] and membrane–electrode assembly (MEA)[10,32–34]. H-cell electrolysers are limited to low reaction rates, only several tens of mA cm^{-2} due to the limited solubility of CO_2 in aqueous solutions[35]. Flow cell electrolysers decouple reactant and electrolyte transport via gas diffusion electrodes (Fig. 1b), thereby overcoming CO_2 mass transport limitations and achieving practical current densities[27,28]. However, ohmic loss across the cathode electrolyte results in high overpotential and low EE[36]. Additionally, the produced liquid products are diluted by

the bulk electrolyte, and salt precipitation limits operational stability[37]. The MEA electrolyser is an emerging platform that combines cathode:membrane:anode in a zero-gap configuration and reduces ohmic loss, liquid product losses and salt formation (Fig. 1c). Integration of selective and active catalysts into flow cell and MEA electrolysers has enabled considerable improvements in Faradaic efficiency (FE)[29,30], productivity[27,29] and stability[28,32] towards C_{2+} products.

Despite advances in FE and current density, present-day CO_2R systems suffer from severe loss of CO_2 reactant[38,39]. The use of alkaline or neutral electrolytes in today's electrolysers leads to carbonate formation ($2OH^- + CO_2 \rightarrow CO_3^{2-} + H_2O$) through the reaction of CO_2 with hydroxides already present in the electrolyte and those locally generated by CO_2R[40] (Fig. 1d). Carbonate formation imposes an unacceptably low upper bound on single pass conversion (SPC)—the fraction of incoming carbon that is converted to target products in benchmark, once-through electrolysers. SPCs are well below fundamental limits due to imperfect FE[41–43]. In alkaline media (pH > 14), fully 95% of CO_2 input is lost, hence for complete CO_2 utilization to be achieved, each CO_2 molecule would have to be separated and recirculated an average of 20 times[44]. Even in milder neutral-electrolyte reactors, 75% of CO_2 is lost to carbonate formation and ensuing crossover in conversion to C_{2+} products (Fig. 1e). The energy demand from separation steps is prohibitive (Fig. 1e). The regeneration of alkaline electrolyte (for example, via calcium caustic loop[9,23]) accounts for 60–75% of total energy input (Table 1). Neutral media MEA electrolysers have less carbonate formation, but do not exceed 50% SPC in the case of C_1 products[45,46] or 25% in the case of C_2[37,47].

A shift from alkaline to neutral media (pH ~14.6 to ~8.2), while maintaining CO_2R performance, could reduce energy penalties associated with carbonate regeneration and cathode separation. However, even under the milder conditions (pH ~8.2), the CO_2R system (with theoretical CO_2-to-ethylene SPC of 25%) requires an extra energy input of ~42 GJ to produce 1 ton of ethylene at typical conditions (Fig. 1e). This energy cost is prohibitive as it is almost equal to the lower heating value of ethylene (~47 GJ ton^{-1}; ref. [48]).

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An analysis of the SPC of CO_2 as a function of carbonate formation ratio (lost-CO_2:reduced-CO_2) indicates that carbon-efficient systems minimize CO_2 loss to carbonate and enable high SPC towards C_{2+} products (for example, ethylene) (Fig. 1f). Strategies to remove these SPC limits are of importance to the field.

This Review provides an overview of opportunities for the field to address the low SPC challenge via carbon-efficient pathways: CO_2 regeneration from carbonate, CO_2R in acidic media, cascade CO_2R-COR and CO_2R direct from a capture liquid. We review the progress and technical challenges in each pathway, discuss the techno-economics and outline future research directions that would make each pathway viable.

CO_2 regeneration via bipolar membrane

Regeneration of CO_2 from carbonate and its ensuing reduction to C_{2+} products can be achieved using a bipolar membrane with anion and cation exchange layers[49,50]. Bipolar membranes can be operated under forward-bias or reverse-bias mode. Under forward bias, the cation exchange layer faces the anode, blocks the transport of (bi) carbonate anions and converts (bi)carbonate back to CO_2 while conducting protons from the anode to the membrane junction[49,51]. The anion exchange layer of the bipolar membrane (facing the cathode) provides the local alkalinity required for CO_2R[52,53] (Fig. 2a). In such a system, anolyte without alkali metal cations (acidic electrolyte or pure water) ensures that protons are the sole charge carrier through the cation exchange membrane and (bi)carbonate can be neutralized at the interface of anion and cation exchange domains. Carbonate crossover can also be mitigated with a bipolar membrane in a reverse-bias configuration, where the cation exchange layer faces the cathode and the anion exchange layer faces the anode[54]. However, the reverse-bias mode requires strict control on the proton flux towards the cathode to mitigate hydrogen evolution and promote C_{2+} products[50].

The forward-bias bipolar membrane approach can be implemented in both flow cells and MEA electrolysers with acidic electrolytes or pure water (pH 1~7). When employed in MEA electrolysers equipped with catalysts selective to liquid CO_2R products (for example, ethanol, acetate, formate and n-propanol), a bipolar membrane would offer the additional benefit of mitigating liquid crossover to the anode[55,56], thereby enabling collection of concentrated liquid products from the cathodic stream. With advantages of high SPC and minimized liquid product crossover, this approach could minimize the downstream energy demand associated with anodic and cathodic separation processes[57].

Although bipolar membrane-based systems could offer a high SPC, they are still at an early stage of development and suffer several shortcomings. One of the biggest challenges is poor operational stability—a result of the accumulation of H_2O and CO_2 at the interface of anion and cation exchange domains[50]. The CO_2/H_2O built up at the interface of the forward-bias bipolar membrane deteriorates performance through increased cell potential and membrane damage[58]. These in turn lead to low EE and poor operational stability. Therefore, gas/water management and electrode/interface engineering have become the focus of research and development to achieve performance breakthroughs.

The forward-bias bipolar membrane-based approach has been demonstrated with both gold and silver catalysts to achieve CO production with minimal CO_2 crossover to the anode[50,54]. The operating potential of these systems is akin to that of electrolysers with conventional anion exchange membranes[27,37] due to the high proton conductivity enabled by the cation exchange layer. Under the reverse-bias mode, augmenting the alkali cation (K^+) availability on the reaction environment overcomes the poor FE limits in CO_2-to-CO conversion, enabling a CO FE of 68%[54]. Strategies that would enable high rate and efficient CO_2R on copper catalysts under the reverse-bias mode are also vital for progress towards C_{2+} products. Under the forward-bias mode, there has been progress in CO_2-to-C_{2+} conversion: a permeable CO_2 regeneration layer coupled with a cation exchange membrane has been developed to minimize the CO_2 crossover in an MEA electrolyser[59], achieving ~65% C_{2+} FE and ~85% SPC of CO_2 towards C_{2+} products at 100 mA cm^{-2}. These productivities suggest that the reaction kinetics of carbonate regeneration are sufficiently rapid to support practical reaction rates. With continued research into electrolyte, electrode and interface engineering, the bipolar membrane approach could enable high SPC, FE and productivity towards C_{2+} products.

