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Coupling electrochemical CO_2 conversion with CO_2 capture

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Electrochemical CO_2 conversion into fuels or chemicals and CO_2 capture from point or dilute sources are two important processes to address the gigaton challenges in reducing greenhouse gas emissions. Both CO_2 capture and electrochemical CO_2 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 CO_2 transport and storage or eliminating the capture media regeneration and molecular CO_2 release. We consider three different levels to couple electrochemical CO_2 reduction with CO_2 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 CO_2 capture and conversion mediated by covalent organic frameworks.

Electrochemical carbon dioxide reduction (CO_2R) 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 CO_2R 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 infrastructures[1]. 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 electrode[3]. Thus far, nearly all lab-scale electrochemical CO_2R demonstrations have used high-purity CO_2 gas cylinders to benchmark catalyst or device performances and eliminate the effects of dilute or impure carbon sources. The role of CO_2 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 CO_2 conversion process with the state-of-the-art CO_2 capture process.

To have an impact on climate change, electrochemical CO_2 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 changes[4]. Currently, this set of factors is disproportionate, leading to net emissions of 4.4 $GtCO_2\,yr^{-1}$ (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 CO_2 emissions are currently at approximately the 40 Gt level and to keep within the 2 °C goal set by the Paris agreement, approximately 10 $GtCO_2$ per year must be captured, with up to 160 $GtCO_2$ stored by 2050[8]. As a benchmark for capture, a recent study found that BECCS has the potential to sequester up to 5.2 $GtCO_2$ per year without large adverse impacts[7].

Large gaps still exist, especially at the demonstrated scale for CO_2 capture and electrochemical CO_2 conversion processes. Various capture technologies are currently being explored to reduce CO_2 emissions[9]. Traditional CO_2 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 source[10]. 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 CO_2 emission[11]. 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, CO_2 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 CO_2 (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 CO_2–bicarbonate–carbonate equilibrium towards gaseous CO_2 release or solid carbonate precipitation to achieve CO_2 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 CO_2 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 cm^2 to hundreds of cm^2, which is the typical size of commercial water electrolysis systems. Production at commercially relevant

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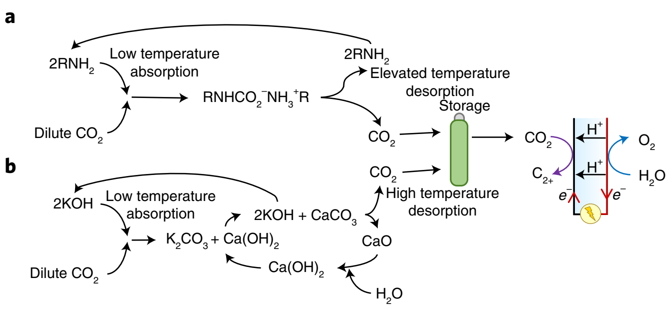

Fig. 1 | Type-I, independent electrochemical CO_2R and CO_2 capture processes. In Type-I-a, CO_2 is captured by an amine-based solution at low temperature, followed by amine regeneration and CO_2 release via temperature swings. In Type-I-b, CO_2 is captured by an alkaline solution to form carbonate species, and is then converted into $CaCO_3$ through the reaction with Ca(OH$_2$). A thermochemical process then releases CO_2 in a pure feed, which allows for use in CO_2R.

scales, even for the simplest two-electron reduction of CO_2 to CO, has yet to be demonstrated. Given that the scaling of electrochemical CO_2 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 CO_2 capture and conversion.

In this Perspective, we explore the synergistic coupling between CO_2 capture processes, especially from dilute sources, and electrochemical CO_2 conversion processes, in which the CO_2 transport and storage or the capture media regeneration and molecular CO_2-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 CO_2R and capture

