



Coupling electrochemical CO₂ conversion with CO₂ capture

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Electrochemical CO₂ conversion into fuels or chemicals and CO₂ capture from point or dilute sources are two important processes to address the gigaton challenges in reducing greenhouse gas emissions. Both CO₂ capture and electrochemical CO₂ conversion are energy intensive, and synergistic coupling between the two processes can improve the energy efficiency of the system and reduce the cost of the reduced products, via eliminating the CO₂ transport and storage or eliminating the capture media regeneration and molecular CO₂ release. We consider three different levels to couple electrochemical CO₂ reduction with CO₂ capture: independent (Type-I), subsequent (Type-II) and fully integrated (Type-III) capture and conversion processes. We focus on Type-II and Type-III configurations and illustrate potential coupling routes of different capture media, which include amine-based solutions and direct carbamate reduction, redox active carriers, aqueous carbonate and bicarbonate solutions, ionic liquids CO₂ capture and conversion mediated by covalent organic frameworks.

Electrochemical carbon dioxide reduction (CO₂R) has made substantial advances in recent years. The selectivity, activity and durability of several multielectron and multiproton reactions has primed this technology for commercialization. Although the techno-economic viability of electrochemical CO₂R is highly dependent on the end product, these performance metrics are pushing this technological pathway to be a viable option, especially with growing renewable energy infrastructures¹. In particular, electrochemical ethylene generation has reached an operating partial current density of 1.3 A cm⁻² and a Faradaic efficiency of 65–75% (ref. ²). Additionally, electrochemical ethanol generation has reached a remarkable Faradaic efficiency of 91% at –0.7 V versus a reversible hydrogen electrode³. Thus far, nearly all lab-scale electrochemical CO₂R demonstrations have used high-purity CO₂ gas cylinders to benchmark catalyst or device performances and eliminate the effects of dilute or impure carbon sources. The role of CO₂ source and its utilization efficiency in the electrochemical conversion process has yet to be carefully examined partly due to the relatively low technical readiness level of this nascent technology. In this perspective, we aim to discuss potential routes to couple the electrochemical CO₂ conversion process with the state-of-the-art CO₂ capture process.

To have an impact on climate change, electrochemical CO₂ capture and conversion must be scalable to the level of the global carbon cycle. This cycle is determined by a balance of ecological factors, such as photosynthesis, forest fires, respiration and ocean–atmosphere exchange, and anthropogenic factors, such as fossil fuel combustion and land use changes⁴. Currently, this set of factors is disproportionate, leading to net emissions of 4.4 GtCO₂ yr⁻¹ (ref. ⁴). This has prompted investigations of the options for carbon capture or negative emissions, which include modified natural processes, such as enhancing the rates of photosynthesis in the oceans by iron or nitrogen seeding, accelerated rock weathering, reforestation, biochar synthesis and enhanced soil carbon sequestration by modified agricultural practice and grassland restoration^{5–7}. Technologically driven processes include bioenergy with carbon capture and storage (BECCS), direct air capture (DAC) and direct ocean capture

(DOC)^{5–7}. Worldwide energy-related CO₂ emissions are currently at approximately the 40 Gt level and to keep within the 2 °C goal set by the Paris agreement, approximately 10 GtCO₂ per year must be captured, with up to 160 GtCO₂ stored by 2050⁸. As a benchmark for capture, a recent study found that BECCS has the potential to sequester up to 5.2 GtCO₂ per year without large adverse impacts⁷.

Large gaps still exist, especially at the demonstrated scale for CO₂ capture and electrochemical CO₂ conversion processes. Various capture technologies are currently being explored to reduce CO₂ emissions⁹. Traditional CO₂ capture from point sources (power plants, oil refineries, cement industry and so on), which involve chemical adsorption and desorption in amine-based solutions via temperature or pressure swings, exists at the mature scale and at a rate of ~20,000 t day⁻¹ from a single point source¹⁰. However, a closed carbon cycle also requires the capture of decentralized emissions from transport, agriculture and small emitters, which are already responsible for approximately 40% of the total CO₂ emission¹¹. These dilute sources will be harder to replace by non-emitting technologies compared with that for point sources. For DAC, Carbon Engineering demonstrated the feasibility of this process in two sequential loops. In the first loop, CO₂ is captured from air using aqueous alkaline solutions. In the second loop, the alkaline solutions are regenerated by a series of chemical steps, followed by calcination and the release of concentrated CO₂ (ref. ¹²). The current largest DAC system is capable of capturing ~4,000 t yr⁻¹ (ref. ¹³), with other future planned systems capable of up to 0.1 Gt yr⁻¹ (ref. ⁹). For DOC, the operating principle is to shift the CO₂–bicarbonate–carbonate equilibrium towards gaseous CO₂ release or solid carbonate precipitation to achieve CO₂ capture^{14,15}. Although the demonstrated scale for DOC is currently low, <1 kg day⁻¹ (refs. ^{14,15}), the vast majority of lab-scale electrochemical or photoelectrochemical CO₂ conversion processes produce fuels at rates of <1 kg day⁻¹. Crucial challenges exist to maintain the delicate gas–liquid interfaces that achieve the optimal operating current density, selectivity and scale up from a few cm² to hundreds of cm², which is the typical size of commercial water electrolysis systems. Production at commercially relevant

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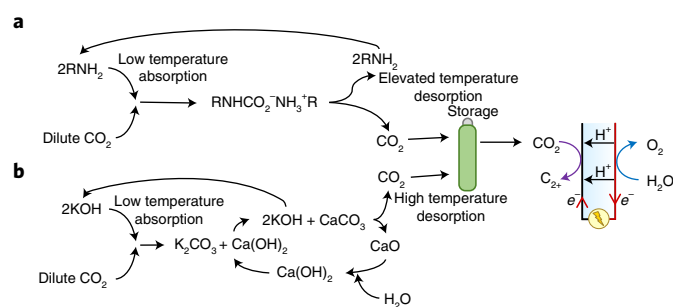


