

## Coupling electrochemical CO<sub>2</sub> conversion with CO<sub>2</sub> capture

Sullivan, Ian; Goryachev, Andrey; Digdaya, Ibadillah A.; Li, Xueqian; Atwater, Harry A.; Vermaas, David A.; Xiang, Chengxiang

**DOI**

[10.1038/s41929-021-00699-7](https://doi.org/10.1038/s41929-021-00699-7)

**Publication date**

2021

**Document Version**

Final published version

**Published in**

Nature Catalysis

**Citation (APA)**

Sullivan, I., Goryachev, A., Digdaya, I. A., Li, X., Atwater, H. A., Vermaas, D. A., & Xiang, C. (2021). Coupling electrochemical CO<sub>2</sub> conversion with CO<sub>2</sub> capture. *Nature Catalysis*, 4(11), 952-958. <https://doi.org/10.1038/s41929-021-00699-7>

**Important note**

To cite this publication, please use the final published version (if applicable). Please check the document version above.

**Copyright**

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

**Takedown policy**

Please contact us and provide details if you believe this document breaches copyrights. We will remove access to the work immediately and investigate your claim.



# Coupling electrochemical CO<sub>2</sub> conversion with CO<sub>2</sub> capture

Ian Sullivan<sup>1</sup>, Andrey Goryachev<sup>2</sup>, Ibadillah A. Digdaya<sup>1</sup>, Xueqian Li<sup>1</sup>, Harry A. Atwater<sup>1</sup>, David A. Vermaas<sup>2</sup> and Chengxiang Xiang<sup>1</sup>

**Electrochemical CO<sub>2</sub> conversion into fuels or chemicals and CO<sub>2</sub> capture from point or dilute sources are two important processes to address the gigaton challenges in reducing greenhouse gas emissions. Both CO<sub>2</sub> capture and electrochemical CO<sub>2</sub> 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<sub>2</sub> transport and storage or eliminating the capture media regeneration and molecular CO<sub>2</sub> release. We consider three different levels to couple electrochemical CO<sub>2</sub> reduction with CO<sub>2</sub> 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<sub>2</sub> capture and conversion mediated by covalent organic frameworks.**

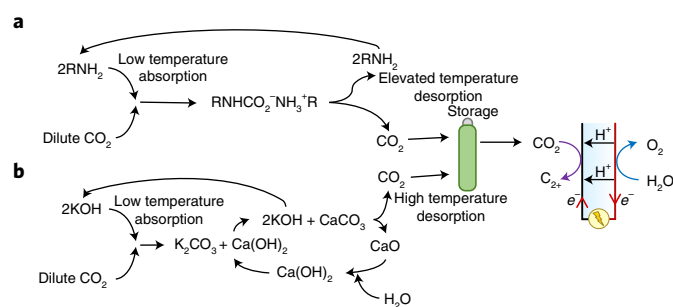
Electrochemical carbon dioxide reduction (CO<sub>2</sub>R) has made substantial advances in recent years. The selectivity, activity and durability of several multielectron and multiproton reactions has primed this technology for commercialization. Although the techno-economic viability of electrochemical CO<sub>2</sub>R 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<sup>1</sup>. In particular, electrochemical ethylene generation has reached an operating partial current density of 1.3 A cm<sup>-2</sup> and a Faradaic efficiency of 65–75% (ref. <sup>2</sup>). Additionally, electrochemical ethanol generation has reached a remarkable Faradaic efficiency of 91% at –0.7 V versus a reversible hydrogen electrode<sup>3</sup>. Thus far, nearly all lab-scale electrochemical CO<sub>2</sub>R demonstrations have used high-purity CO<sub>2</sub> gas cylinders to benchmark catalyst or device performances and eliminate the effects of dilute or impure carbon sources. The role of CO<sub>2</sub> 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<sub>2</sub> conversion process with the state-of-the-art CO<sub>2</sub> capture process.

To have an impact on climate change, electrochemical CO<sub>2</sub> 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<sup>4</sup>. Currently, this set of factors is disproportionate, leading to net emissions of 4.4 GtCO<sub>2</sub> yr<sup>-1</sup> (ref. <sup>4</sup>). 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<sup>5–7</sup>. Technologically driven processes include bioenergy with carbon capture and storage (BECCS), direct air capture (DAC) and direct ocean capture

(DOC)<sup>5–7</sup>. Worldwide energy-related CO<sub>2</sub> 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<sub>2</sub> per year must be captured, with up to 160 GtCO<sub>2</sub> stored by 2050<sup>8</sup>. As a benchmark for capture, a recent study found that BECCS has the potential to sequester up to 5.2 GtCO<sub>2</sub> per year without large adverse impacts<sup>7</sup>.