Future numerical and experimental investigations into the underlying mechanisms of CO_2/H_2O accumulation will be key to developing sound strategies that prolong operational stability beyond 1,000 h. We suggest the following foci to achieve performance breakthroughs (lower cell potential and higher CO_2R activity) and prolong operational stability under both forward- and reverse-bias modes: (1) engineering the physical, chemical and mechanical properties of anion and cation layers in the bipolar membrane (for example, thickness, porosity, tortuosity, ionic conductivity, electroosmotic drag, liquid uptake, hydraulic permeability, sorption/ desorption and chemical/mechanical stability); (2) optimizing the interfaces between the anion/cation layers and anode/cathode electrodes; and (3) optimizing operating conditions (temperature and type/concentration of aqueous electrolytes).

CO_2R in acid

CO_2 loss to carbonate is acute in alkaline conditions. Performing CO_2R in acidic media could eliminate carbonate formation, thereby eliminating CO_2 crossover. In an acidic system, cathode and anode electrodes are physically separated by a proton exchange membrane. Consequently, the crossover of both carbonate ions and charged/uncharged CO_2R products is minimized (for example, the ion flow is reversed relative to traditional systems). Ideally, if H_3O^+ is the proton source, there would be no generation of OH^-, hence CO_2R can occur without carbonate formation. However, if H_2O is the proton source, local OH^- generation and carbonate formation is inevitable. Under certain conditions, any carbonate generated locally could be converted back to CO_2 by protons available in the acidic bulk electrolyte[60,61] (Fig. 2b). In this case, any formed
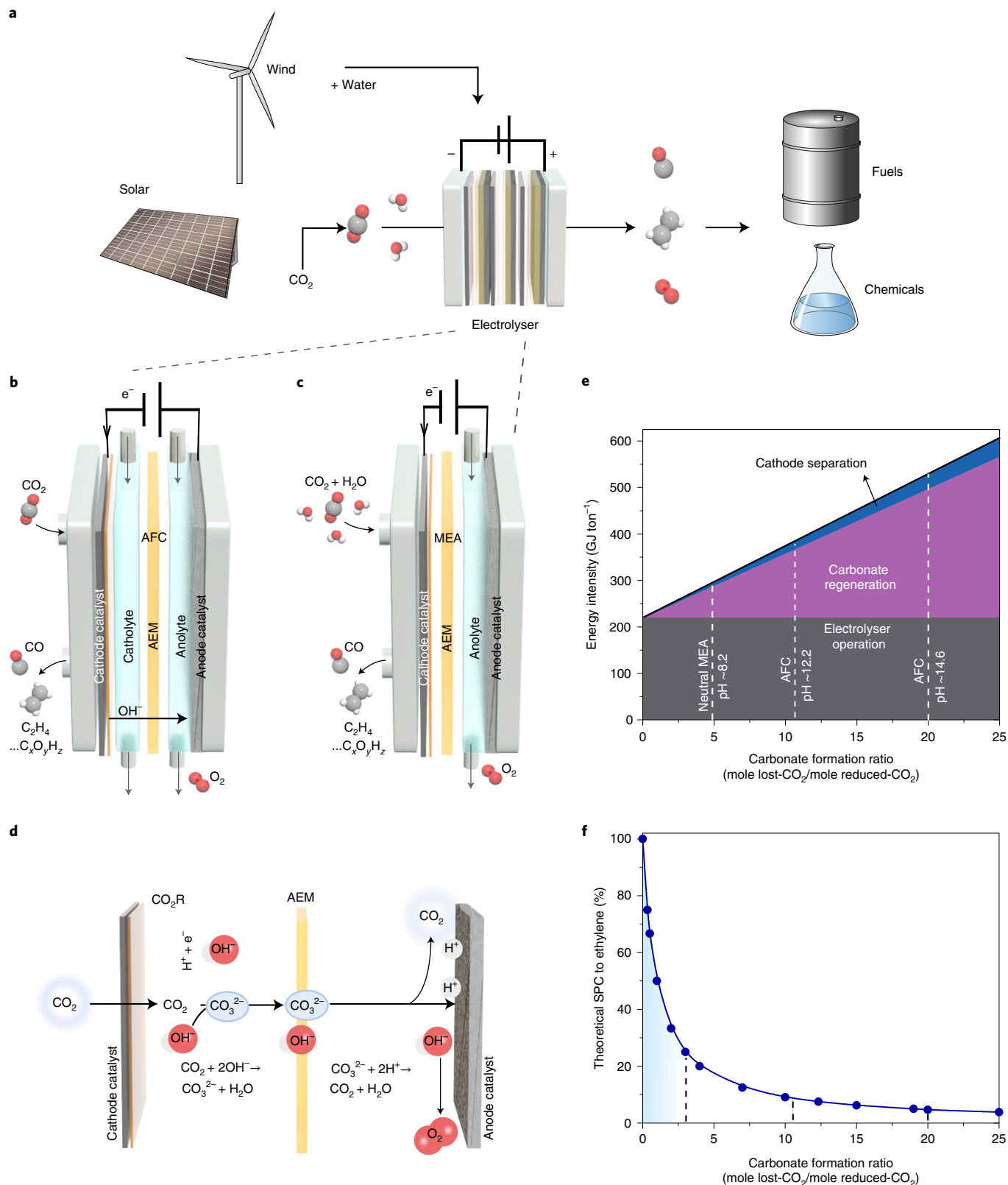
Fig. 1 | Carbonate formation and associated energy consumption/production penalty in alkaline and neutral media CO_2R. a, CO_2R to fuels and chemicals. **b**, Schematic of a liquid-electrolyte alkaline flow cell (AFC) electrolyser. AEM, anion exchange membrane. **c**, Schematic of a neutral media MEA electrolyser. **d**, Carbonate formation and crossover in alkaline and neutral media. **e**, Energy penalty associated with carbonate formation and cathode separation versus SPC. **f**, SPC of CO_2 towards ethylene versus carbonate formation ratio. Carbon-efficient systems minimize CO_2 loss to carbonate and enable high SPC. The dashed lines represent SPC limits for ethylene in AFCs and MEA electrolysers. CO_2 separation from the anolyte in the neutral case is treated similarly to the carbonate regeneration in the alkaline case. The energy penalty associated with regeneration of alkaline electrolyte is based on calcium caustic loop[9,23]. The carbonate formation ratio of <3 (light blue-shaded area) represents the carbon-efficient systems. The carbonate formation ratios were obtained by performing CO_2R at 300 mA cm^{-2}. The product and CO_2 concentrations at the cathodic and anodic streams were monitored to determine the ratio of lost-CO_2 to reduced-CO_2 on a molar basis. Performing the analysis with various electrolytes, including neutral (pH ~8.2) and alkaline (pH ~12.2 and ~14.6) electrolytes, we determined the minima and maxima of carbonate formation ratio in neutral and alkaline systems. The energy intensity versus carbonate formation ratio and the SPC to ethylene versus carbonate formation ratio were obtained at a current density of 300 mA cm^{-2}, a cell potential of 3.7 V and an ethylene FE of 70%.