Conceptually, we consider three different levels to couple electrochemical CO_2R with CO_2 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 CO_2 stored and utilized elsewhere. Minimal coupling between the two processes provides flexibility in varied approaches. The incompatibility in operating temperatures for electrochemical CO_2R, thermochemical CO_2 release and solvent regeneration requires the complete separation of the two processes. For example, Type-I-a shows amine regeneration via temperature swings[10], and Type-I-b shows regeneration of an alkaline solution, KOH(aq.), in multistep thermochemical processes[12]. A Type-II configuration involves coupling of the capture and conversion processes at a local level (Fig. 2). Here, molecular CO_2 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. CO_2 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 electrodialysis[23] (Type-II-c) and proton coupled electron transfer (PCET)-based CO_2 capture[24] (Type-II-d). The capture approaches described in the Type-II configuration all fall under the broad concept of electrochemical CO_2 capture, in which electrochemical potentials are applied to alter the nucleophilicity to mediate the capture and release of CO_2 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 CO_2 capture from dilute sources and anodic release of CO_2 into concentrated outputs. It is also important to note that CO_2 capture from sources that could contain air (DAC and point sources) may introduce O_2 to the cell, and possibly cause degradation of the capture solvents and competition between the oxygen reduction reaction and cathodic CO_2 capture. A Type-III approach bypasses the traditional release of CO_2 from the capture agent and instead involves the direct electroreduction of CO_2-loaded capture agents (Fig. 3). Here, electrochemical conversion of CO_2 into fuels or chemicals uses physisorbed or chemisorbed CO_2 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, CO_2 capture from sources that could contain air (DAC and point sources) may introduce O_2 to the cell, and possibly cause degradation of the capture solvents and competition between the oxygen reduction reaction and cathodic CO_2 capture or CO_2R. A major advantage of Type-III configurations is the formation of CO_2 adducts or carbamates, which result in a bent CO_2 configuration and so lower the overpotential needed for electrochemical conversion. These catalysts could further be optimized by changing the bond strength of the CO_2 binding site with additional functional groups, which results in lower energy penalties for bond formation and breaking, or selective product distributions during CO_2R.

CO_2 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 CO_2 from dilute sources, such as DAC, to give concentrated CO_2 at 1 bar. In comparison, electrochemical CO_2R, 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 CO_2 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 CO_2 capture are close to those of CO_2 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 CO_2 (ref. [11]). For CO_2 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 CO_2 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 CO_2 capture and conversion process, the regeneration of the capture media and the conversion of the CO_2 in the form of a CO_2–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 CO_2R 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 CO_2–adduct-rich local environment could be used to increase the local concentration of CO_2 at the electrode and lower the overpotential for CO_2R. 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 H_2 compression, tends to dominate the cost of the overall system; as a result, Type-III configurations with a single