Large gaps still exist, especially at the demonstrated scale for CO<sub>2</sub> capture and electrochemical CO<sub>2</sub> conversion processes. Various capture technologies are currently being explored to reduce CO<sub>2</sub> emissions<sup>9</sup>. Traditional CO<sub>2</sub> 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<sup>-1</sup> from a single point source<sup>10</sup>. 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<sub>2</sub> emission<sup>11</sup>. 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<sub>2</sub> 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<sub>2</sub> (ref. <sup>12</sup>). The current largest DAC system is capable of capturing ~4,000 t yr<sup>-1</sup> (ref. <sup>13</sup>), with other future planned systems capable of up to 0.1 Gt yr<sup>-1</sup> (ref. <sup>9</sup>). For DOC, the operating principle is to shift the CO<sub>2</sub>–bicarbonate–carbonate equilibrium towards gaseous CO<sub>2</sub> release or solid carbonate precipitation to achieve CO<sub>2</sub> capture<sup>14,15</sup>. Although the demonstrated scale for DOC is currently low, <1 kg day<sup>-1</sup> (refs. <sup>14,15</sup>), the vast majority of lab-scale electrochemical or photoelectrochemical CO<sub>2</sub> conversion processes produce fuels at rates of <1 kg day<sup>-1</sup>. 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<sup>2</sup> to hundreds of cm<sup>2</sup>, which is the typical size of commercial water electrolysis systems. Production at commercially relevant

<sup>1</sup>Liquid Sunlight Alliance (LiSA) and Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA, USA. <sup>2</sup>Department of Chemical Engineering, Delft University of Technology, Delft, the Netherlands. ✉e-mail: [haa@caltech.edu](mailto:haa@caltech.edu); [D.A.Vermaas@tudelft.nl](mailto:D.A.Vermaas@tudelft.nl); [cxx@caltech.edu](mailto:cxx@caltech.edu)



**Fig. 1 | Type-I, independent electrochemical CO<sub>2</sub>R and CO<sub>2</sub> capture processes.** In Type-I-a, CO<sub>2</sub> is captured by an amine-based solution at low temperature, followed by amine regeneration and CO<sub>2</sub> release via temperature swings. In Type-I-b, CO<sub>2</sub> is captured by an alkaline solution to form carbonate species, and is then converted into CaCO<sub>3</sub> through the reaction with Ca(OH)<sub>2</sub>. A thermochemical process then releases CO<sub>2</sub> in a pure feed, which allows for use in CO<sub>2</sub>R.

scales, even for the simplest two-electron reduction of CO<sub>2</sub> to CO, has yet to be demonstrated. Given that the scaling of electrochemical CO<sub>2</sub> conversion is evolving rapidly<sup>16,17</sup>, and expected to grow to large-scale production in the next decade, we aim to reflect on the possibilities to match CO<sub>2</sub> capture and conversion.

In this Perspective, we explore the synergistic coupling between CO<sub>2</sub> capture processes, especially from dilute sources, and electrochemical CO<sub>2</sub> conversion processes, in which the CO<sub>2</sub> transport and storage or the capture media regeneration and molecular CO<sub>2</sub>-release step can be minimized or eliminated, to improve the energy efficiency of the system and lower the cost of the reduced products.