carbonate would be confined to the local environment at the cathode surface (locally alkaline). Consequently, acidic media CO_2R holds substantial potential to circumvent the low SPC limits that are fundamental to neutral and alkaline systems.

Acidic media CO_2R can be implemented in flow cells or MEA electrolysers with pH 0~5 electrolytes. This approach could provide the additional benefit of suppressing liquid product crossover to the anode if employed in MEA electrolysers, with catalysts selective to liquid products (for example, formic acid or acetic acid at bulk pH < 3.7) and a proton exchange membrane[49,56].

Unfortunately, in acidic media CO_2R, the hydrogen evolution reaction dominates as proton reduction is kinetically favoured. As a

Table 1 | Energy assessment of literature benchmark carbon-efficient and alkaline/neutral media CO_2R systems towards ethylene under their highest EE operation mode

Parameters	Conventional alkaline media CO_2R (ref. [28])	Conventional neutral media CO_2R (ref. [10])	CO_2 regeneration via bipolar membrane[59]	CO_2R in acid[47]	Cascade CO_2R-COR (ref. [9])	CO_2R from a capture liquid[a]
	Flow cell	MEA	MEA	Flow cell	SOEC[d]/MEA	MEA
Full-cell voltage (V)	**2.4**	**3.9**	3.8	4.2	1.4/2.4	4.1
FE (%)[b]	**70**	**66**	45	30	95/63	30
Current density (mA cm^{-2})	**150**	**315**	100	1200	700/120	200
SPC (%)	**1.1**	**3.3**	0.7	11.4	45/2.2	100
Carbonate formation ratio[c]	**20**	**3**	0	0	0	0
Electrolyser specific energy distribution (GJ (ton product)$^{-1}$)[e]						
Electrolyser electricity	**141.8**	**244.4**	349.2	578.9	20.4/105.0	565.1
Cathode separation	**144.2**	**49.3**	229.6	24.0	3.6/69.8	0.0
Anode separation	**0.0**	**68**	0.0	0.0	0.0/0.0	0.0
Carbonate regeneration	**278.1**	**0.0**	0.0	0.0	0.0/0.0	0.0
Upstream energy credit[f]	**0.0**	**0.0**	0.0	0.0	0.0/0.0	−17.5
Heating	**0.0**	**0.0**	0.0	0.0	8/0.0	0.0
Overall energy	**564**	**362**	579	602	207	548

Results for conventional alkaline and neutral media are shown in bold for comparison. This table provides insights into the energy intensity of producing ethylene in various electrolyser configurations using the readily achieved performance metrics in CO_2-to-ethylene conversion, CO-to-ethylene conversion (COR step in cascade CO_2R-COR) and CO_2-to-CO (CO_2R step in cascade CO_2R-COR). [a]The CO_2 from a capture liquid system with performance metrics that are expected in the next few years. [b]The highest energy efficiency operation mode refers to the performance metrics achieved under high reactant availability (input CO_2 flow rate of >10 sccm cm^{-2}). [c]Carbonate formation ratio represents the molar ratio between CO_2 lost to carbonate and CO_2 reduced to any product. [d]Heating required for SOEC is obtained from ref. [9]. Energy intensities listed for SOEC (CO_2-to-CO conversion) are given for 2 tons of CO produced, which is required to produce 1 ton of ethylene. [e]Electrolyser specific energy distribution for each system is calculated by using the model and assumptions reported in refs. [9,23]. Details of assumptions and a sample calculation for electrolyser electricity, cathode separation, anode separation and carbonate regeneration are provided in Supplementary Note 1. [f]For CO_2R from a capture liquid approach, the total energy requirement associated with CO_2 capture and conditioning is estimated to be 5.66 GJ ton^{-1} CO_2 (3.1 × 5.66 = 17.5 GJ ton^{-1} ethylene produced)[95,96]. This is subtracted from the overall energy requirement to produce ethylene and is referred to as an upstream energy credit.

result, acidic CO_2R has typically been limited to acidic electrolyte at pH 2~5, where local alkalinity can be maintained as long as reaction rates are sufficient: for example, to produce only C_1 products[60,62–65]. Promoting C_{2+} products in acidic media systems is a challenge as carbon–carbon (C–C) coupling is favourable in alkaline conditions[27,28]. Therefore, development of catalysts/systems that would control the pH (or proton activity) gradient near the cathode via catalyst/electrolyte/operating condition engineering will be critical to realize acidic media CO_2R.

Operation at higher current densities would surpass proton transport and avoid competition with proton reduction. However, high-current-density operation imposes additional cathodic overpotential that lowers EE. This could be compensated by the use of a proton exchange membrane, which in acidic systems would enable lower resistance, lower pH gradients, lower anodic overpotentials and overall lower voltage losses.

Recently, a cation-augmenting strategy has achieved CO_2R in acidic electrolyte (pH ~0.6) with a C_{2+} FE of 50% at 1.2 A cm^{-2} and ~4.2 V (ref. [47]). In contrast, the literature benchmark alkaline media CO_2R system uses strongly alkaline electrolytes (pH ~14.8) and requires a full-cell potential of ~3.8 V for a similar C_{2+} productivity (900 mA cm^{-2} and 75% C_{2+} FE)[27]. Although the acidic system results in higher cell potential and lower C_{2+} FE, the SPC of 77% exceeds that achieved in neutral and alkaline media.