Fig. 1 | Type-I, independent electrochemical CO₂R and CO₂ capture processes. In Type-I-a, CO₂ is captured by an amine-based solution at low temperature, followed by amine regeneration and CO₂ release via temperature swings. In Type-I-b, CO₂ is captured by an alkaline solution to form carbonate species, and is then converted into CaCO₃ through the reaction with Ca(OH)₂. A thermochemical process then releases CO₂ in a pure feed, which allows for use in CO₂R.

scales, even for the simplest two-electron reduction of CO₂ to CO, has yet to be demonstrated. Given that the scaling of electrochemical CO₂ conversion is evolving rapidly^{16,17}, and expected to grow to large-scale production in the next decade, we aim to reflect on the possibilities to match CO₂ capture and conversion.

In this Perspective, we explore the synergistic coupling between CO₂ capture processes, especially from dilute sources, and electrochemical CO₂ conversion processes, in which the CO₂ transport and storage or the capture media regeneration and molecular CO₂-release step can be minimized or eliminated, to improve the energy efficiency of the system and lower the cost of the reduced products.

Conceptual coupling between electrochemical CO₂R and capture

Conceptually, we consider three different levels to couple electrochemical CO₂R with CO₂ capture: independent (Type-I), subsequent stage (Type-II) and fully integrated (Type-III) capture and conversion processes. In each type of configuration, we aim to give notable examples to illustrate the unique features of the coupling. It is important to note that additional or alternative pathways are and will become available in each configuration as both the capture and reduction technology progress. With a Type-I configuration (Fig. 1), capture and conversion occur independently, with the captured CO₂ stored and utilized elsewhere. Minimal coupling between the two processes provides flexibility in varied approaches. The incompatibility in operating temperatures for electrochemical CO₂R, thermochemical CO₂ release and solvent regeneration requires the complete separation of the two processes. For example, Type-I-a shows amine regeneration via temperature swings¹⁰, and Type-I-b shows regeneration of an alkaline solution, KOH(aq.), in multistep thermochemical processes¹². A Type-II configuration involves coupling of the capture and conversion processes at a local level (Fig. 2). Here, molecular CO₂ is still the reactant for the conversion process, but a flux match between the capture and conversion process is required to achieve the optimal system performance. CO₂ capture technologies applicable for local coupling include electrochemically mediated amine regeneration^{18,19} (Type-II-a), redox active carrier^{20–22} (Type-II-b), bipolar membrane-based electro dialysis²³ (Type-II-c) and proton coupled electron transfer (PCET)-based CO₂ capture²⁴ (Type-II-d). The capture approaches described in the Type-II configuration all fall under the broad concept of electrochemical CO₂ capture, in which electrochemical potentials are applied to alter the nucleophilicity to mediate the capture and release of CO₂ from dilute sources to

concentrated sources^{11,25–27}. It is important to note that most electrochemical approaches involve cathodic activation of the capture media for CO₂ capture from dilute sources and anodic release of CO₂ into concentrated outputs. It is also important to note that CO₂ capture from sources that could contain air (DAC and point sources) may introduce O₂ to the cell, and possibly cause degradation of the capture solvents and competition between the oxygen reduction reaction and cathodic CO₂ capture. A Type-III approach bypasses the traditional release of CO₂ from the capture agent and instead involves the direct electroreduction of CO₂-loaded capture agents (Fig. 3). Here, electrochemical conversion of CO₂ into fuels or chemicals uses physisorbed or chemisorbed CO₂ from the capture medium as the reactant with simultaneous regeneration of the capture media. Several capture agents can be utilized in the Type-III configuration, which include amine based^{28–35} (Type-III-a) and bicarbonate and/or carbonate based^{36,37} (Type-III-b) agents, ionic liquids (ILs)³⁸ (Type-III-c) and covalent organic frameworks (COFs) (Type-III-d)³⁹. For both Type-II and Type-III approaches, CO₂ capture from sources that could contain air (DAC and point sources) may introduce O₂ to the cell, and possibly cause degradation of the capture solvents and competition between the oxygen reduction reaction and cathodic CO₂ capture or CO₂R. A major advantage of Type-III configurations is the formation of CO₂ adducts or carbamates, which result in a bent CO₂ configuration and so lower the overpotential needed for electrochemical conversion. These catalysts could further be optimized by changing the bond strength of the CO₂ binding site with additional functional groups, which results in lower energy penalties for bond formation and breaking, or selective product distributions during CO₂R.

CO₂ capture and conversion energetics in Type-I and II versus Type-III configurations were compared, as illustrated in Fig. 4. At the thermodynamic limit, only ~20 kJ mol⁻¹ is required to capture CO₂ from dilute sources, such as DAC, to give concentrated CO₂ at 1 bar. In comparison, electrochemical CO₂R, which involves bond making and bond breaking, requires orders of magnitude higher energy input at the thermodynamic limit. For example, at the thermodynamic limit, to convert CO₂ to CO electrochemically or photoelectrochemically requires a minimum voltage of 1.33 V, or 257 kJ mol⁻¹ at 25 °C, with typical realistic operations at ~3 V (579 kJ mol⁻¹) (ref. 16). Practically, however, energy requirements for CO₂ capture are close to those of CO₂ conversion, with a large regeneration energy in the range of 100–300 kJ mol⁻¹ from either temperature or pressure swings, or from electrochemical energy to regenerate the capture media and release concentrated CO₂ (ref. 11). For CO₂ capture from point sources, such as synthetic flue gas, a lower energy consumption of <100 kJ mol⁻¹ has been achieved in various approaches^{40–42}. The released CO₂ from the capture step could then be supplied to an electrochemical cell for conversion in the Type-I and Type-II configurations, as illustrated by the red pathway in Fig. 4.