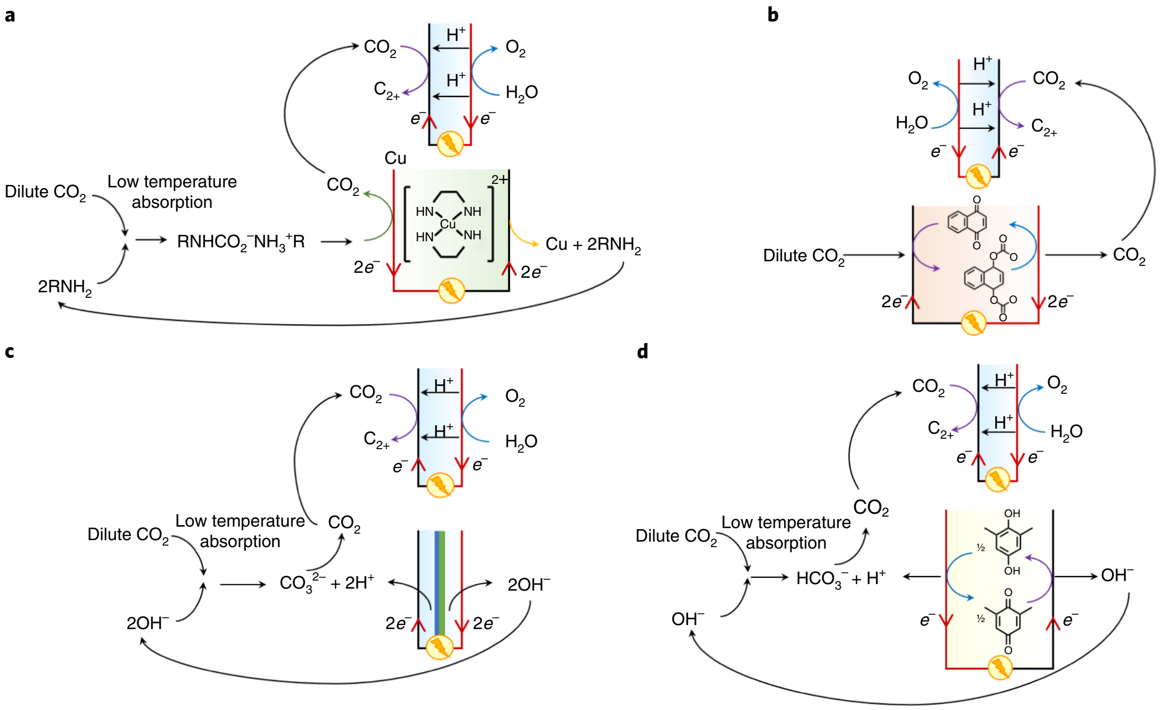

Fig. 2 | Type-II, subsequent stage electrochemical CO_2R and CO_2 capture processes. Technologies for local coupling include electrochemically mediated amine regeneration (Type-II-a), redox active carrier (Type-II-b), bipolar membrane-based electrodialysis (Type-II-c) and PCET-based CO_2 capture (Type-II-d). Type-II-a and b rely on anodic release of CO_2 through a redox mediator, whereas Type-II-c and d rely on the local generation and reaction of protons to release CO_2.

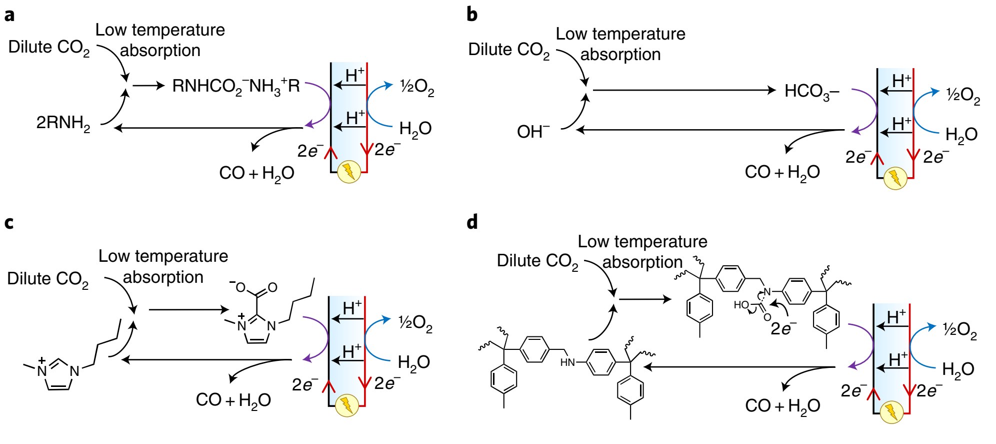

Fig. 3 | Type-III, fully integrated electrochemical CO_2R and CO_2 capture processes. Direct electroreduction of CO_2-loaded capture agents based on amines (Type-III-a), bicarbonates and/or carbonates (Type-III-b), ILs (Type-III-c) and COFs (Type-III-d). Type-III processes eliminate the capture media regeneration and molecular CO_2 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 CO_2R products.

To date, coupling between CO_2 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 CO_2 capture and utilization process from the overall cost point of view[43]. 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 CO_2 capture and conversion.

Amine-based media for CO_2 storage and direct carbamate reduction

CO_2 can be captured by nucleophilic reaction with diamines, alkanolamines and their derivatives to yield the corresponding carbamates. Depending on the application, CO_2 can be released via thermal or electrocatalytic routes, which results in amine regeneration. Electrochemically mediated amine regeneration cannot be readily coupled to electrochemical CO_2R at the same electrode due to the anodic release step[18,19]. However, using a separate electrode for CO_2R 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