Overall, acidic media CO_2R offers the benefit of high SPC; however, current systems suffer from poor C_{2+} FE and high cell potential, and these must be addressed to achieve competitive EE. Recent work has shown progress in this regard[47], and suggests that achieving viable acidic CO_2R (Table 1) will require advances in the following areas: (1) promoting CO_2 adsorption on the catalyst surface in a low-pH environment through cation effects[47,66,67]; (2) isolating the cathode electrode from harsh acidic conditions imposed by the cation exchange membrane through a neutral buffer layer[68,69]; and (3) maintaining a locally alkaline reaction environment using

alkalinity-enabling porous layers separating the catalyst and the cation exchange membrane. Lastly, acidic electrolytes present additional considerations for the design of anode electrodes[70], motivating continued research/development into robust electrocatalysts for oxidation reactions in acidic media[71].

Cascade CO_2R-COR

Dividing CO_2-to-C_{2+} conversion into two cascading steps—CO_2-to-CO and CO-to-C_{2+} (COR)—offers another route to carbonate-free electrosynthesis of C_{2+} products. The cascade CO_2R-COR approach would involve (1) CO_2 reduction to CO with established high-temperature solid-oxide electrolysis cell (SOEC) technology that does not suffer from carbonate formation and achieves moderate SPC (40–50%)[72]; followed by (2) COR to C_{2+} products in a COR electrolyser[73–78] (Fig. 2c).

Although the cascade CO_2R-COR approach requires two electrolysers, as well as heating and an additional separation step, it has potential to outcompete direct CO_2R with neutral or alkaline electrolytes[9,23]. The cascade approach benefits from high energy and SPC in both steps. Recent calculations and experiments demonstrate that the CO_2-to-CO conversion step accounts for only 10–15% of the overall energy input[9,23]. Thus, in the cascade process the SOEC step is not limiting, although improvements in SPC and reductions in operating temperatures would be welcome[21]. Herein, it is also worth noting that SOECs do not employ iridium (Ir) on their electrodes (instead they typically use nickel-based catalysts), hence would not suffer from high capital costs and scalability limitations.

The COR step of the cascade approach can be performed in flow cell or MEA electrolysers with neutral or alkaline electrolytes (pH 7~15). Although both neutral and alkaline electrolytes can be used to perform CO-to-C_{2+} conversion, alkaline electrolytes would improve C–C coupling and reduce ohmic losses, enabling higher EEs. As CO does not react with OH$^-$, the alkaline COR system will not suffer from carbonate formation. Similarly, the use of
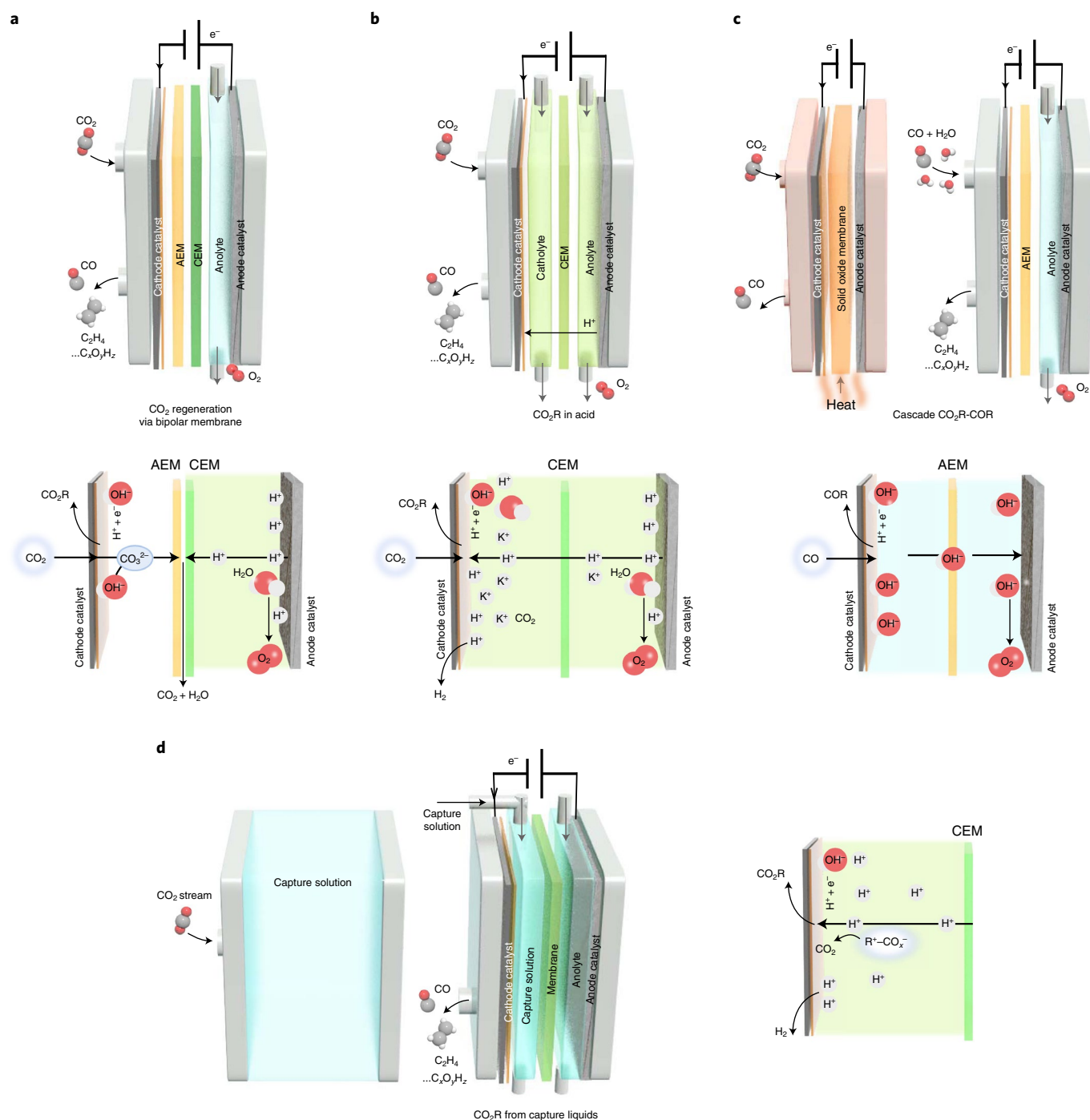
Fig. 2 | Carbon-efficient technologies for CO_2R. a, Schematic illustration of CO_2 regeneration from carbonate and its subsequent upgrading in a catholyte-free MEA equipped with a bipolar membrane. CEM, cation exchange membrane. **b**, Schematic illustration of CO_2R in an acidic media flow cell through augmenting the availability of cations in the cathodic local reaction environment. **c**, Schematic illustration of cascade CO_2R-COR. This approach uses CO (produced in a carbonate-free SOEC) as the starting feedstock and upgrades it to C_{2+} products (for example, ethylene) in an MEA electrolyser without incurring CO_2 loss to carbonate. **d**, Schematic illustration of CO_2R from capture liquids. In (bi)carbonate solutions, the acid/base reaction between protons and (bi)carbonate anions allows CO_2 to be generated in situ at the catalyst layer to initiate CO_2R. In amine-based solvents, the amine-CO_2 adduct (R-CO_2) is directly reduced at the catalyst surface.

thin electrolysers would further reduce ohmic losses and improve EE in the CO-to-C_{2+} step.

