Sequential vs integrated CO_2 capture and electrochemical conversion: An energy comparison

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Abstract

Integrating carbon dioxide (CO_2) electrolysis with CO_2 capture provides new exciting opportunities for energy reductions by simultaneously removing the energy-demanding regeneration step in CO_2 capture and avoiding critical issues faced by CO_2 gas-fed electrolysers. However, understanding the potential energy advantages of an integrated capture and conversion process is not straightforward. There are only early-stage demonstrations of CO_2 conversion from capture media very recently, and an evaluation of the broader process is paramount before claiming any energy gains from the integration. Here we identify the upper limits of the integrated capture and conversion from an energy perspective by comparing the working principles and performance of integrated and sequential CO_2 conversion approaches. Our high-level energy analyses unveil that an integrated electrolysis unit must operate below 1000 kJ/mol$_{CO_2}$ to ensure an energy benefit of up to 44% versus the existing state-of-the-art sequential route. However, such energy benefits diminish if future gas-fed electrolysers resolve the carbonation issue and if an integrated electrolyser has poor conversion efficiencies. We conclude with opportunities and limitations to develop industrially relevant integrated electrolysis, providing performance targets for novel integrated electrolysis processes.

Keywords: CO_2 electrolysis; CO_2 capture; energy cost; process intensification; carbonate regeneration.

Introduction

Carbon dioxide (CO_2) capture and subsequent conversion is a necessary step to mitigate anthropogenic climate change. In the past two decades, these capture and conversion steps have separately been advanced through innovations that have led to continuously lower implementation costs and higher energy efficiencies for each process. [1] For example, CO_2 capture can operate at an overall cost of US$50 – 150 to capture one tonne CO_2 using commercially mature amine scrubbing processes from industrial sources [2,3]. Larger-scale pilot capture processes are also now operating using alkaline capture sorbents[4] at $94 – 232 or solid sorbents[5,6] at about $600 to capture one tonne CO_2 from air, providing more refined large-scale cost estimates. On the conversion side, low-temperature CO_2 electrolysis using pure CO_2 feeds have achieved a current density beyond 1 A cm^{-2} to convert CO_2 selectively to feedstocks (*e.g.*, carbon monoxide (CO) and ethylene (C_2H_4)). [7-10] To prove viable, however, conversion efforts now require integration with upstream CO_2 capture and downstream processes to better define their role in offsetting existing emissions and define the impacts of the processes associated energy penalties (e.g. electrolyte recovery, product separation).[11,12]

Given the eventual need to combine CO_2 capture and electrochemical conversion processes, and the diminishing energy efficiency returns from optimizing each process separately, researchers have considered the techno-economic and energy benefits of combining capture and conversion.[13,14] For chemical processes, the discussion of whether 'to integrate, or not to integrate' CO_2 capture processes with conversion has been proposed to reduce overall energy requirements. For example, in a techno-economic study, CO_2 capture and chemical conversion showed a potential energy advantage of up to 46% when integrated to produce chemicals such as methyl formate from hydrogen, CO_2, and methanol (where the methanol serving as the capture media) at high pressures.[15,16] With the potential for CO_2 electrolysis at room temperature to act as a means of CO_2 conversion, we ask a similar question. Does an *integrated CO_2 capture and conversion process* offer potential energy or process advantages over a *sequential capture and electrochemical conversion process*? Here an integrated approach implies that the electrochemical process converts the captured CO_2 (e.g., carbamate) in a captured medium. In this work, we construct and compare these two scenarios to answer two key questions: (1) does an integrated route have energy advantages over the sequential route; (2) what performance metrics need to be met within the integrated electrolysis for such a route to be viable?

Shown in Fig. 1 are two comparable scenarios for a sequential capture and conversion process (Fig. 1a) and an envisioned integrated approach where the converted reactant is carbamate (Fig. 1b). In the sequential route, captured CO_2 is released at high purity via an amine-scrubbing step and then fed as a gas to a CO_2 electrolyser unit. Product separation and (bi)carbonate regeneration processes are included in the conversion step. The product will be separated from CO_2 through pressure-swing adsorption. The potassium (bi)carbonates in the electrolyte can be regenerated back to potassium hydroxide by reacting

calcium hydroxide to form $CaCO_3$ precipitates. The precipitates will then be calcinated to release CO_2 and produce CaO that will be hydrated to become $Ca(OH)_2$ in the final step. [4]