However, in a fully integrated CO₂ capture and conversion process, the regeneration of the capture media and the conversion of the CO₂ in the form of a CO₂-adduct take place simultaneously, which offers a potential route to lower the overall capture and conversion energy. As illustrated in Fig. 4, if Type-I, II and III have the same energetic level for CO₂R intermediates, Type-III configurations could achieve lower overall energy requirements due to the energy saving through bypassing the capture media regeneration step. In addition, a CO₂-adduct-rich local environment could be used to increase the local concentration of CO₂ at the electrode and lower the overpotential for CO₂R. In addition to a potentially higher energy efficiency, the Type-III configuration only needs a single electrochemical device instead of multiple electrochemical devices for the capture and conversion process. The capital expenditure of electrochemical devices, such as water electrolysis and electrochemical H₂ compression, tends to dominate the cost of the overall system; as a result, Type-III configurations with a single

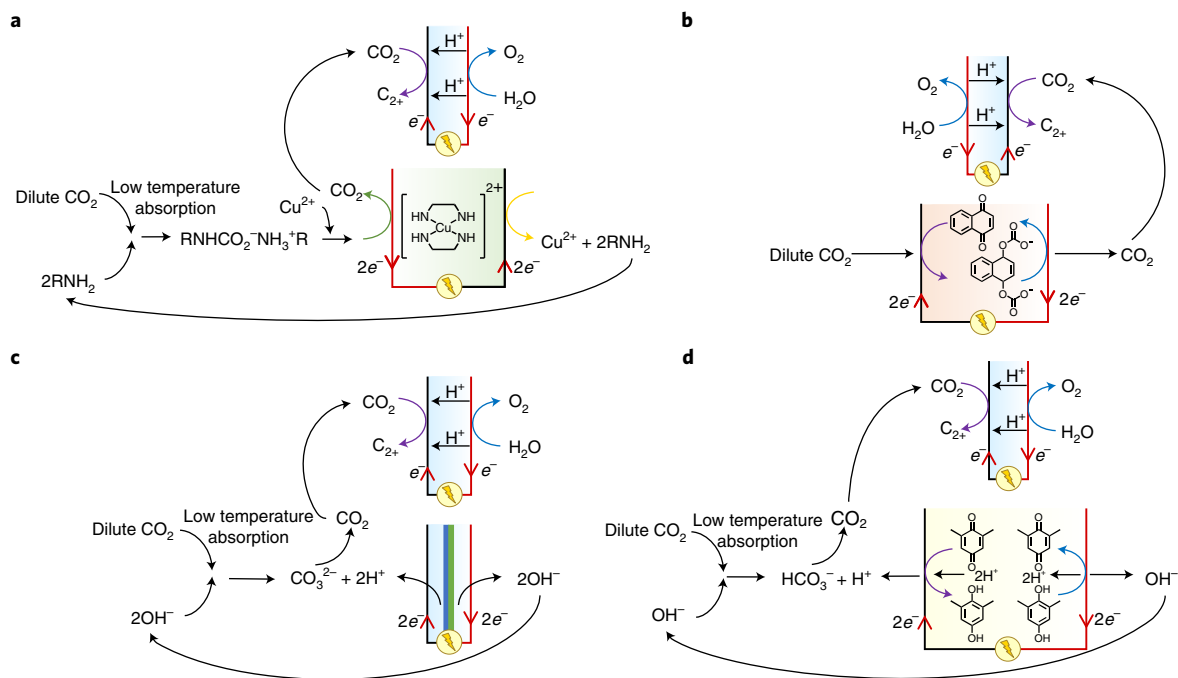


Fig. 2 | Type-II, subsequent stage electrochemical CO₂R and CO₂ capture processes. Technologies for local coupling include electrochemically mediated amine regeneration (Type-II-a), redox active carrier (Type-II-b), bipolar membrane-based electro dialysis (Type-II-c) and PCET-based CO₂ capture (Type-II-d). Type-II-a and b rely on anodic release of CO₂ through a redox mediator, whereas Type-II-c and d rely on the local generation and reaction of protons to release CO₂.

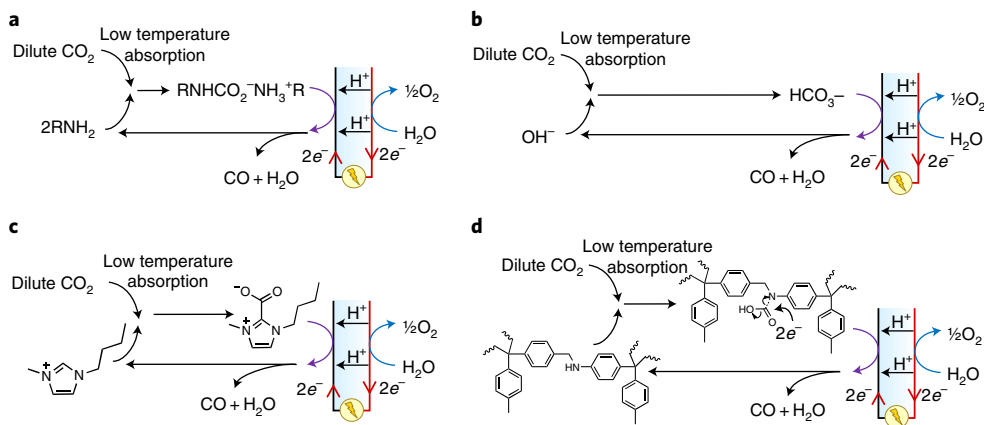


Fig. 3 | Type-III, fully integrated electrochemical CO₂R and CO₂ capture processes. Direct electroreduction of CO₂-loaded capture agents based on amines (Type-III-a), bicarbonates and/or carbonates (Type-III-b), ILs (Type-III-c) and COFs (Type-III-d). Type-III processes eliminate the capture media regeneration and molecular CO₂ release step, which has the potential to improve the energy efficiency of the system and to lower the cost of the reduced products.

electrochemical cell that accomplishes both the capture and conversion process will probably have an advantage in lowering the cost of CO₂R products.