The viability of the cascade CO_2R-COR approach depends on the development of a CO-to-C_{2+} electrolyser with EE well beyond demonstrations to date. Recently, we demonstrated cascade CO_2R-COR to C_{2+} products without incurring CO_2 loss to carbonate and associated

energy penalties[9]. In the full SOEC-MEA cascade approach, we achieved stable CO_2-to-ethylene conversion for 40 h and an energy requirement of ~138 GJ ton^{-1}. This energy requirement is 48% lower than the best-case single-reactor CO_2R system[32] and bodes well for the cascade pathway. Although the electrolyser integration enables record-low energy requirement, electrosynthesis of C_{2+} products

with cascade CO_2R-COR remains far from the target energy intensity of 80 GJ ton^{-1}. Considering the current literature performance metrics for SOEC and MEA systems, major improvements in productivity, EE and SPC are still required in the CO-to-C_{2+} step. Another important goal is to increase operational stability of the electrolyser integration from today's 40 h (ref. [9]) to >1,000 h.

In the CO_2R step, SOECs—among all the electrolysis strategies—enable the highest EE and productivity[72]. Present-day nickel catalyst-based SOECs already achieve the productivity and EE levels suitable for economic production of CO. However, the challenge is to combine this performance with stability and SPC. These systems suffer from carbon deposition (CO_2 (g) $\rightarrow$ C + O_2 (g))[79], known as 'coking', which limits stability[80]. Operating parameters can be tuned to reduce coking but not without sacrificing SPC (<50%)[81]. This low SPC doubles the capital cost in the CO_2-to-CO conversion[21,23], and thus limits the whole process in cascade fashion. Addressing the coking problem in high-temperature CO_2-to-CO conversion or developing alternative low-temperature carbon-efficient approaches will be key to achieving the needed SPC of >75% in the first step (Table 1). To realize this performance, SOECs require targeted research into selective, active and stable catalysts (to improve EE)[82], electrolytes (to increase ionic conductivity and lower operating temperatures)[83,84], intermediate layers (to ensure physico-chemical compatibility)[83] and interconnectors (to mitigate coking and delamination)[85].

The biggest challenge for the COR step is to combine high productivity, EE and stability with present-day levels of SPC. Current CO-to-C_{2+} conversion systems achieve SPC exceeding 70% (refs. [75,86]), but not at conditions that provide viable EE and current density. These gaps, and the notable competitive advantage of the cascade approach, motivate targeted research in the following areas: (1) cathode catalysts that enable high productivity at low overpotentials for CO-to-C_{2+} conversion; (2) electrolyser architectures that minimize voltage loss and optimize mass, electron and ion transport; (3) electrodes that are porous, electrically conductive and hydrophobic, and suppress hydrogen evolution under low reactant availability conditions; and (4) anode catalysts that enable high-rate, low-overpotential and stable oxidation reactions in alkaline media.

CO_2R from capture liquids

The generation of high-purity CO_2 reactant from CO_2 capture liquids is a costly step in the overall process of capture and conversion. Employing CO_2 capture liquids as the reactant in the conversion system avoids this costly step, with potential to improve overall process efficiency and reduce capital costs[87]. Promising recent approaches to electrocatalytically convert CO_2 capture liquid rely on cation exchange or bipolar membranes to block the transfer of CO_2 adducts, such as (bi)carbonate and carbamate, from cathode to anode (Fig. 2d). There is precedent for CO_2R from two types of capture liquids, (bi)carbonates and amines.

Alkaline capture processes use (bi)carbonate liquids to capture CO_2. The process is typically composed of two connected chemical loops and four major units: an air contactor, pellet reactor, calciner and slaker[44]. In the air contactor, CO_2 reacts with an alkaline hydroxide solution (for example, KOH or Ca(OH)$_2$) to form an alkaline carbonate (for example, K_2CO_3 or $CaCO_3$) and water. The carbonate anion is precipitated out as a calcium carbonate salt in the pellet reactor and the regenerated alkaline hydroxide solution is recycled back to the air contactor. In the calciner, calcium carbonate is heated (to ~900 °C) and CO_2 is released. The leftover CaO is then hydrated back to Ca(OH)$_2$ in the slaker and cycled back to the pellet reactor. The CO_2 evolved in the calciner is compressed and processed into a high-purity stream for storage or downstream applications such as CO_2R.

An alternative approach is to feed the alkaline carbonate stream directly from the air contactor to an electrolyser, thereby eliminating three major unit operations and the calcium loop. Based on a recent analysis, this approach would avoid 4.05 GJ ton^{-1} CO_2 from calcination and 70% of electrical energy costs[44]. Recent efforts have used cation exchange or bipolar membranes in MEA reactors to enable the electroreduction of CO_2 derived in situ from carbonate[51] and bicarbonate[61,88,89] solutions. At the electrode–membrane interface, protons originating from the membrane react with CO_3^{2-} and/or HCO_3^{-} to produce CO_2 at the electrode surface.

A syngas stream has been produced from carbonate solutions with an EE of 35%, an SPC of 100% and stability over 145 h (at 180 mA cm^{-2}; ref. [51]). Starting from bicarbonate, higher reaction rates have been achieved, including a partial current density of >100 mA cm^{-2} towards CO (ref. [89]). Operando pH studies of bicarbonate-based systems showed that higher current densities lead to higher surface pH, thereby suppressing hydrogen evolution. Similar pH gradient trends have also been observed for carbonate-based systems[88].