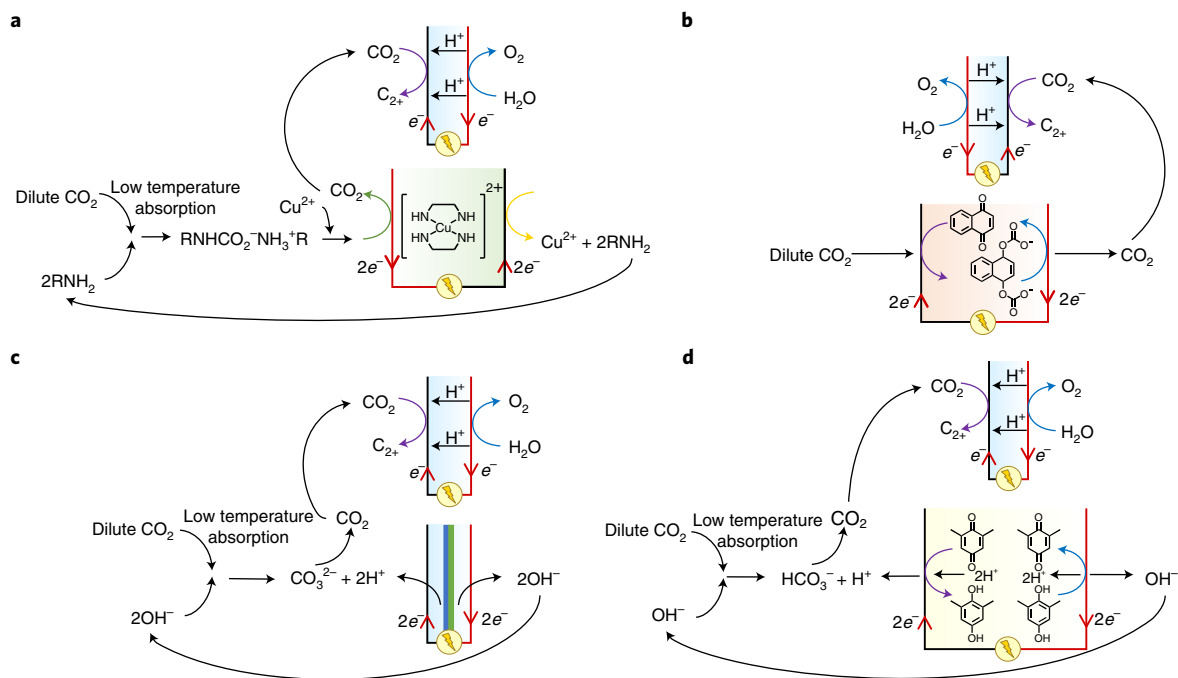
### Conceptual coupling between electrochemical CO<sub>2</sub>R and capture

Conceptually, we consider three different levels to couple electrochemical CO<sub>2</sub>R with CO<sub>2</sub> 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<sub>2</sub> stored and utilized elsewhere. Minimal coupling between the two processes provides flexibility in varied approaches. The incompatibility in operating temperatures for electrochemical CO<sub>2</sub>R, thermochemical CO<sub>2</sub> release and solvent regeneration requires the complete separation of the two processes. For example, Type-I-a shows amine regeneration via temperature swings<sup>10</sup>, and Type-I-b shows regeneration of an alkaline solution, KOH(aq.), in multistep thermochemical processes<sup>12</sup>. A Type-II configuration involves coupling of the capture and conversion processes at a local level (Fig. 2). Here, molecular CO<sub>2</sub> 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<sub>2</sub> capture technologies applicable for local coupling include electrochemically mediated amine regeneration<sup>18,19</sup> (Type-II-a), redox active carrier<sup>20–22</sup> (Type-II-b), bipolar membrane-based electro dialysis<sup>23</sup> (Type-II-c) and proton coupled electron transfer (PCET)-based CO<sub>2</sub> capture<sup>24</sup> (Type-II-d). The capture approaches described in the Type-II configuration all fall under the broad concept of electrochemical CO<sub>2</sub> capture, in which electrochemical potentials are applied to alter the nucleophilicity to mediate the capture and release of CO<sub>2</sub> from dilute sources to