To date, coupling between CO₂ capture and conversion has been studied in a few non-electrochemical conversion processes. These initial studies show a potential synergy between capture and conversion, with specific operating regimes that favour a single integrated CO₂ capture and utilization process from the overall cost point of view⁴³. The following sections focus on Type-II and Type-III approaches; we illustrate potential coupling routes of different capture media and present scientific challenges to integrate CO₂ capture and conversion.

Amine-based media for CO₂ storage and direct carbamate reduction

CO₂ can be captured by nucleophilic reaction with diamines, alkanolamines and their derivatives to yield the corresponding carbamates. Depending on the application, CO₂ can be released via thermal or electrocatalytic routes, which results in amine regeneration. Electrochemically mediated amine regeneration cannot be readily coupled to electrochemical CO₂R at the same electrode due to the anodic release step^{18,19}. However, using a separate electrode for CO₂R in the vicinity of the anode for amine regeneration enables a Type-II-a configuration. Moreover, the relative stability of unhindered carbamates allows for a one-step carbamate reduction on a

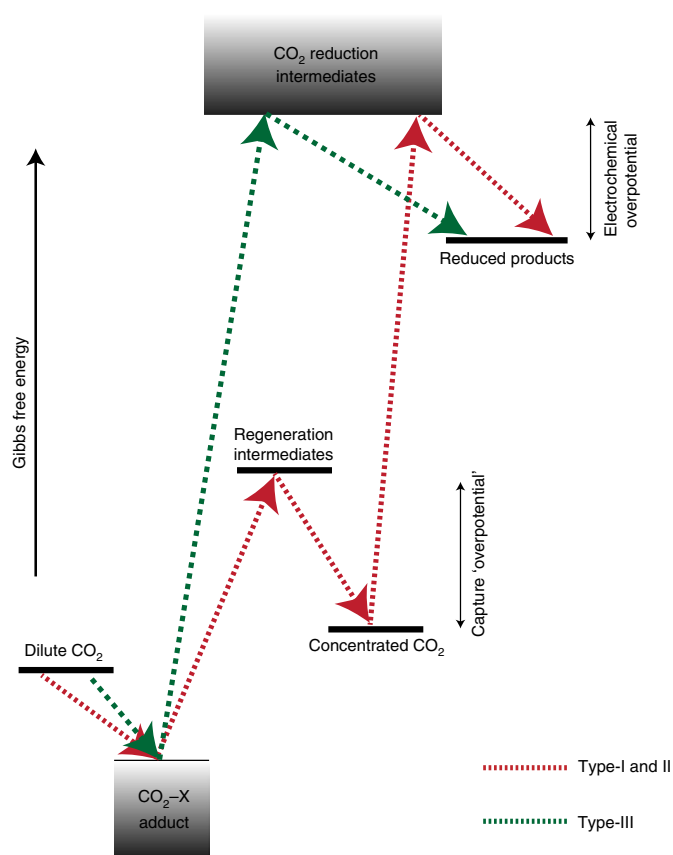


Fig. 4 | CO₂ capture and conversion energetics for Type-I and II (red) and Type-III (green). Dilute CO₂ can be captured through the formation of a CO₂-adduct species for all the routes; however, Type-I and II require an additional regeneration step to produce concentrated molecular CO₂, which can then be used for electrocatalysis. The Type-III configuration integrates the capture media regeneration with electrochemical CO₂R, which results in an improved energy efficiency of the overall capture and conversion system.

cathode for a Type-III-a configuration^{28–35}. Available reports suggest that amine addition drastically improves the CO₂R current densities along with C1 selectivity^{34,35}. The carbamate stability depends on many parameters, such as the structure of the precursor amine, the type of counterion and the presence of water, which allows for further improvements in CO₂R via fine-tuning through, for example, the use of additives²⁹, a supporting electrolyte²⁸ and varying the amine structure²⁸. Electrode stability is also an area of concern as high concentrations of amines may also result in corrosion of the metal surfaces. Careful consideration of the electrode composition and proper characterization must be taken into account for long-term performances. Given the novelty of the concept, the exact mechanism of carbamate reduction has yet to be described. There are two major hypotheses on the role of carbamates during electrochemical CO₂R, with the debate largely over the direct involvement of carbamate species as a possible reactant. Most studies suggest that carbamate acts as an electrolyte for CO₂R reaction because they show an improved CO₂ uptake and promote electrolyte conductivity as compared with those of conventional (bi)carbonate solutions^{29,35}. However, a detailed NMR investigation of an isolated carbamate reduction in non-aqueous electrolytes points towards the direct involvement of these species as the carbon source²⁸. Furthermore, the authors linked carbamate stability to CO₂R performance, which provides a possible explanation for previously observed performance improvements by utilizing cationic additives. This was

confirmed by Lee et al., who observed an improved Faradaic efficiency for CO in the presence of alkali cations⁴⁴.