The technical challenge for (bi)carbonate-based approaches is achieving sufficient reactant CO_2 concentration at the catalyst. This is complicated by the CO_2 acid–base equilibria at the membrane–electrode interface, hydrogen evolution from the influx of protons at the membrane and mass transport of the locally generated CO_2 to catalyst sites. At high current densities, a high flux of protons aids in regenerating CO_2 from carbonate, but also promotes hydrogen evolution. At the catalyst, hydroxide generation from CO_2R converts locally regenerated CO_2 back to (bi)carbonate, thereby depleting available CO_2. Reduced performance at high current density is attributed to this shortage of locally generated CO_2 and the competing hydrogen evolution. An increased availability of CO_2 and thus increased catalyst surface coverage of *CO intermediates (adsorbed CO on catalyst surface) would enable the C−C coupling required for C_{2+} products. Catalysts that stabilize these intermediate species in conditions that are acidic, or more acidic, could improve FE markedly. Creative approaches to improve the mass transport of CO_2 to catalyst sites—in a way that avoids the re-formation of carbonate—would enable high current density, suppressed hydrogen evolution and a direct path from a shortened capture process to C_{2+} products.

Amine-based solvents are another capture liquid from which direct CO_2R is reported. Amine scrubbing is a widely used chemisorption-based CO_2 capture technology commonly applied to point sources of CO_2[90]. Amine-based chemicals react with CO_2 to form carbamate salts, and upon heating to 120–150 °C, release CO_2 and regenerate the amine. The CO_2 is then compressed and is available for electrochemical upgrading to C_1 and C_{2+} products.

Directly upgrading the amine-CO_2 adduct by electrochemical means in an integrated capture–conversion system would eliminate the temperature swing and compression steps, and reduce process energy and capital costs. Monoethanolamine is the most studied amine capture solvent, which with exposure to CO_2 produces carbamate and ethanolammonium. Recent studies have pursued the electrolysis of CO_2 dissolved in aqueous monoethanolamine solutions[91] and the direct electrolysis of the amine-CO_2 adduct[92,93]. Due to CO_2 solubility limitations in aqueous solutions, the direct electrolysis of amine-CO_2 adducts is the more promising pathway moving forward.

Recently, the direct electrolysis of an amine-CO_2 adduct to CO has been achieved with a FE of 72% (at 50 mA cm^{-2}; ref. [93]). By introducing alkali cations to the electrochemical double layer, the distance from the amine-CO_2 adduct to the catalyst surface was reduced, enabling improved heterogeneous electron transfer to the carbamate ion. This system uses a cation exchange membrane that acts as a barrier to anion transport and prevents carbon crossover (in the form of the amine-CO_2 adduct, carbamate) to the anode. As with the direct conversion of (bi)carbonates, there is a tremendous opportunity to achieve viability with direct conversion from amine-based capture liquids (Table 1).
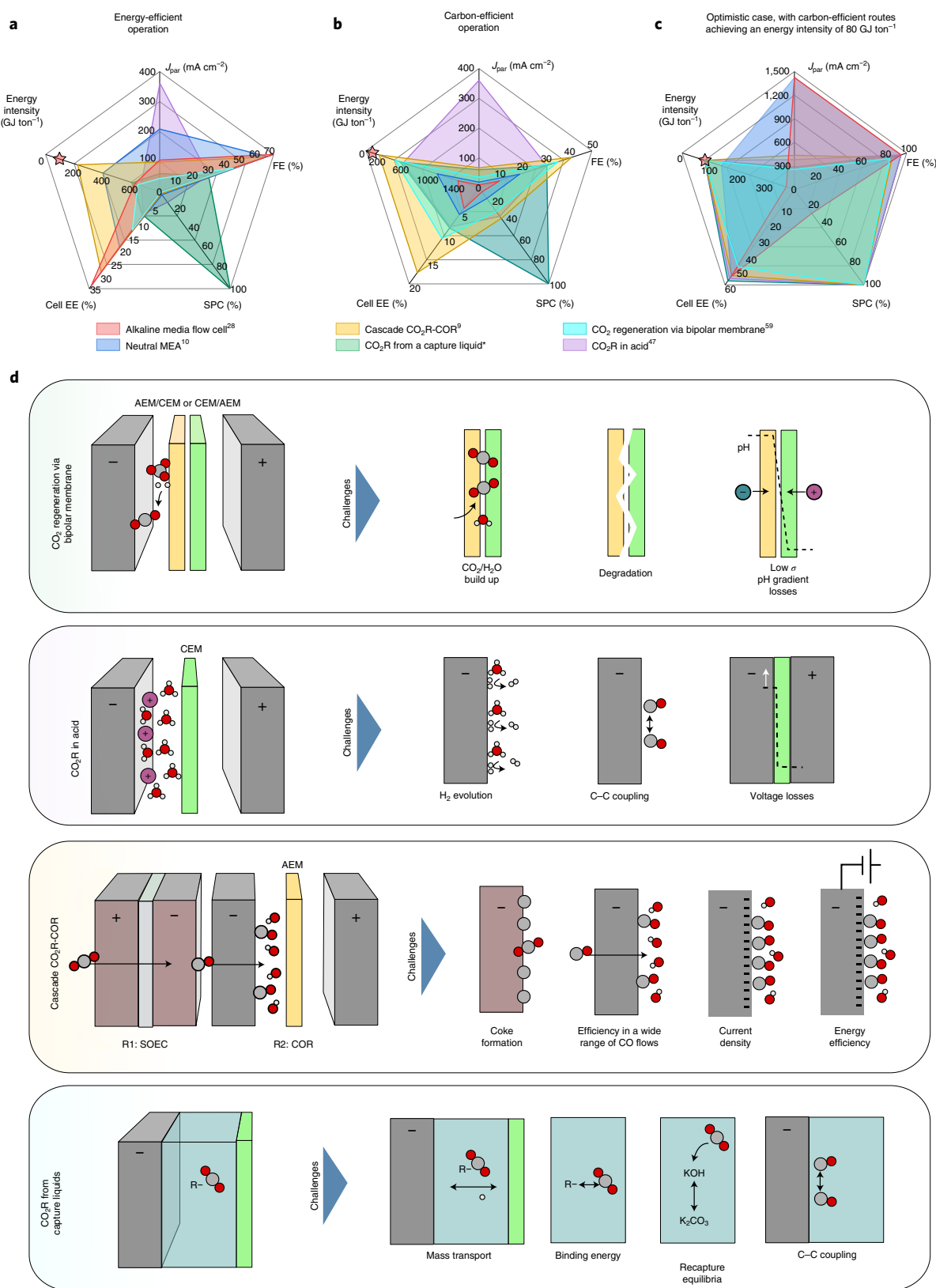
Fig. 3 | Performance and energy assessment of literature benchmark carbon-efficient and conventional alkaline/neutral media CO₂R systems and challenges associated with carbon-efficient routes. a, Performance metrics and energy intensity of producing ethylene under their highest EE operation mode. **b**, Performance metrics and energy intensity of producing ethylene under their highest SPC operation mode. **c**, Energy intensity of producing ethylene with the performance metrics close to their upper bounds in conventional alkaline/neutral media and carbon-efficient CO₂R systems. Red stars in **a**–**c** represent the target energy intensity of 80 GJ ton⁻¹ in ethylene electrosynthesis. J_{par} represents the partial current density towards ethylene. **d**, Remaining challenges associated with carbon-efficient CO₂R systems. *CO₂R from a capture liquid system with performance metrics that are expected in the next few years.