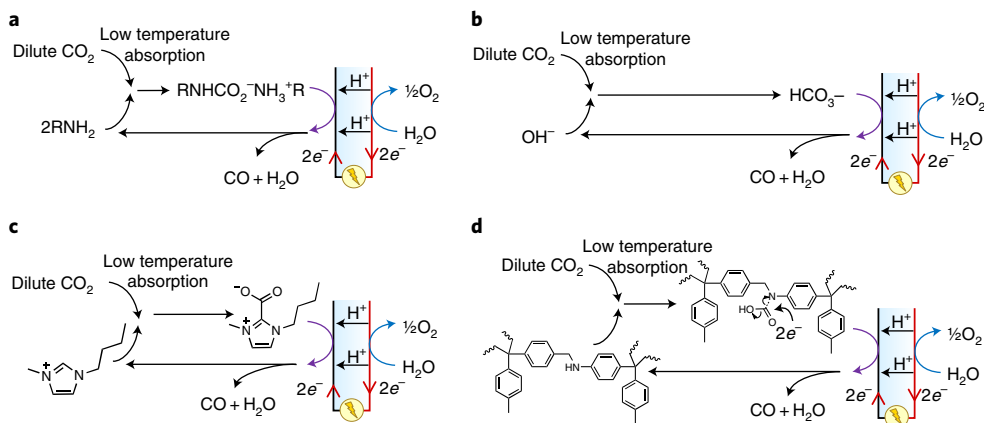
concentrated sources<sup>11,25–27</sup>. It is important to note that most electrochemical approaches involve cathodic activation of the capture media for CO<sub>2</sub> capture from dilute sources and anodic release of CO<sub>2</sub> into concentrated outputs. It is also important to note that CO<sub>2</sub> capture from sources that could contain air (DAC and point sources) may introduce O<sub>2</sub> to the cell, and possibly cause degradation of the capture solvents and competition between the oxygen reduction reaction and cathodic CO<sub>2</sub> capture. A Type-III approach bypasses the traditional release of CO<sub>2</sub> from the capture agent and instead involves the direct electroreduction of CO<sub>2</sub>-loaded capture agents (Fig. 3). Here, electrochemical conversion of CO<sub>2</sub> into fuels or chemicals uses physisorbed or chemisorbed CO<sub>2</sub> 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<sup>28–35</sup> (Type-III-a) and bicarbonate and/or carbonate based<sup>36,37</sup> (Type-III-b) agents, ionic liquids (ILs)<sup>38</sup> (Type-III-c) and covalent organic frameworks (COFs) (Type-III-d)<sup>39</sup>. For both Type-II and Type-III approaches, CO<sub>2</sub> capture from sources that could contain air (DAC and point sources) may introduce O<sub>2</sub> to the cell, and possibly cause degradation of the capture solvents and competition between the oxygen reduction reaction and cathodic CO<sub>2</sub> capture or CO<sub>2</sub>R. A major advantage of Type-III configurations is the formation of CO<sub>2</sub> adducts or carbamates, which result in a bent CO<sub>2</sub> configuration and so lower the overpotential needed for electrochemical conversion. These catalysts could further be optimized by changing the bond strength of the CO<sub>2</sub> binding site with additional functional groups, which results in lower energy penalties for bond formation and breaking, or selective product distributions during CO<sub>2</sub>R.

CO<sub>2</sub> 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<sup>-1</sup> is required to capture CO<sub>2</sub> from dilute sources, such as DAC, to give concentrated CO<sub>2</sub> at 1 bar. In comparison, electrochemical CO<sub>2</sub>R, 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<sub>2</sub> to CO electrochemically or photoelectrochemically requires a minimum voltage of 1.33 V, or 257 kJ mol<sup>-1</sup> at 25 °C, with typical realistic operations at ~3 V (579 kJ mol<sup>-1</sup>) (ref. 16). Practically, however, energy requirements for CO<sub>2</sub> capture are close to those of CO<sub>2</sub> conversion, with a large regeneration energy in the range of 100–300 kJ mol<sup>-1</sup> from either temperature or pressure swings, or from electrochemical energy to regenerate the capture media and release concentrated CO<sub>2</sub> (ref. 11). For CO<sub>2</sub> capture from point sources, such as synthetic flue gas, a lower energy consumption of <100 kJ mol<sup>-1</sup> has been achieved in various approaches<sup>40–42</sup>. The released CO<sub>2</sub> 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<sub>2</sub> capture and conversion process, the regeneration of the capture media and the conversion of the CO<sub>2</sub> in the form of a CO<sub>2</sub>-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<sub>2</sub>R 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<sub>2</sub>-adduct-rich local environment could be used to increase the local concentration of CO<sub>2</sub> at the electrode and lower the overpotential for CO<sub>2</sub>R. 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<sub>2</sub> 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<sub>2</sub>R and CO<sub>2</sub> 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 CO<sub>2</sub> capture (Type-II-d). Type-II-a and b rely on anodic release of CO<sub>2</sub> through a redox mediator, whereas Type-II-c and d rely on the local generation and reaction of protons to release CO<sub>2</sub>.