In an integrated process, there is an opportunity for the CO_2 electrolyser to displace the stripper unit by converting captured CO_2 while regenerating the capture medium simultaneously [17] (see Fig. 1). In the amine-scrubbing cases, such a displacement could save $155 - 203$ kJ/mol_{CO2} from amine regeneration, which takes up to 90% of the total energy cost of the capture process. [18] Further, due to the absence of CO_2 gas in the integrated electrolysis step, the integrated CO_2 electrolysis may further avoid the critical issue of CO_2 loss to (bi)carbonates faced by the gas-fed electrolysers[19-24]. If fulfilled, the integrated process may save > 230 kJ/mol_{CO2} to regenerate (bi)carbonates to hydroxide. [4,19] Finally, an additional $30 - 79.2$ kJ/mol_{CO2} for product separation [12,25] can also be avoided because gas products can separate from the capture media spontaneously as a result of their low solubility (*e.g.*, 1 mM for CO and 5 mM for C_2H_4 at 20 °C and 1 atm)[26]. Such a high-level analysis indicates that an ideal integrated route could save a total energy benefit of about 500 kJ/mol_{CO2} converted to CO versus the sequential route.
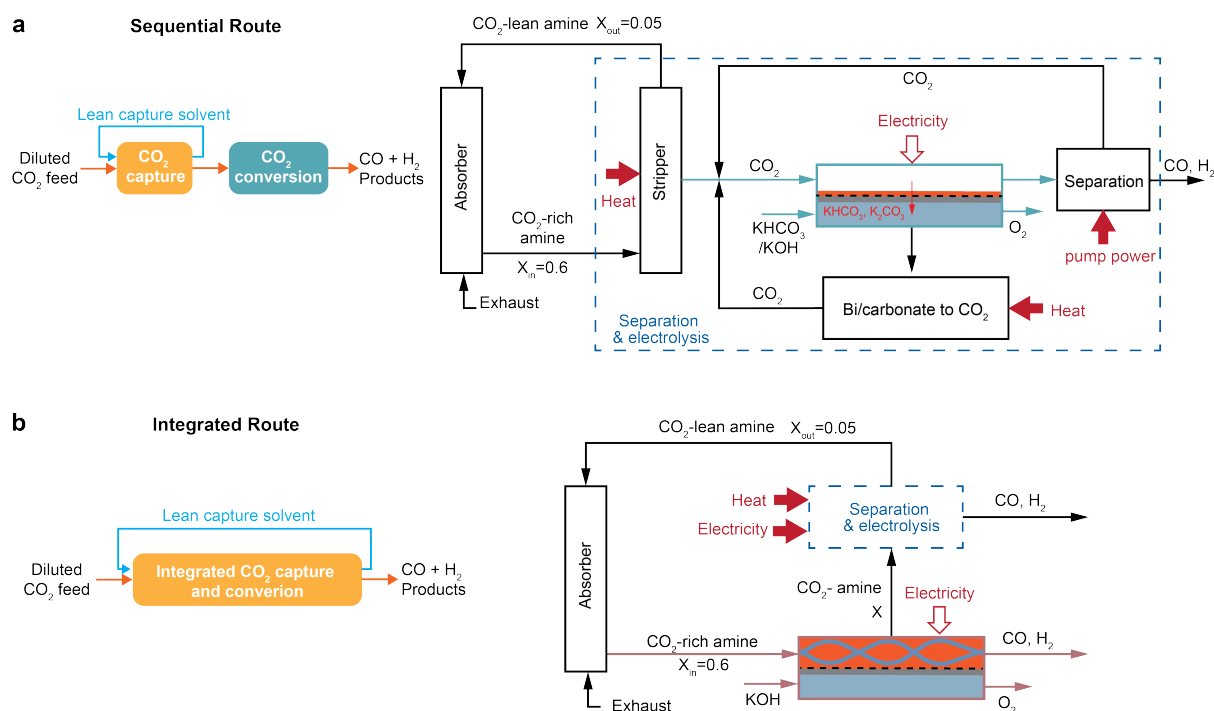

Fig. 1 Sequential and integrated routes of CO_2 capture and conversion. a, Schematic illustration and block diagrams of the sequential route for amine-based CO_2 capture and electrolysis to produce CO. CO_2 electrolyser is based on membrane-electrode assemblies. **b,** Schematic illustration and block diagrams of integrated CO_2 capture and direct CO_2 electrochemical conversion from capture medium. The separation and electrolysis process is symbolic, similar to the one highlighted with a dashed line to regenerate the capture medium fully. X represents the CO_2 loading in the capture medium, with a unit of mol CO_2 per mol amine molecule.

However, there are also stringent requirements for integrated electrolysis to be beneficial and actually replace the amine regeneration in the sequential process. First, the integrated electrolyser must recover

the capture medium to its original state (*i.e.*, CO$_2$-lean medium), implying a requirement of a high carbamate utilisation efficiency for the integrated electrolyser. If the capture medium is not fully recovered in the initial electrolysis step, then a secondary stripping unit and conversion process are still required to maintain a similar process as the sequential route. Such a regeneration step is shown in Fig. 1 and again includes a stripper unit and gas-fed electrolyser, reducing the benefit of integrated electrolysis. Alternatively, a medium-level CO$_2$-loaded capture media can be used, but this will lead to an energy and capital-cost penalty for the absorption step. Second, to provide an overall energy benefit in the process, the integrated electrochemical conversion step should show at least similar performance metrics (cell voltage, Faradaic efficiency) as the gas-fed electrolysis unit in the sequential process. To date, there are few reports of integrated electrolysis, but their current performance is far inferior to the gas-fed electrolysis performance. [17,27] (see Fig. 2) These above two constraints then prevent a straightforward comparison of the energy benefits of an integrated process and thus warrant a more detailed analysis to help determine the upper limits of this new research direction.