Table 2 | Energy assessment of literature benchmark carbon-efficient and alkaline/neutral media CO_2R systems towards ethylene under their highest SPC operation mode

	Conventional alkaline media CO_2R (ref. [28])	Conventional neutral media CO_2R (ref. [10])	CO_2 regeneration via bipolar membrane[59]	CO_2R in acid[47]	Cascade CO_2R-COR (ref. [9])	CO_2R from a capture liquid[a]
Parameters	Flow cell	MEA	MEA	Flow cell	SOEC[d]/MEA	MEA
Full-cell voltage (V)	**2.4**	**3.7**	3.8	4.2	1.4/2.45	4.1
FE (%)[b]	**9**	**18**	35	30	95/41	30
Current density (mA cm^{-2})	**100**	**100**	100	1,200	700/160	200
SPC (%)	**4.4**	**11.4**	25	30	45/32	100
Carbonate formation ratio[c]	**20**	**3**	0	0	0	0
Electrolyser specific energy distribution (GJ (ton product)$^{-1}$)[e]						
Electrolyser electricity	**1102.7**	**849.9**	448.9	578.9	20.4/164.7	565.1
Cathode separation	**82.6**	**34.4**	14.3	15.5	3.6/8.7	0.0
Anode separation	**0.0**	**250**	0.0	0.0	0.0/0.0	0.0
Carbonate regeneration	**278.1**	**0.0**	0.0	0.0	0.0/0.0	0.0
Upstream energy credit[f]	**0.0**	**0.0**	0.0	0.0	0.0/0.0	−17.5
Heating	**0.0**	**0.0**	0.0	0.0	8/0.0	0.0
Overall energy	**1463**	**1133**	463	594	205	548

Results for conventional alkaline and neutral media are shown in bold for comparison. This table provides insights into the energy intensity of producing ethylene in various electrolyser configurations using the readily achieved performance metrics in CO_2-to-ethylene conversion, CO-to-ethylene conversion (COR step in cascade CO_2R-COR) and CO_2-to-CO (CO_2R step in cascade CO_2R-COR). [a]The CO_2R from a capture liquid system with performance metrics that are expected in the next few years. [b]The highest SPC operation mode refers to the performance metrics achieved under low reactant (CO_2) availability (input CO_2 flow rate of 0.4–3 sccm cm^{-2}). [c]Carbonate formation ratio represents the molar ratio between CO_2 lost to carbonate and CO_2 reduced to any product. [d]Heating required for SOEC is obtained from ref. [9]. Energy intensities listed for SOEC (CO_2-to-CO conversion) are given for 2 tons of CO produced, which is required to produce 1 ton of ethylene. [e]Electrolyser specific energy distribution for each system is calculated by using the model and assumptions reported in refs. [9,23]. Details of assumptions and a sample calculation for electrolyser electricity, cathode separation, anode separation and carbonate regeneration are provided in Supplementary Note 1. [f]For CO_2R from a capture liquid approach, the total energy requirement associated with CO_2 capture and conditioning is estimated to be 5.66 GJ ton^{-1} CO_2 (3.1 × 5.66 = 17.5 GJ ton^{-1} ethylene produced)[95,96]. This is subtracted from the overall energy requirement to produce ethylene and is referred to as an upstream energy credit.

Further development of CO_2R from amine-based solvents should focus on the binding strength of amine-CO_2 adducts, catalyst design and mass transport of amine-CO_2 adducts to the cathode. Industrial-scale amine capture systems use a mixture of amines and additives to extend their stability over repeated capture and release cycles. The binding strength of amine-CO_2 adducts and solution composition will impact FE, current density and stability of the reaction. Catalyst studies that compare the conversion of the amine-CO_2 adduct with the conversion of free CO_2 would provide crucial insight into this process. In particular, breaking the N−C bond of the amine-CO_2 adduct, and understanding adduct and reaction intermediate interactions at the catalyst surface are challenges unique to this system. Additionally, reactor engineering advances are also required to control the transport of amine-CO_2 adducts in the local reaction environment and achieve viable productivities.

Current status and future priorities

We provide here a comparative analysis of these emerging carbon-efficient pathways and present-day alkaline/neutral systems, and offer minimum target performance metrics required for large-scale deployment. We focus on ethylene, the world's most-produced organic compound[94], and apply reported energy assessment approach and assumptions[9,23] (Supplementary Note 1). Energy intensities are typically determined using literature benchmarks for (1) CO_2 regeneration from carbonate and its ensuing reduction in a bipolar membrane-based system[59], (2) CO_2R in acidic media[47], (3) cascade CO_2R-COR[9] and (4) CO_2R direct from a capture liquid. The analysis considers two distinct operation modes: highest EE (high reactant availability) and highest SPC (low reactant availability) (Fig. 3a,b).

In operation modes that offer the highest EE, the alkaline and neutral media systems require energy inputs of 564 and 362 GJ to produce 1 ton of ethylene, respectively (Table 1 and Fig. 3a). Considering the possibility of future strategies that would bring ethylene electrosynthesis close to the upper bound performance metrics (for example, FE of 95%, cell potential of 2 V and CO_2-to-ethylene SPC of 25%), the energy intensities of alkaline and neutral systems could be as low as 371 and 140 GJ ton^{-1}, respectively (Fig. 3c). These energy intensities are still much higher than the target intensity of 80 GJ ton^{-1} (Table 3), suggesting that, as they stand, these conventional systems do not have a pathway to practical application. An energy analysis of these high SPC systems suggests that, at present, cascade CO_2R-COR enables the lowest energy intensity for ethylene electrosynthesis. The cascade CO_2R-COR approach enables substantial energy savings over the alkaline/neutral CO_2R systems as well (Table 1 and Fig. 3a). This, in part, originates from the high FE and low voltage requirement. At present, the other pathways—including CO_2 regeneration via bipolar membrane, CO_2R in acid and CO_2R from a capture liquid—are more energy intensive than conventional neutral/alkaline systems under conditions that maximize EE (Table 1 and Fig. 3a).