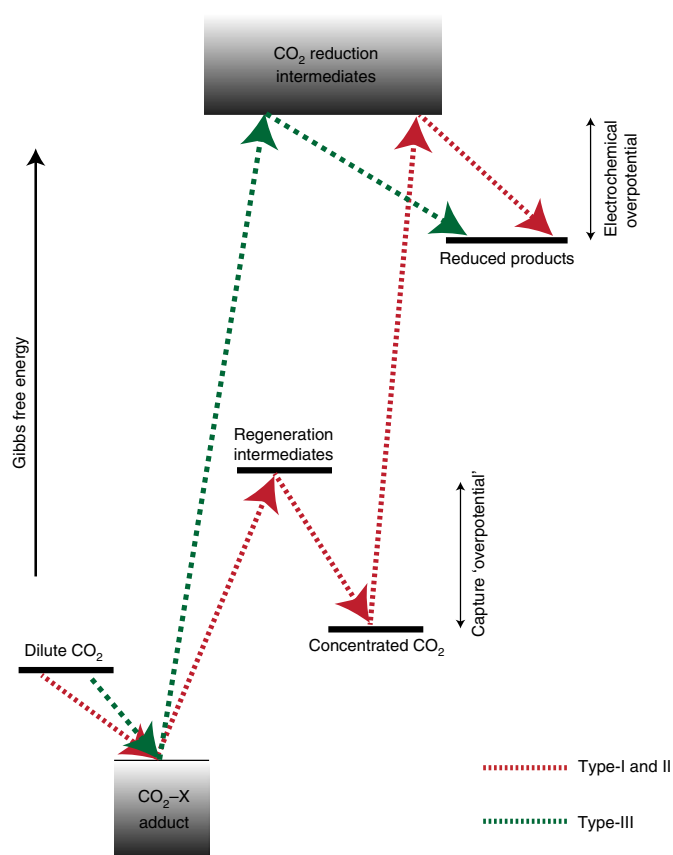
**Fig. 3 | Type-III, fully integrated electrochemical CO<sub>2</sub>R and CO<sub>2</sub> capture processes.** Direct electroreduction of CO<sub>2</sub>-loaded capture agents based on amines (Type-III-a), bicarbonates and/or carbonates (Type-III-b), ILs (Type-III-c) and COFs (Type-III-d). Type-III processes eliminate the capture media regeneration and molecular CO<sub>2</sub> 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<sub>2</sub>R products.

To date, coupling between CO<sub>2</sub> 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<sub>2</sub> capture and utilization process from the overall cost point of view<sup>43</sup>. 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<sub>2</sub> capture and conversion.

### Amine-based media for CO<sub>2</sub> storage and direct carbamate reduction

CO<sub>2</sub> can be captured by nucleophilic reaction with diamines, alkanolamines and their derivatives to yield the corresponding carbamates. Depending on the application, CO<sub>2</sub> can be released via thermal or electrocatalytic routes, which results in amine regeneration. Electrochemically mediated amine regeneration cannot be readily coupled to electrochemical CO<sub>2</sub>R at the same electrode due to the anodic release step<sup>18,19</sup>. However, using a separate electrode for CO<sub>2</sub>R 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<sub>2</sub> capture and conversion energetics for Type-I and II (red) and Type-III (green).** Dilute CO<sub>2</sub> can be captured through the formation of a CO<sub>2</sub>-adduct species for all the routes; however, Type-I and II require an additional regeneration step to produce concentrated molecular CO<sub>2</sub>, which can then be used for electrocatalysis. The Type-III configuration integrates the capture media regeneration with electrochemical CO<sub>2</sub>R, which results in an improved energy efficiency of the overall capture and conversion system.

cathode for a Type-III-a configuration<sup>28–35</sup>. Available reports suggest that amine addition drastically improves the CO<sub>2</sub>R current densities along with C1 selectivity<sup>34,35</sup>. 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<sub>2</sub>R via fine-tuning through, for example, the use of additives<sup>29</sup>, a supporting electrolyte<sup>28</sup> and varying the amine structure<sup>28</sup>. 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<sub>2</sub>R, 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<sub>2</sub>R reaction because they show an improved CO<sub>2</sub> uptake and promote electrolyte conductivity as compared with those of conventional (bi)carbonate solutions<sup>29,35</sup>. 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<sup>28</sup>. Furthermore, the authors linked carbamate stability to CO<sub>2</sub>R 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<sup>44</sup>.