Carbonate and bicarbonate in aqueous alkaline capture media

CO₂ can be captured by aqueous solutions of inorganic hydroxides to yield the corresponding (bi)carbonates. Aside from their use as a conductive medium, (bi)carbonates can serve as an indirect carbon source in CO₂R reactions. In contrast to carbamates, a direct electroreduction of a bicarbonate or carbonate has not been observed; instead, the electrochemical reduction reaction in the bicarbonate or carbonate solutions took place because of the CO₂-bicarbonate equilibrium and used molecular CO₂ as the reactant⁴⁵. Recent work leveraged the local acidification and local generation of molecular CO₂ for CO₂R at the membrane-catalyst interfaces^{36,37}. Type-II-c and Type-II-d illustrate the local acidification of (bi)carbonates for CO₂R via bipolar membrane-based electro dialysis and PCET, respectively. In this concept, in situ produced (bi)carbonate is circulated in a cathodic compartment of an electrochemical cell in which CO₂R is expected^{36,37} (Fig. 2c,d). In parallel, a H⁺ flux is produced at an ion-exchange membrane via an applied potential bias or a PCET reaction²⁴. As the result of catholyte acidification, CO₂ is released and eventually converted into target products at the cathode. Advantages of this approach include the local generation of CO₂, which could potentially break the CO₂ transport limitation in water and increase the local concentration of reactive species.

From a mass balance point of view, it is possible to realize the electrochemical conversion of CO₂ and release of the alkaline regenerative agent in a single electrochemical cell, as illustrated as a Type-III-b configuration in Fig. 3. Two protons from the anodic water oxidation locally regenerate molecular CO₂ in contact with the bicarbonate solution. Water instead of protons would participate in the CO₂R reaction and produce OH⁻ locally at the electrode surface, which closes the carbon capture loop. Practically, the low solubility of CO₂ in this alkaline environment presents a challenge in sustaining the CO₂R at a reasonable rate. Hence, to obtain a cyclic process for a Type-III configuration, the challenge lies in removing the produced OH⁻ from the CO₂R surface before it reacts with bicarbonate.

Redox active carriers for coupled catalysis

Similar to amine-based CO₂ capture, other redox active carriers (for example, quinones and thiocarbonates) can be used to form adducts with CO₂ (refs. 20–22). Unlike unhindered primary amines, bulk redox carriers cannot spontaneously form adducts with CO₂ and thus require the addition of electrons or holes. Mechanistically, C=O, RN- and RS- functional groups are first activated via cathodic reaction and then used to form an adduct with CO₂ via nucleophilic addition (Type-II-b). Owing to the requirement of cathodic activation, the use of such species is typically limited to a multi-step capture-release concept (Type-I or Type-II), as with amine scrubbing, in which the CO₂ release step occurs at the anode. A potential coupling strategy of Type-II-b is illustrated in Fig. 2 using quinone-based redox active carriers. Note that these redox active carriers are only soluble in non-aqueous electrolytes, and do not rely on proton transport for CO₂ capture. This drastically reduces competition from the hydrogen evolution reaction observed in aqueous electrolytes. Although a single-step adduct reduction (Type-III) has not been demonstrated with redox carriers for CO₂ capture, it is not intrinsically excluded either.

IL-mediated CO₂ capture and conversion

ILs have been investigated as carbon capture media due to their favourable physical and chemical properties for CO₂ absorption and allow for the combination of capture and conversion. ILs have high CO₂ absorption capabilities and are more selective for CO₂ than

for other gases (that is, N₂ and O₂), have low vapour pressures, are thermally stable and are ionically conductive due to their charged species⁴⁶. Their ionic compositions vary, but generally include imidazolium cations. ILs are promising candidates for CO₂ capture owing to their ability to specifically absorb and desorb CO₂. CO₂ can be released from conventional ILs by heating, purging with inert gases (such as Ar or N₂) or through pressure swings⁴⁷.

ILs can be separated into conventional and task-specific ionic liquids (TSILs). Each interacts differently with CO₂ and results in varying degrees of absorption. Conventional ILs physically absorb CO₂ and have weaker chemical interactions with it (compared with those of TSILs). These are typically imidazolium based and have been used in a wide variety of applications for CO₂ capture and conversion. A Type-III-c configuration, such as the reduction of the imidazolium–CO₂ adduct and regeneration of imidazolium, represents an opportunity for simultaneous CO₂ capture and electrochemical CO₂R. The binding of CO₂ in ILs is advantageous for electrocatalysis, as it bends the CO₂ molecule and allows for lower overpotentials for reduction^{38,48}. Several studies reported an increased CO₂R selectivity when using ILs as an electrolyte or as an additive in aqueous solution to suppress the hydrogen evolution^{38,49,50}. The challenge in Type-III-c is the relatively low CO₂ uptake by the conventional imidazolium-based ILs, which becomes especially critical when dilute CO₂ sources are used from DAC or DOC processes. To improve the CO₂ capture uptake, TSILs with typically amine^{51–53} functional groups that strongly interact with CO₂ were developed. The amine functional group strongly binds to CO₂ to form carbamates, which allows a CO₂ to IL molar ratio of 1:2 to be realized. Although these are promising characteristics, the direct CO₂R of carbamates in TSILs has yet to be demonstrated with functional catalysts.

Although there are several obvious advantages to using ILs for CO₂ capture and for electrochemical conversion, there are several issues to take into account. ILs can act as hydrogen evolution reaction suppressors during CO₂R and stabilize intermediates, but stability of the cation group, and in some instances electrode restructuring, was found to be an issue during electrocatalysis^{49,54}. However, several groups have studied ILs for CO₂R and reported impressive yields for CO and formate, but very few C–C products are reported, even for Cu electrodes, which are well known for producing C₂₊ products. Considering the interactions of CO₂ with ILs, the heat of adsorption of carbamate formation in ILs is often higher than that for imidazolium adduct formation. CO₂ therefore more strongly binds as a carbamate in TSILs compared with the physical absorption in conventional ILs. Carbamate formation may be better suited to capturing CO₂, but conventional ILs are favoured for electrocatalytic conversion.