In operation modes that offer the highest SPC, the alkaline and neutral systems require prohibitive energy inputs of 1,463 and 1,133 GJ ton^{-1}, respectively (Table 2 and Fig. 3b). The carbon-efficient systems, however, benefit from high SPC to minimize the energy cost associated with anodic/cathodic separations (Table 2). Albeit suffering from low FEs at present, these systems are still competitive under low reactant availability, under which alkaline/neutral systems suffer from poor CO_2R activity due to CO_2 loss to carbonate (Table 2 and Fig. 2b). Unlike the neutral/alkaline systems, the carbon-efficient systems—with no carbonate formation and associated energy penalties—hold the potential for achieving the target intensity of 80 GJ ton^{-1} (Fig. 3c). Achieving this impressively low energy intensity and, eventually, practicality, will require achieving high SPC and stability simultaneously with the best performance metrics of today's neutral/alkaline systems: an ethylene FE of 85–95%, a current density of 300–500 mA cm^{-2} and a full-cell potential of 1.7–2.0 V (Table 3 and Fig. 3c). Progress

Table 3 | A set of performance metrics required for carbon-efficient systems to achieve 80 GJ ton^{-1} (based on ethylene's lower heating value and a total process efficiency of 60%) ethylene production

	Conventional alkaline media CO$_2$R	Conventional neutral media CO$_2$R	CO$_2$ regeneration via bipolar membrane	CO$_2$R in acid	Cascade CO$_2$R-COR	CO$_2$R from a capture liquid
Parameters	Flow cell	MEA	MEA	Flow cell	SOEC/MEA	MEA
Full-cell voltage (V)	**2**	**2**	1.9	1.95	1.28/1.7	2
FE (%)	**95**	**95**	95	95	100/87	85
Current density (mA cm^{-2})	**1,500**	**1,500**	300	400	800/500	300
SPC (%)	**25**	**25**	100	100	100/100	100
Carbonate formation ratio	**20**	**3**	0	0	0	0
Electrolyser specific energy distribution (GJ (ton product)$^{-1}$)						
Electrolyser electricity	**87.1**	**87.1**	79.1	79.4	17.2/53.8	97.7
Cathode separation	**5.8**	**5.8**	1.0	1.0	0.0/1.3	0.0
Anode separation	**0.0**	**47.4**	0.0	0.0	0.0/0.0	0.0
Carbonate regeneration	**278.1**	**0.0**	0.0	0.0	0.0/0.0	0.0
Upstream energy credit	**0.0**	**0.0**	0.0	0.0	0.0/0.0	−17.5
Heating	**0.0**	**0.0**	0.0	0.0	8/0.0	0.0
Overall energy	**371**	**140**	80	80	80	80

This table provides insights into the performance metrics towards ethylene that would need to be achieved for economically compelling production of ethylene. The columns in bold provide the peak-performance levels of conventional systems with alkaline and neutral electrolytes. The performance metrics are those required to be achieved in CO$_2$-to-ethylene conversion, CO-to-ethylene conversion (COR step in cascade CO$_2$R-COR) and CO$_2$-to-CO conversion (CO$_2$R step in cascade CO$_2$R-COR). [a]The CO$_2$R from a capture liquid system with performance metrics that are expected in the next few years. [b]The highest SPC operation mode refers to the performance metrics achieved under low reactant (CO$_2$) availability (input CO$_2$ flow rate of 0.4–3 sccm cm^{-2}). [c]Carbonate formation ratio represents the molar ratio between CO$_2$ lost to carbonate and CO$_2$ reduced to any product. [d]Heating required for SOEC is obtained from ref. [9]. Energy intensities listed for SOEC (CO$_2$-to-CO conversion) are given for 2 tons of CO produced, which is required to produce 1 ton of ethylene. [e]Electrolyser specific energy distribution for each system is calculated by using the model and assumptions reported in refs. [9,23]. Details of assumptions and a sample calculation for electrolyser electricity, cathode separation, anode separation and carbonate regeneration are provided in Supplementary Note 1. [f]For CO$_2$R from a capture liquid approach, the total energy requirement associated with CO$_2$ capture and conditioning is estimated to be 5.66 GJ ton^{-1} CO$_2$ (3.1 × 5.66 = 17.5 GJ ton^{-1} ethylene produced)[95,96]. This is subtracted from the overall energy requirement to produce ethylene and is referred to as an upstream energy credit.

here will require overcoming remaining challenges associated with each carbon-efficient route (Fig. 3d). This would in turn require high-resolution modelling to improve our understanding of CO$_2$R at these conditions, reaction environment/electrolyte/interface engineering, and rationally designed catalysts, electrodes and reactor configurations.

Outlook

As governments, corporations and individuals pursue greater sustainability, there is a growing need to reduce the carbon intensity of heavy industries. CO$_2$R—when powered by renewable electricity—provides a sustainable means to convert would-be emissions into valuable feedstocks for manufacturing, transport and chemical production. By recycling CO$_2$, this process could help close the carbon loop, enable the penetration of renewables into the petrochemical sector and facilitate the storage of renewable energy.

The feasibility of this process requires operation with a rate, energy intensity and feedstock that brings operational and capital costs in line with incumbents. Recent advances in electrocatalysts and electrolyser architectures have generated impressive gains in productivity and energy efficiency. The challenge before the field is to eliminate CO$_2$ reactant loss and the associated process energy penalties that render all current approaches uneconomic. Strategies to eliminate CO$_2$ reactant loss in the upgrade of CO$_2$ to C$_{2+}$ products are crucial to make low-temperature CO$_2$R technology commercially viable.

We examined four emerging approaches with potential to achieve carbon-efficient electrosynthesis of commodity chemicals from CO$_2$: CO$_2$ regeneration from carbonate, CO$_2$R in acid, cascade CO$_2$R-COR and CO$_2$R from capture liquids. A high-level analysis of each pathway—with ethylene production as the common basis—indicates the potential for each carbon-efficient strategy and specific performance gaps in each case. These performance targets motivate a broader research effort in catalysts and systems, with clear objectives informed by the full process energy intensity and the shared goal of viable renewably powered CO$_2$R.

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Author contributions

D.S. and E.H.S. supervised the work; A.O., D.S. and E.H.S. conceptualized the manuscript; A.O. prepared the first draft of the manuscript with input from D.S., F.P.G.d.A., J.E.H. and J.W.; J.S., R.K.M., C.P.O.'B., G.L., X.W. and A.H.I. assisted in literature review. All authors discussed the results and assisted during manuscript preparation.

Competing interests

The authors declare no competing interests.

Additional information

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