Herein we compare the sequential and integrated scenarios from an energy perspective, bringing in a wealth of current knowledge from both fields to give a perspective on the outlook of integrated CO$_2$ capture and electrochemical conversion. To perform this analysis, we compare the performance and working principles of the electrochemical reduction of molecular CO$_2$ and carbamate and discuss the essential roles of product Faradaic efficiency and cell voltages in the overall energy cost. We then compare the sensitivity of various parameters to observe the parameter space where each process is favourable, which gives clear and targeted performance metrics for the novel integrated electrochemical conversion process. We then conclude with an outlook on challenges and future potential for the integrated routes.

Performance comparison for the electrolysis of molecular CO$_2$ vs. captured CO$_2$

Here we compare the operation of existing gas-fed CO$_2$ electrolysers with an electrochemical process utilizing CO$_2$ in a captured form. We discuss the performance metrics for both conversion processes in-depth to provide perspective on the comparative energy cost of each route under different scenarios. As shown in Fig. 2a, the blue region highlights the energy to produce CO with varied Faradaic efficiencies and cell voltages. [28] Overlayed within Fig. 2a are the existing state-of-the-art Faradaic efficiencies and current densities for the electrolysis of molecular CO$_2$ (blue circles). The electrolysis of captured CO$_2$ in amines (red circles) is relevant to the integrated route described in Fig. 1. For context, Fig. 2b communicates that product Faradaic efficiency has a more profound impact on energy consumption toward target CO than the cell voltages.

Electrolysis of molecular CO₂

Recent reports have shown that electrolysis of molecular CO_2 outperforms the electrolysis of captured CO_2 in product selectivity, current densities, and energy efficiency. [17,27] (see Fig. 2a) The state-of-the-art gas-fed CO_2 electrolysers can operate at >100 mA cm^{-2} with a cell voltage below 3 – 3.5 V and a product Faradaic efficiency of 80 - 90% (*e.g.*, CO). (see Table S4) When converting these performance metrics into the energy required to convert CO_2 into CO, we can estimate the benchmark gas-fed electrolyser to be in the range of 600 – 800 kJ/mol$_{CO2converted}$. Our analysis uses only near-room-temperature flow cells and membrane-electrode assemblies (MEAs) for CO_2-to-CO as the model for the sequential route because this technology has a relatively high level of technical readiness. [28-30]
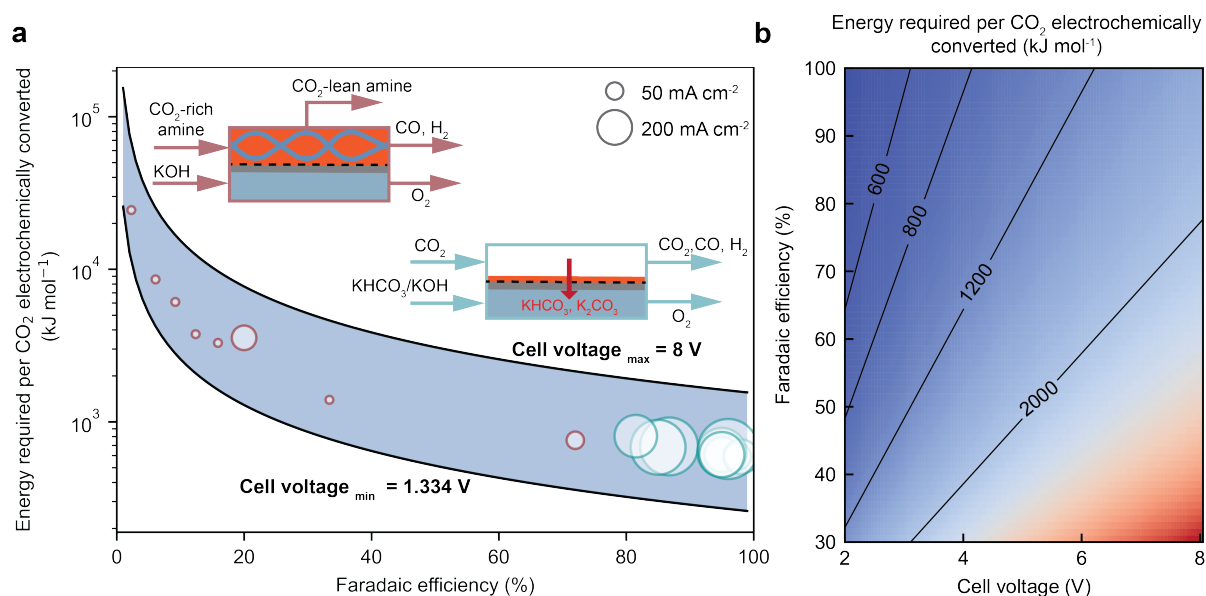