COF-mediated CO₂ capture and conversion

COFs, which comprise organic precursors linked by strong covalent bonds, have emerged as a relatively new class of crystalline porous materials. COFs were recently explored as sorption material for CO₂ capture⁵⁵. Like metal organic frameworks, the high affinity between COFs and CO₂ can be leveraged for CO₂ capture either in an adsorption process or embedded in a membrane sheet. At the same time, COFs have been widely investigated as potential catalysts for CO₂ electrocatalysis, either decorated with a metal^{56–58} or as a molecular catalyst^{59–61}.

Demonstrations of both CO₂ capture and conversion using COFs open the opportunity for the integration into a single step. For electrochemical reduction, Liu et al showed a similar process to exploit the strong affinity between the amine linkage in the COF backbone to form carbamates, and so enhance the CO₂R reduction at a silver electrode³⁹. Using the concerted electrochemical CO₂R at the silver electrode in the presence of COFs, a Type-III-d simultaneous CO₂ capture and electrochemical CO₂R can be realized. The sorption

properties of COFs (and metal organic frameworks) could potentially alleviate the limitations posed by low CO₂ concentrations in air or water, and possibly allow an integrated DAC and CO₂ conversion. The particular COF used in earlier COF-enhanced catalysis, COF-300, is proved to be water-resilient, unlike most metal organic framework structures for CO₂ capture⁶². From a materials standpoint, challenges remain in the limited electronic conductivity and chemical stability of COFs.

Summary and outlook

As the simplest case, Type-I configurations can readily couple independent CO₂ capture and conversion technologies. Nevertheless, the integrated nature of Type-II and Type-III configurations has unique advantages, which include reduced capital expenditure. Type-II approaches eliminate the storage and transportation of captured CO₂, whereas converted fuels or chemicals, especially liquid products, can be readily stored and transported. Type-II approaches involve multiple sets of cathodes and anodes (Type-II-a, b and d) or multiple sets of heterogeneous interfaces (Type-II-c) for electrochemical CO₂R at the vicinity of the CO₂ release in the capture process. Placement of the catalysts, engineering of the local environments and development of reactor designs are important for the efficient usage of CO₂ and flux matching the two processes in the Type-II approach. Meanwhile, Type-III configurations leverage the CO₂-rich capture agent to bypass energy-intensive steps for regeneration of the capture agent and the release of CO₂, which has the potential to improve the overall energy efficiency of the system. Vast potential for research and development exists in Type-III configurations to overcome catalytic materials challenges as well as to investigate fundamental mechanistic understandings of electrochemical CO₂R in various CO₂-rich capture agents. To overcome the limited C₂₊ product distributions generally favoured in aqueous CO₂R, an alternative strategy can be found through producing CO at high Faradaic efficiencies from CO₂R and further conversion to higher-order products via Fisher–Tropsch type reactions. Additionally, coupling electrochemical CO₂R with dilute CO₂ capture from air or ocean water presents long-term opportunities for neutral or negative CO₂ emission. Ultimately, the realization of integrated CO₂ capture and conversion systems requires advancements in efficiency and scale for the CO₂R process, and also overcoming the limitations in chemical stability and compatibility for CO₂ capture technology.

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References

- Jouny, M., Luc, W. & Jiao, F. General techno-economic analysis of CO₂ electrolysis systems. *Ind. Eng. Chem. Res.* **57**, 2165–2177 (2018).
- García de Arquer, F. P. et al. CO₂ electrolysis to multicarbon products at activities greater than 1 A cm⁻². *Science* **367**, 661–666 (2020).
- Xu, H. et al. Highly selective electrocatalytic CO₂ reduction to ethanol by metallic clusters dynamically formed from atomically dispersed copper. *Nat. Energy* **5**, 623–632 (2020).
- Cavallaro, N. et al. *Second State of the Carbon Cycle Report* (US Global Change Research Program, 2018); <https://doi.org/10.7930/SOCCR2.2018>
- McLaren, D. A comparative global assessment of potential negative emissions technologies. *Process Saf. Environ. Prot.* **90**, 489–500 (2012).
- Fridahl, M., Hansson, A. & Haikola, S. Towards indicators for a negative emissions climate stabilisation index: problems and prospects. *Climate* **8**, 75 (2020).
- National Academies of Sciences, Engineering, and Medicine *Negative Emissions Technologies and Reliable Sequestration. Negative Emissions Technologies and Reliable Sequestration* (National Academies, 2019); <https://doi.org/10.17226/25259>
- Mac Dowell, N., Fennell, P. S., Shah, N. & Maitland, G. C. The role of CO₂ capture and utilization in mitigating climate change. *Nat. Clim. Chang.* **7**, 243–249 (2017).
- Bettenhausen, C. The life-or-death race to improve carbon capture. *Chem. Eng. News* **99**, 28–35 (2021).