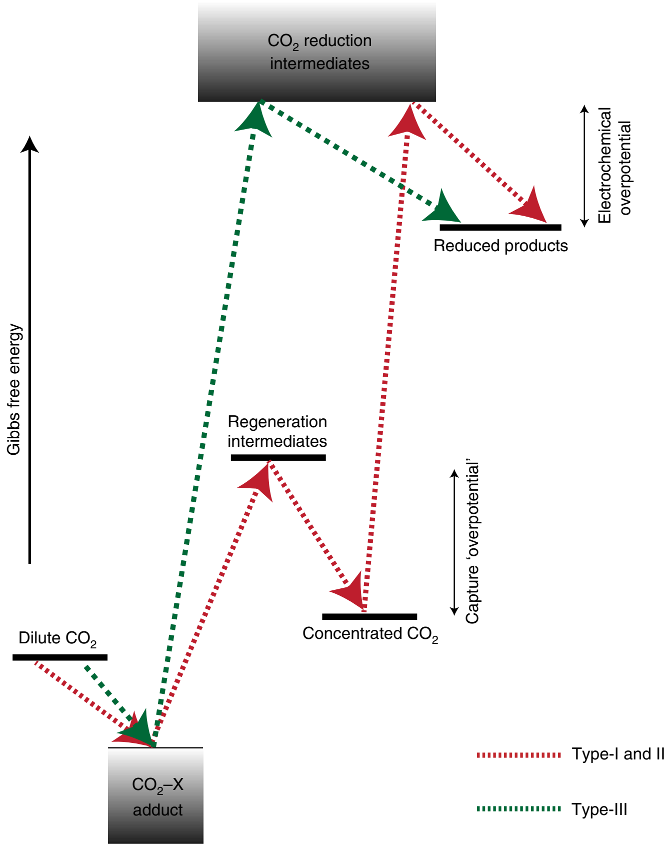

Fig. 4 | CO_2 capture and conversion energetics for Type-I and II (red) and Type-III (green). Dilute CO_2 can be captured through the formation of a CO_2–adduct species for all the routes; however, Type-I and II require an additional regeneration step to produce concentrated molecular CO_2, which can then be used for electrocatalysis. The Type-III configuration integrates the capture media regeneration with electrochemical CO_2R, 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 CO_2R 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 CO_2R via fine-tuning through, for example, the use of additives[29], a supporting electrolyte[28] and varying the amine structure[28]. 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 CO_2R, 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 CO_2R reaction because they show an improved CO_2 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 source[28]. Furthermore, the authors linked carbamate stability to CO_2R 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 cations[44].

Carbonate and bicarbonate in aqueous alkaline capture media

CO_2 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 CO_2R 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 CO_2–bicarbonate equilibrium and used molecular CO_2 as the reactant[45]. Recent work leveraged the local acidification and local generation of molecular CO_2 for CO_2R at the membrane–catalyst interfaces[36,37]. Type-II-c and Type-II-d illustrate the local acidification of (bi)carbonates for CO_2R via bipolar membrane-based electrodialysis and PCET, respectively. In this concept, in situ produced (bi)carbonate is circulated in a cathodic compartment of an electrochemical cell in which CO_2R 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 reaction[24]. As the result of catholyte acidification, CO_2 is released and eventually converted into target products at the cathode. Advantages of this approach include the local generation of CO_2, which could potentially break the CO_2 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 CO_2 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 CO_2 in contact with the bicarbonate solution. Water instead of protons would participate in the CO_2R reaction and produce OH^- locally at the electrode surface, which closes the carbon capture loop. Practically, the low solubility of CO_2 in this alkaline environment presents a challenge in sustaining the CO_2R 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 CO_2R surface before it reacts with bicarbonate.

Redox active carriers for coupled catalysis

Similar to amine-based CO_2 capture, other redox active carriers (for example, quinones and thiocarbonates) can be used to form adducts with CO_2 (refs. [20–22]). Unlike unhindered primary amines, bulk redox carriers cannot spontaneously form adducts with CO_2 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 CO_2 via nucleophilic addition (Type-II-b). Owing to the requirement of cathodic activation, the use of such species is typically limited to a multistep capture–release concept (Type-I or Type-II), as with amine scrubbing, in which the CO_2 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 CO_2 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 CO_2 capture, it is not intrinsically excluded either.