Fig. 2 Energy cost to convert CO₂ to CO for gas-fed CO₂ electrolyser and direct CO₂ electrochemical upgrade from capture medium. a, The energy cost to convert CO_2 to CO as a function of CO Faradaic efficiency with recently reported values for two different CO_2 electrolysers. The bubble size represents the magnitude of current densities for these cells as indicated in the legend. The insets illustrate the operating conditions of these two cells. **b,** Impacts of CO Faradaic efficiency and cell voltages on the energy cost of the CO_2 electrolysers.

In molecular CO_2 reduction, dissolved CO_2 is the main catalytically reactant for the conversion. [31,32] High rates (up to 1 A cm^{-2}) are achieved by applying gas-diffusion electrodes, [8-10] where the gases transport from the gas channel to the catalyst facing the liquid electrolyte. Therefore, maintaining a stable electrode wettability is challenging for long-term operation. [33]

In these gas-fed systems, the CO_2 utilisation efficiency is usually low (*e.g.*, capped at 50% if producing CO) due to carbonation between CO_2 and hydroxide ions (OH⁻) generated from electrochemical reductions at the cathode interface [19-21]. In an MEA configuration using an anion-exchange membrane, the carbonate will migrate to the anode and are reported to evolve back to CO_2 by reacting with the generated protons. [22-24] Such CO_2 evolution should occur at the cost of increasing anode overpotentials.

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[34] When the carbonate requires regeneration into CO_2, an energy penalty of at least 230 kJ/mol$_{CO2\text{-converted}}$ is associated with it in the case of 50% CO_2 utilisation efficiency. Our analysis then takes this energy penalty into account.

We acknowledge the recent efforts that attempt to remove the energy penalty associated with carbonate formation and low CO_2 utilisations, but these have not been demonstrated with substantial overall performance metrics as compared to those presented in Fig. 2a. Such strategies use acidic environments and bipolar membranes to introduce protons to regenerate carbonate[35,36] or optimize local reaction environments or operating conditions [37,38]. For simplicity of this model, however, our analysis assumes a gas-fed CO_2 conversion of 50% with additional steps for product separation and carbonate regeneration processes.

<u>Electrolysis of captured CO_2 in amine solutions</u>

In contrast to the gas-fed system above, reported electrolysis of captured CO_2 presently suffers from a high energy requirement at low current densities (Fig. 2a and Table S3). Such poor performance is due to product selectivities below 72% with relatively high cell voltages (see Figure S1). In these systems, most cell potentials were unreported. So we estimated the potentials associated with the anode, membrane, and electrolytes to perform a parameter sweep and evaluate the energy cost for conversion (see Supporting Information).

Taking Lee *et al.*'s result as an example, the estimated cell voltage is 3.7 V to achieve 100 mA cm^{-2} with 20% Faradaic efficiency for CO production. [17] The high cell voltage should be related to (1) the limited number of active sites over the utilised planar electrode and (2) the low ionic conductivity of the amine solutions (i.e. 3.7 S m^{-1} for 5 M monoethanolamine solutions with about 0.4 mol$_{CO2}$/mol$_{amine}$ [39] *cf.*. 21.5 S m^{-1} for 1M KOH solution [40]). Due to the low CO Faradaic efficiency and high cell voltage, we estimate the reported electrolysis of captured CO_2 to be at an energy cost at 10^3 - 10^5 kJ/mol$_{CO2}$, as compared to the 600 – 800 kJ/mol$_{CO2}$ for the gas-fed system. From a state-of-the-art perspective, it is then clear that substantial energy reductions in the integrated electrolysis process are needed to make the overall integrated route more energetically favourable. The most straightforward path to reduce the energy load is through an increase in Faradaic efficiency for CO, which requires an understanding of the underlying mechanisms and reactant species (e.g., carbamate) dominating the conversion process. The outlook of this article provides a detailed discussion on the mechanism for electrochemical conversion of carbamates and its challenges.

Determination of dominant energy contributors

With the conversion processes described for the sequential and integrated routes, we can compare the expected energy costs for both routes. Here Fig. 3 explores the potential energy advantages of the integrated route under optimistic, baseline, and pessimistic scenarios based upon reported information

for the electrochemical conversion processes. Detailed conditions for these scenarios are summarized in Table 1 using the three most critical parameters for the integrated electrolysis process: Faradaic efficiency, cell voltage and the CO_2 content (X) of the effluent amine stream. A broader parameter sweep is further available in the following section.