10. Dutcher, B., Fan, M. & Russell, A. G. Amine-based CO₂ capture technology development from the beginning of 2013—a review. *ACS Appl. Mater. Interfaces* **7**, 2137–2148 (2015).
11. Sharifian, R., Wagterveld, R. M., Digdaya, I. A., Xiang, C. & Vermaas, D. A. Electrochemical carbon dioxide capture to close the carbon cycle. *Energy Environ. Sci.* **14**, 781–814 (2021).
12. Keith, D. W., Holmes, G., St. Angelo, D. & Heidel, K. A process for capturing CO₂ from the atmosphere. *Joule* **2**, 1573–1594 (2018).
13. Skydsgaard, N. & Evans, D. World's largest plant capturing carbon from air starts in Iceland. *Reuters* (13 September 2021); <https://www.reuters.com/business/environment/worlds-largest-plant-capturing-carbon-air-starts-iceland-2021-09-08/>
14. Digdaya, I. A. et al. A direct coupled electrochemical system for capture and conversion of CO₂ from oceanwater. *Nat. Commun.* **11**, 4412 (2020).
15. Eisaman, M. D. et al. CO₂ extraction from seawater using bipolar membrane electrodialysis. *Energy Environ. Sci.* **5**, 7346–7352 (2012).
16. Endrödi, B. et al. Multilayer electrolyzer stack converts carbon dioxide to gas products at high pressure with high efficiency. *ACS Energy Lett.* **4**, 1770–1777 (2019).
17. Sánchez, O. G. et al. Recent advances in industrial CO₂ electroreduction. *Curr. Opin. Green. Sustain. Chem.* **16**, 47–56 (2019).
18. Stern, M. C., Simeon, F., Herzog, H. & Hatton, T. A. Post-combustion carbon dioxide capture using electrochemically mediated amine regeneration. *Energy Environ. Sci.* **6**, 2505–2517 (2013).
19. Stern, M. C. & Alan Hatton, T. Bench-scale demonstration of CO₂ capture with electrochemically-mediated amine regeneration. *RSC Adv.* **4**, 5906–5914 (2014).
20. Gurkan, B., Simeon, F. & Hatton, T. A. Quinone reduction in ionic liquids for electrochemical CO₂ separation. *ACS Sustain. Chem. Eng.* **3**, 1394–1405 (2015).
21. Apaydin, D. H., Glowacki, E. D., Portenkirchner, E. & Sariciftci, N. S. Direct electrochemical capture and release of carbon dioxide using an industrial organic pigment: quinacridone. *Angew. Chem. Int. Ed.* **53**, 6819–6822 (2014).
22. Singh, P. et al. Electrochemical capture and release of carbon dioxide using a disulfide–thiocarbonate redox cycle. *J. Am. Chem. Soc.* **139**, 1033–1036 (2017).
23. Nagasawa, H., Yamasaki, A., Iizuka, A., Kumagai, K. & Yanagisawa, Y. A new recovery process of carbon dioxide from alkaline carbonate solution via electrodialysis. *AIChE J.* **55**, 3286–3293 (2009).
24. Watkins, J. D. et al. Redox-mediated separation of carbon dioxide from flue gas. *Energy Fuels* **29**, 7508–7515 (2015).
25. Renfrew, S. E., Starr, D. E. & Strasser, P. Electrochemical approaches toward CO₂ capture and concentration. *ACS Catal.* **10**, 13058–13074 (2020).
26. Kang, J. S., Kim, S. & Hatton, T. A. Redox-responsive sorbents and mediators for electrochemically based CO₂ capture. *Curr. Opin. Green Sustain. Chem.* **31**, 100504 (2021).
27. Rheinhardt, J. H., Singh, P., Tarakeshwar, P. & Buttry, D. A. Electrochemical capture and release of carbon dioxide. *ACS Energy Lett.* **2**, 454–461 (2017).
28. Khurram, A., Yan, L., Yin, Y., Zhao, L. & Gallant, B. M. Promoting amine-activated electrochemical CO₂ conversion with alkali salts. *J. Phys. Chem. C* **123**, 18222–18231 (2019).
29. Chen, L. et al. Electrochemical reduction of carbon dioxide in a monoethanolamine capture medium. *ChemSusChem* **10**, 4109–4118 (2017).
30. Pilotás, D., Nagy, T., Nagy, L., Mizsey, P. & Nagy, G. Extended investigation of electrochemical CO₂ reduction in ethanolamine solutions by SECM. *Electroanalysis* **30**, 690–697 (2018).
31. Bhattacharya, M., Sebhathi, S., Vercella, Y. M. & Saouma, C. T. Electrochemical reduction of carbamates and carbamic acids: implications for combined carbon capture and electrochemical CO₂ recycling. *J. Electrochem. Soc.* **167**, 086507 (2020).
32. Bhattacharya, M., Sebhathi, S., Vanderlinden, R. T. & Saouma, C. T. Toward combined carbon capture and recycling: addition of an amine alters product selectivity from CO to formic acid in manganese catalyzed reduction of CO₂. *J. Am. Chem. Soc.* **142**, 17589–17597 (2020).
33. Margarit, C. G., Asimow, N. G., Costentin, C. & Nocera, D. G. Tertiary amine-assisted electroreduction of carbon dioxide to formate catalyzed by iron tetraphenylporphyrin. *ACS Energy Lett.* **5**, 72–78 (2020).
34. Abdinejad, M., Mirza, Z., Zhang, X. A. & Kraatz, H. B. Enhanced electrocatalytic activity of primary amines for CO₂ reduction using copper electrodes in aqueous solution. *ACS Sustain. Chem. Eng.* **8**, 1715–1720 (2020).
35. Hossain, M. N., Ahmad, S., da Silva, I. S. & Kraatz, H. B. Electrochemical reduction of CO₂ at coinage metal nanodendrites in aqueous ethanolamine. *Chem. Eur. J.* **27**, 1346–1355 (2021).
36. Li, Y. C. et al. CO₂ electroreduction from carbonate electrolyte. *ACS Energy Lett.* **4**, 1427–1431 (2019).
37. Li, T. et al. Electrolytic conversion of bicarbonate into CO in a flow cell. *Joule* **3**, 1487–1497 (2019).
38. Rosen, B. A. et al. Ionic liquid-mediated selective conversion of CO₂ to CO at low overpotentials. *Science* **334**, 643–644 (2011).