IL-mediated CO_2 capture and conversion

ILs have been investigated as carbon capture media due to their favourable physical and chemical properties for CO_2 absorption and allow for the combination of capture and conversion. ILs have high CO_2 absorption capabilities and are more selective for CO_2 than for other gases (that is, N_2 and O_2), have low vapour pressures, are thermally stable and are ionically conductive due to their charged species[46]. Their ionic compositions vary, but generally include imidazolium cations. ILs are promising candidates for CO_2 capture owing to their ability to specifically absorb and desorb CO_2. CO_2 can be released from conventional ILs by heating, purging with inert gases (such as Ar or N_2) or through pressure swings[47].

ILs can be separated into conventional and task-specific ionic liquids (TSILs). Each interacts differently with CO_2 and results in varying degrees of absorption. Conventional ILs physically absorb CO_2 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 CO_2 capture and conversion. A Type-III-c configuration, such as the reduction of the imidazolium–CO_2 adduct and regeneration of imidazolium, represents an opportunity for simultaneous CO_2 capture and electrochemical CO_2R. The binding of CO_2 in ILs is advantageous for electrocatalysis, as it bends the CO_2 molecule and allows for lower overpotentials for reduction[38,48]. Several studies reported an increased CO_2R 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 CO_2 uptake by the conventional imidazolium-based ILs, which becomes especially critical when dilute CO_2 sources are used from DAC or DOC processes. To improve the CO_2 capture uptake, TSILs with typically amine[51–53] functional groups that strongly interact with CO_2 were developed. The amine functional group strongly binds to CO_2 to form carbamates, which allows a CO_2 to IL molar ratio of 1:2 to be realized. Although these are promising characteristics, the direct CO_2R of carbamates in TSILs has yet to be demonstrated with functional catalysts.

Although there are several obvious advantages to using ILs for CO_2 capture and for electrochemical conversion, there are several issues to take into account. ILs can act as hydrogen evolution reaction suppressors during CO_2R 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 CO_2R 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 C_{2+} products. Considering the interactions of CO_2 with ILs, the heat of adsorption of carbamate formation in ILs is often higher than that for imidazolium adduct formation. CO_2 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 CO_2, but conventional ILs are favoured for electrocatalytic conversion.

COF-mediated CO_2 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 CO_2 capture[55]. Like metal organic frameworks, the high affinity between COFs and CO_2 can be leveraged for CO_2 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 CO_2 electrocatalysis, either decorated with a metal[56–58] or as a molecular catalyst[59–61].

Demonstrations of both CO_2 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 CO_2R reduction at a silver electrode[39]. Using the concerted electrochemical CO_2R at the silver electrode in the presence of COFs, a Type-III-d simultaneous CO_2 capture and electrochemical CO_2R can be realized. The sorption properties of COFs (and metal organic frameworks) could potentially alleviate the limitations posed by low CO_2 concentrations in air or water, and possibly allow an integrated DAC and CO_2 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 CO_2 capture[62]. 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 CO_2 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 CO_2, 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 CO_2R at the vicinity of the CO_2 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 CO_2 and flux matching the two processes in the Type-II approach. Meanwhile, Type-III configurations leverage the CO_2-rich capture agent to bypass energy-intensive steps for regeneration of the capture agent and the release of CO_2, 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 CO_2R in various CO_2-rich capture agents. To overcome the limited C_{2+} product distributions generally favoured in aqueous CO_2R, an alternative strategy can be found through producing CO at high Faradaic efficiencies from CO_2R and further conversion to higher-order products via Fisher–Tropsch type reactions. Additionally, coupling electrochemical CO_2R with dilute CO_2 capture from air or ocean water presents long-term opportunities for neutral or negative CO_2 emission. Ultimately, the realization of integrated CO_2 capture and conversion systems requires advancements in efficiency and scale for the CO_2R process, and also overcoming the limitations in chemical stability and compatibility for CO_2 capture technology.

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Author contributions

C.X., H.A.A. and D.A.V. conceptualized and organized different levels of coupling between electrochemical CO_2 conversion with CO_2 capture in the manuscript. I.S. and A.G. contributed to writing and editing of the various approaches for coupling CO_2 capture with CO_2 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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