Table 1: Summary of CO FE, cell voltage, and CO_2 loading in the effluent for electrochemical upgrade reactor in different scenarios

Scenarios	CO FE (%)	Cell voltage (V)	X (mol CO_2 per mol amine)
Optimistic	90	3	0.05
Baseline	70	4	0.3
Pessimistic	40	5	0.1

In the sequential route, the energy consumption is shown to be dominated by CO_2 electrochemical conversion to produce CO, which includes CO_2 electrolysis (643 kJ/mol$_{CO2}$), carbonate regeneration (230 kJ/mol$_{CO2}$), and product purification (110 kJ/mol$_{CO2}$). These are all in terms of the amount of converted CO_2 (see Supporting Information for the carbon balance). The gas-fed CO_2 electrolyser was assumed to operate at a cell voltage of 3 V and a CO FE of 90% which has been demonstrated experimentally (Fig. 2). The single-pass conversion rate is assumed to be 50%, including 25% CO_2 conversion to CO and 25% CO_2 loss to (bi)carbonate. When compared to the baseline integrated route, there is then no foreseen energy advantage between the two routes (Fig. 4). The primary reason is the appreciable amount of CO_2 (i.e., 0.3 mol CO_2 per mol amine) retained in the amine solution at the electrolyser outlet stream. A substantial amount of energy is then still required to recover the amine for CO_2 re-absorption, which then offsets any foreseen energy benefits from process intensification.

We have chosen an effluent concentration of X = 0.3 in the baseline case because the integrated electrolyser is unlikely to regenerate the capture medium to the level achieved by the conventional thermal treatment (e.g., X = 0.05) due to the mass transport limitations in the reactor. A relatively high CO_2 loading (or high carbamate concentration) would be necessary to ensure a sufficient concentration gradient to drive carbamate diffusion to the catalyst through the stagnant layer at meaningful current densities. The mass transport limitation is then similar to that faced in H-cell CO_2 gas-fed electrolysers where CO_2 molecules transport from the liquid bulk to the electrode surface.

It is possible to operate the integrated process with a richer effluent stream of X = 0.3, but the absorption rate and capacity of the regenerated amine would be degraded in the absorber unit. A larger absorber size would therefore be required to ensure an identical capture capacity, penalizing the processes' capital cost. However, this is a techno-economic trade-off and brings further complexity to our energy analysis. Hence, we kept the same CO_2 loading conditions for both processes as a CO_2-lean amine amount of X = 0.05. In this case, we include a symbolic process (including amine regeneration, CO_2 electrolysis, product separation, and (bi)carbonate regeneration) to fully regenerate the solvents and convert the rest of captured CO_2 to CO, similar to the sequential route as shown in Fig. 1a. We find that

the carbamate utilisation efficiency has a profound impact on the total energy cost if the integrated electrolyser performs far worse than the gas-fed electrolyser. If the integrated route has a poor CO FE (40%), in the pessimistic case, the energy to drive integrated conversion is far higher (2193 kJ/mol$_{CO2}$) than the gas-fed electrolysis, making the sequential route much more attractive than the integrated route.
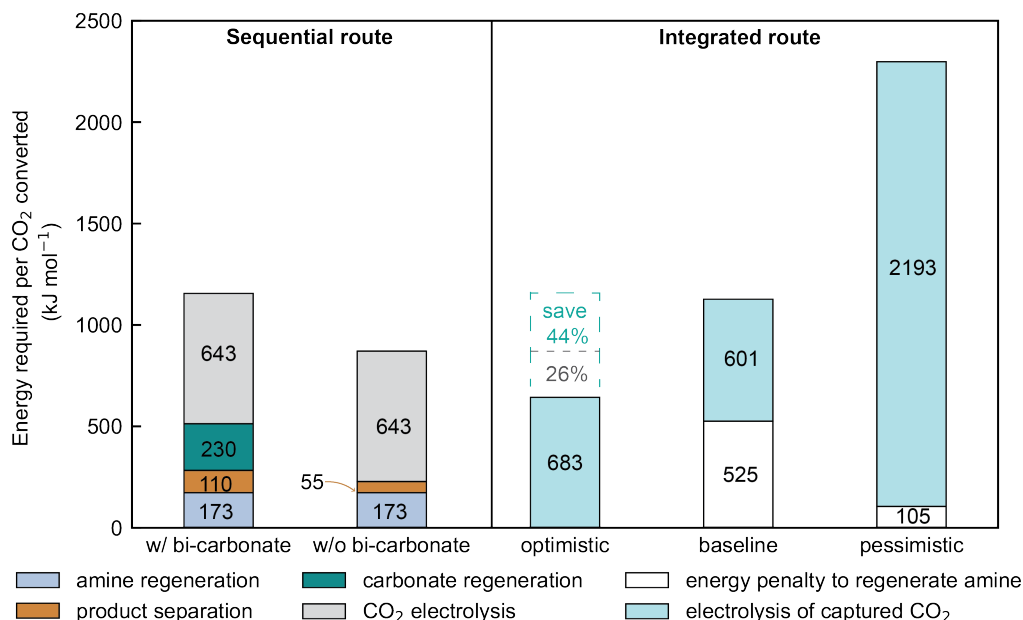

Fig. 3 Scenario analysis of overall energy cost for sequential and integrated routes. In the sequential route, the CO_2 electrolyser includes state-of-the-art gas-fed electrolysers that have CO_2 loss to (bi)carbonate or future scenarios with 100% CO_2 utilisation. The optimistic, baseline and pessimistic cases for the integrated route are compared against the sequential route.