39. Liu, H. et al. Covalent organic frameworks linked by amine bonding for concerted electrochemical reduction of CO₂. *Chem* **4**, 1696–1709 (2018).
40. Legrand, L., Shu, Q., Tedesco, M., Dykstra, J. E. & Hamelers, H. V. M. Role of ion exchange membranes and capacitive electrodes in membrane capacitive deionization (MCDI) for CO₂ capture. *J. Colloid Interface Sci.* **564**, 478–490 (2020).
41. Liu, Y., Ye, H.-Z., Diederichsen, K. M., Van Voorhis, T. & Hatton, T. A. Electrochemically mediated carbon dioxide separation with quinone chemistry in salt-concentrated aqueous media. *Nat. Commun.* **11**, 2278 (2020).
42. Lin, Y.-J., Chen, E. & Rochelle, G. T. Pilot plant test of the advanced flash stripper for CO₂ capture. *Faraday Discuss.* **192**, 37–58 (2016).
43. Jens, C. M., Müller, L., Leonhard, K. & Bardow, A. To integrate or not to integrate—techno-economic and life cycle assessment of CO₂ capture and conversion to methyl formate using methanol. *ACS Sustain. Chem. Eng.* **7**, 12270–12280 (2019).
44. Lee, G. et al. Electrochemical upgrade of CO₂ from amine capture solution. *Nat. Energy* **6**, 46–53 (2021).
45. Hori, Y. & Suzuki, S. Electrolytic reduction of bicarbonate ion at a mercury electrode. *J. Electrochem. Soc.* **130**, 2387–2390 (1983).
46. Aghaie, M., Rezaei, N. & Zendejboudi, S. A systematic review on CO₂ capture with ionic liquids: current status and future prospects. *Renew. Sustain. Energy Rev.* **96**, 502–525 (2018).
47. Park, Y., Lin, K.-Y. A., Park, A.-H. A. & Petit, C. Recent advances in anhydrous solvents for CO₂ capture: ionic liquids, switchable solvents, and nanoparticle organic hybrid materials. *Front. Energy Res.* **3**, 42 (2015).
48. Tanner, E. E. L., Batchelor-McAuley, C. & Compton, R. G. Carbon dioxide reduction in room-temperature ionic liquids: the effect of the choice of electrode material, cation, and anion. *J. Phys. Chem. C* **120**, 26442–26447 (2016).
49. Feaster, J. T. et al. Understanding the influence of [EMIM]Cl on the suppression of the hydrogen evolution reaction on transition metal electrodes. *Langmuir* **33**, 9464–9471 (2017).
50. Rosen, B. A. et al. In situ spectroscopic examination of a low overpotential pathway for carbon dioxide conversion to carbon monoxide. *J. Phys. Chem. C* **116**, 15307–15312 (2012).
51. Yang, Z. Z., Zhao, Y. N. & He, L. N. CO₂ chemistry: task-specific ionic liquids for CO₂ capture/activation and subsequent conversion. *RSC Adv.* **1**, 545–567 (2011).
52. Bates, E. D., Mayton, R. D., Ntai, I. & Davis, J. H. CO₂ capture by a task-specific ionic liquid. *J. Am. Chem. Soc.* **124**, 926–927 (2002).
53. Luo, X. et al. Significant improvements in CO₂ capture by pyridine-containing anion-functionalized ionic liquids through multiple-site cooperative interactions. *Angew. Chem. Int. Ed.* **53**, 7053–7057 (2014).
54. Medina-Ramos, J. et al. Structural dynamics and evolution of bismuth electrodes during electrochemical reduction of CO₂ in imidazolium-based ionic liquid solutions. *ACS Catal.* **7**, 7285–7295 (2017).
55. Zeng, Y., Zou, R. & Zhao, Y. Covalent organic frameworks for CO₂ capture. *Adv. Mater.* **28**, 2855–2873 (2016).
56. Johnson, E. M., Haiges, R. & Marinescu, S. C. Covalent–organic frameworks composed of rhenium bipyridine and metal porphyrins: designing heterobimetallic frameworks with two distinct metal sites. *ACS Appl. Mater. Interfaces* **10**, 37919–37927 (2018).
57. Su, P., Iwase, K., Harada, T., Kamiya, K. & Nakanishi, S. Covalent triazine framework modified with coordinatively-unsaturated Co or Ni atoms for CO₂ electrochemical reduction. *Chem. Sci.* **9**, 3941–3947 (2018).
58. Wu, Q. et al. Integration of strong electron transporter tetrathiafulvalene into metalloporphyrin-based covalent organic framework for highly efficient electroreduction of CO₂. *ACS Appl. Mater. Interfaces* **5**, 1005–1012 (2020).
59. Lin, S. et al. Covalent organic frameworks comprising cobalt porphyrins for catalytic CO₂ reduction in water. *Science* **349**, 1208–1213 (2015).
60. Lin, C. Y., Zhang, D., Zhao, Z. & Xia, Z. Covalent organic framework electrocatalysts for clean energy conversion. *Adv. Mater.* **30**, 170364 (2018).
61. Wang, Y., Chen, J., Wang, G., Li, Y. & Wen, Z. Perfluorinated covalent triazine framework derived hybrids for the highly selective electroconversion of carbon dioxide into methane. *Angew. Chem. Int. Ed.* **57**, 13120–13124 (2018).
62. Uribe-Romo, F. J. et al. A crystalline imine-linked 3-D porous covalent organic framework. *J. Am. Chem. Soc.* **131**, 4570–4571 (2009).

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Author contributions

C.X., H.A.A. and D.A.V. conceptualized and organized different levels of coupling between electrochemical CO₂ conversion with CO₂ capture in the manuscript. I.S. and A.G. contributed to writing and editing of the various approaches for coupling CO₂ capture with CO₂ conversion. I.A.D. and X.L. contributed to preparing the figures and references, as well as editing of the manuscript.

Competing interests

The authors declare no competing interests.

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