In the optimistic case, we assume the electrolysis of captured CO_2 performs the same as the gas-fed electrolysis and the integrated electrolyser can fully recover the capture medium. In this scenario, the integrated route can save up to 44% of total energy due to a low cell voltage, high CO Faradaic efficiency, and no cost associated with full amine regeneration. Such reduction in energy consumption renders the integrated route a more attractive option. We then find that most research emphasis should be placed on enhancing the Faradaic efficiency and cell voltages in order to reduce the energy of the overall process. Further, the amine stream leaving the electrolyser must have a low CO_2 loading. Without these conditions, the sequential route remains favourable.

Lastly, we assessed the energy cost of the sequential route based on future CO_2 gas-fed electrolysis with no carbonate formation. Very recent reports demonstrated the potential to improve CO_2 utilisation efficiency [41] by developing catalyst-membrane interface [35,42], optimising cell operating conditions (*e.g.*, reducing CO_2 flow rates, increasing current densities, and optimising anolyte compositions and ionic strength)[37], or supplying protons towards the cathode to regenerate CO_2 from the (bi)carbonates, *e.g.*, flowing strong acidic catholyte[20,43], applying cation-exchange membranes[35] or bipolar membrane[42] in a reverse mode. The single-pass conversion rate remains 50% in this optimistic sequential model,

meaning that 50% of the inputted CO_2 feed converts to CO product and reduces the required pressure-swing absorption separation energy cost. The total energy of such a sequential route is only 871 kJ mol^{-1}$_{CO2}$ (see Fig. 3). Here the integrated optimistic case then only maintains a maximum energy advantage of 26%. We then conclude that if the energy penalty associated with carbonate regeneration is solved, there would be substantially lower energy gain possible by integrating capture and conversion even in the most optimistic scenario as described in this article.

Overall, our comparison highlights that energy benefits brought by the integrated route strongly depend on the progress in enhancing the energy efficiencies of electrolysis of molecular CO_2 and captured CO_2. This trend makes sense because the CO_2 electrochemical conversion is the dominant contributor to the overall energy cost, which is the primary reason preventing straightforward CO_2 capture and utilisation at a low cost.

Parameter sweeps of the integrated route

Here we briefly highlight how varied performance metrics of Faradaic efficiency and cell voltage impact the overall energy requirements for the integrated route. Such an analysis provides deeper context than the described optimistic, baseline and pessimistic scenarios above.

Fig. 4a shows that the energy advantage from the integrated route plummets linearly with the energy consumption of electrolysis of captured CO_2. This trend highlights the core role of the electrolyser in determining the overall energy efficiency. The breakeven point for the integrated route is at the energy cost of 1156 kJ mol^{-1} for the integrated electrolyser (see Fig. 4a). The value of the breakeven point should vary with the energy efficiency of the gas-fed electrolyser and the operating conditions, such as the effluent CO_2 loading (X) and the use of the capture solvents. (see Fig. S4)
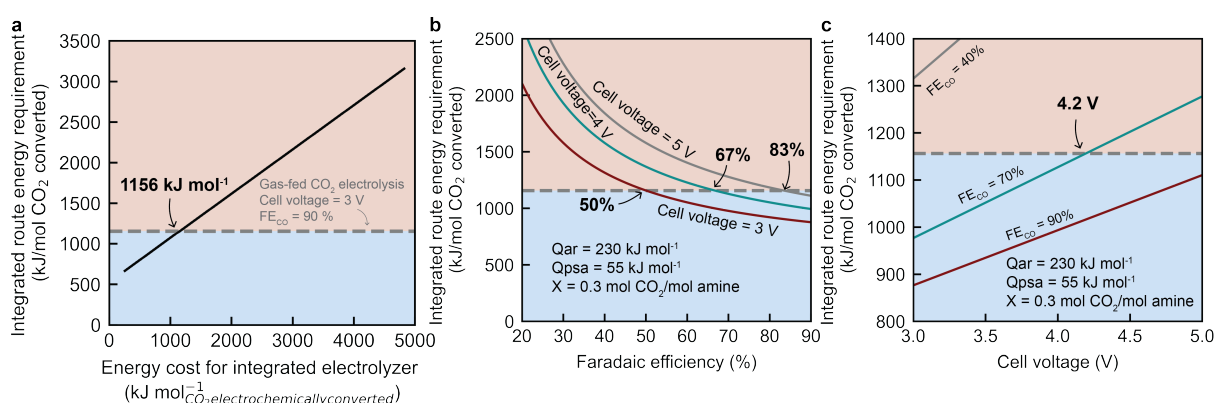

Fig. 4 Impacts on overall integrated energy cost from integrated conversion cells. a, Effect of energy cost from direct CO_2 conversion on the overall energy cost of the integrated route. Effect of **b,** CO FE at a cell voltage at 3, 4, and 5 V and **c,** cell voltages with CO Faradaic efficiency (FE) of 40%, 70%, and 90% on the overall energy cost of the integrated route. The grey dashed line represents the energy cost of the sequential route based on state-of-the-art gas-fed CO_2 electrolysers. The blue region means that the integrated route is more energy-efficient than the sequential route, while the orange region indicates vice-versa.

The role of CO Faradaic efficiency and cell voltages were examined individually in influencing the energy gain from an integrated route. Fig. 4b shows the breakeven point for CO Faradaic efficiency with varied cell voltages: the breakeven Faradaic efficiency is 50% at 3 V, 67% at 4 V, and 83% at 5 V. The impact from the Faradaic efficiency is more significant than from the cell voltages, as shown in Fig. 4b and c. The energy advantage from the integrated route decreases linearly with an increase of cell voltages and diminishes at 4.2 V when the Faradaic efficiency is 70%. Similarly, the breakeven cell voltages increase if the CO Faradaic efficiency could be further enhanced. The state-of-the-art integrated CO_2 conversion, as reported by Lee *et al.*[17] at 50 mA cm^{-2} as shown in Fig. 2, has the potential to achieve a more energy-efficient integrated route, while most of the reported Faradaic efficiencies are below 40% at high rates. Our model did not consider the cost associated with the current densities, which predetermine the capital cost of the electrolysers. Like the gas-fed CO_2 electrolysers, we believe operating at more than 100 mA cm^{-2} with a high product selectivity is a prerequisite for an industrially relevant CO_2 electrochemical upgrade system. [44]

Outlook for future integrated electrolysis

Our results identified that the electrochemical CO_2 conversion is the primary energy contributor for both sequential and integrated CO_2 capture and electrochemical conversion process. The reported energy efficiency of the integrated electrolyser is generally lower than the gas-fed CO_2 electrolysis. Such limitation originates from (1) the low surface coverage of anionic reactants at the negatively charged catalyst surface at industrially relevant rates and (2) the limited number of active sites the medium can reach over the hydrophobic gas-diffusion electrodes. [17]

Although the catalysts for CO_2 electroreduction are selective to reduce CO_2 captured by amine-based capture media (RNH_2), [17,27,45] the carbamate ions (*i.e.*, $RNHCO_2$) could be the main active reagent for the conversion. [17,46] This is different from the reduction mechanisms in CO_2 electrolysis[31] and direct bicarbonate reduction [47,48]. The carbamate ions together with protonated amines (RNH_3^+) are the major products when CO_2 is in contact with amines when the CO_2 loading is below 0.4 – 0.6 mol CO_2 per mol amine in the case of 30 % wt. monoethanolamine aqueous solution. [49,50]
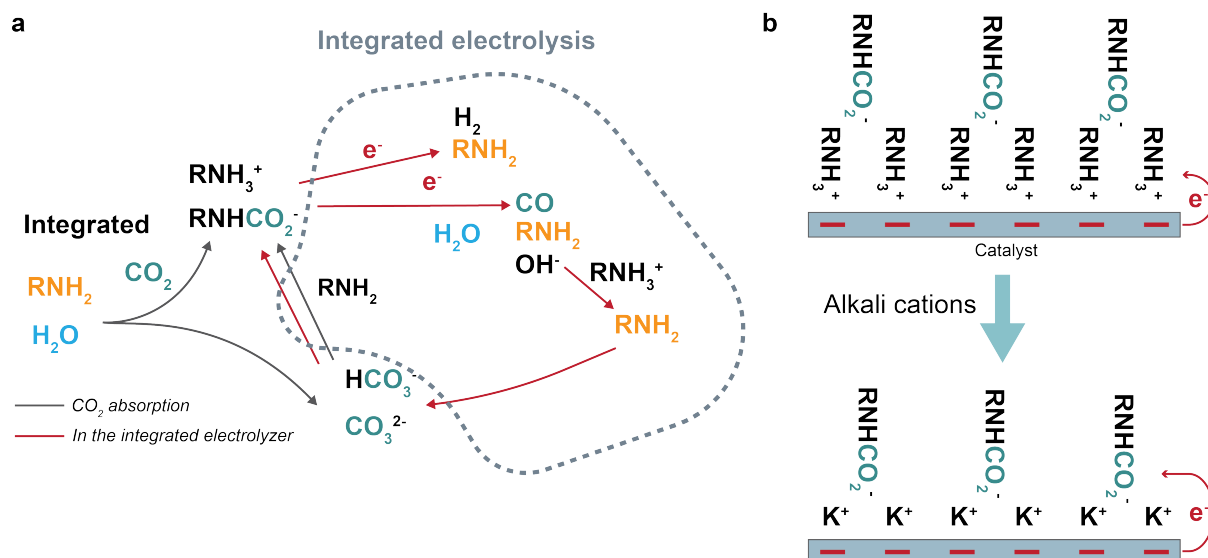
Fig. 5 Speciation of amine-based capture media in sequential and integrated routes and their impacts on CO$_2$ electrochemical conversion. a, Proposed integrated CO$_2$ absorption and electrolysis routes in amine-based solvents. **b,** Schematic illustration of the role of alkali cations which promote interfacial charge transfer from the catalyst surface to the carbamate ions, adapted from [17].

The heating is required to reverse the carbamate hydrolysis and separate CO$_2$ from the amine solutions in a sequential route. Whereas in the integrated route, as shown in Fig. 5a, electrical energy is required to convert carbamate into CO or protonated amine into hydrogen while regenerating the carbamate and producing OH$^-$ ions. [51] The OH$^-$ should react with protonated amines to regenerate the amines. If there are (bi)carbonates present in the CO$_2$-rich amines, the electrochemically regenerated amines at the catalyst surface thermodynamically tend to react with the (bi)carbonate to form carbamate. It means that direct bicarbonate reduction is unlikely the primary mechanism for conversion. However, the carbamate ions are anions and could be repelled by the negatively charged cathode surface, which likely contributes to the observed low CO Faradaic efficiency. Therefore, such electrostatic repulsion limits the coverage of reactants, especially at a high overpotential, and causes a poor product Faradaic efficiency usually lower than 10%.

This issue can be alleviated by including alkali cations such as potassium ions (K$^+$) or caesium ions (Cs$^+$) in the amine capture medium. [17] In this case, the carbamate reduction can occur through an interfacial charge transfer mechanism proposed by Lee *et al.*[17], where the alkali cations can be packed (instead of protonated amines) at the electrode surface and facilitate charge transfer from the electrode surface to the carbamate ions. (Fig. 5b) Meanwhile, an increasing number of reports also highlighted the essential role of alkali cations in activating gas-fed CO$_2$ electrochemical conversion. [22,52,53] Hence, the cations could synergistically suppress the hydrogen evolution by minimizing surface coverage of protonated amines activate electrochemical reduction of carbamates. Nevertheless, the electrochemical reduction of captured CO$_2$ is still low in CO Faradaic efficiency at > 100 mA cm^{-2}, which could also be

partially related to the limited electrochemical area due to the use of planar metal electrodes[27] or the hydrophobic nature of the gas-diffusion electrodes that are frequently used for gas-fed electrolysis.[17]

We anticipate a significant improvement of gas product Faradaic efficiency and cell voltages at an improved rate (> 100 mA cm^{-2}) by implementing new electrode structures such as hydrophilic 3D structured flow-through electrodes and optimised capture media.[54,55] The desired wetting condition for direct carbamate reduction should have maximized solid-liquid interfaces with a minimal contact area of the gas bubble with the electrode surface. This means that the electrode surface should be hydrophilic, which is different from the wettability of gas-diffusion electrodes. Using metallic porous flow through electrodes is expected to achieve a high rate of CO_2 conversion by maximizing the electrochemical surface area and accelerating the detachment of gas products.

Further, including conversion-active cations could weaken the solvent capability to absorb CO_2. For instance, Khurram et al.[46] reported that including alkali cations such as K^+ and Cs^+ could promote direct carbamate reduction but may destabilize the formation of carbamate, which is essential for CO_2 absorption. However, the results of our analysis (see Fig. 3) indicate that the capture media for the integrated route could be designed to favour CO_2 conversion at a reasonable cost on CO_2 absorption and loading. Therefore, an interdisciplinary collaboration between CO_2 capture and electrolysis is highly important to advance the integrated route. On the other hand, more experimental and theoretical efforts are also essential to understand the potential catalyst surface restructuring, local reaction environment (e.g., pH and local concentration of amine species), and multiphase and ion transports in the cells, which have been demonstrated important for the stability and efficiency of the gas-fed CO_2 electrolysis.[56-58]

Lastly, a directly coupled CO_2 capture and electrochemical conversion could potentially save close to 44% energy cost versus a sequential process based on the state-of-the-art gas-fed CO_2 electrolysers if the integrated electrolysis performs similarly to the gas-fed electrolysis (3 V and 90% CO FE). However, this energy benefit could drop to only 26% if new gas-fed CO_2 electrolysers with no CO_2 loss to (bi)carbonates emerged at high current densities. Our sensitivity analysis results suggest that research efforts should target an overall energy cost at least below 1000 kJ mol$^{-1}_{CO2}$ for the integrated conversion cells so that the operational cost would not diminish the capital cost reduction from the process intensification. Collectively we hope this work provides a benchmark for integrated electrolysis research and provides a perspective to researchers and funding bodies seeking to achieve low-cost carbon capture and electrochemical utilisation processes through process integration.

Acknowledgement

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