### Carbonate and bicarbonate in aqueous alkaline capture media

CO<sub>2</sub> 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<sub>2</sub>R 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<sub>2</sub>-bicarbonate equilibrium and used molecular CO<sub>2</sub> as the reactant<sup>45</sup>. Recent work leveraged the local acidification and local generation of molecular CO<sub>2</sub> for CO<sub>2</sub>R at the membrane-catalyst interfaces<sup>36,37</sup>. Type-II-c and Type-II-d illustrate the local acidification of (bi)carbonates for CO<sub>2</sub>R 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 CO<sub>2</sub>R is expected<sup>36,37</sup> (Fig. 2c,d). In parallel, a H<sup>+</sup> flux is produced at an ion-exchange membrane via an applied potential bias or a PCET reaction<sup>24</sup>. As the result of catholyte acidification, CO<sub>2</sub> is released and eventually converted into target products at the cathode. Advantages of this approach include the local generation of CO<sub>2</sub>, which could potentially break the CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> in contact with the bicarbonate solution. Water instead of protons would participate in the CO<sub>2</sub>R reaction and produce OH<sup>-</sup> locally at the electrode surface, which closes the carbon capture loop. Practically, the low solubility of CO<sub>2</sub> in this alkaline environment presents a challenge in sustaining the CO<sub>2</sub>R at a reasonable rate. Hence, to obtain a cyclic process for a Type-III configuration, the challenge lies in removing the produced OH<sup>-</sup> from the CO<sub>2</sub>R surface before it reacts with bicarbonate.

### Redox active carriers for coupled catalysis

Similar to amine-based CO<sub>2</sub> capture, other redox active carriers (for example, quinones and thiocarbonates) can be used to form adducts with CO<sub>2</sub> (refs. 20–22). Unlike unhindered primary amines, bulk redox carriers cannot spontaneously form adducts with CO<sub>2</sub> 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<sub>2</sub> 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 CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> capture, it is not intrinsically excluded either.

### IL-mediated CO<sub>2</sub> capture and conversion

ILs have been investigated as carbon capture media due to their favourable physical and chemical properties for CO<sub>2</sub> absorption and allow for the combination of capture and conversion. ILs have high CO<sub>2</sub> absorption capabilities and are more selective for CO<sub>2</sub> than



for other gases (that is, N<sub>2</sub> and O<sub>2</sub>), have low vapour pressures, are thermally stable and are ionically conductive due to their charged species<sup>46</sup>. Their ionic compositions vary, but generally include imidazolium cations. ILs are promising candidates for CO<sub>2</sub> capture owing to their ability to specifically absorb and desorb CO<sub>2</sub>. CO<sub>2</sub> can be released from conventional ILs by heating, purging with inert gases (such as Ar or N<sub>2</sub>) or through pressure swings<sup>47</sup>.

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

Although there are several obvious advantages to using ILs for CO<sub>2</sub> capture and for electrochemical conversion, there are several issues to take into account. ILs can act as hydrogen evolution reaction suppressors during CO<sub>2</sub>R and stabilize intermediates, but stability of the cation group, and in some instances electrode restructuring, was found to be an issue during electrocatalysis<sup>49,54</sup>. However, several groups have studied ILs for CO<sub>2</sub>R 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<sub>2+</sub> products. Considering the interactions of CO<sub>2</sub> with ILs, the heat of adsorption of carbamate formation in ILs is often higher than that for imidazolium adduct formation. CO<sub>2</sub> 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<sub>2</sub>, but conventional ILs are favoured for electrocatalytic conversion.

### COF-mediated CO<sub>2</sub> 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<sub>2</sub> capture<sup>55</sup>. Like metal organic frameworks, the high affinity between COFs and CO<sub>2</sub> can be leveraged for CO<sub>2</sub> 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<sub>2</sub> electrocatalysis, either decorated with a metal<sup>56–58</sup> or as a molecular catalyst<sup>59–61</sup>.

Demonstrations of both CO<sub>2</sub> 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<sub>2</sub>R reduction at a silver electrode<sup>39</sup>. Using the concerted electrochemical CO<sub>2</sub>R at the silver electrode in the presence of COFs, a Type-III-d simultaneous CO<sub>2</sub> capture and electrochemical CO<sub>2</sub>R can be realized. The sorption

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

Received: 19 May 2021; Accepted: 6 October 2021;  
Published online: 18 November 2021

### References

- Jouny, M., Luc, W. & Jiao, F. General techno-economic analysis of CO<sub>2</sub> electrolysis systems. *Ind. Eng. Chem. Res.* **57**, 2165–2177 (2018).
- García de Arquer, F. P. et al. CO<sub>2</sub> electrolysis to multicarbon products at activities greater than 1 A cm<sup>-2</sup>. *Science* **367**, 661–666 (2020).
- Xu, H. et al. Highly selective electrocatalytic CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> from oceanwater. *Nat. Commun.* **11**, 4412 (2020).
15. Eisaman, M. D. et al. CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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. Filotás, D., Nagy, T., Nagy, L., Mizsey, P. & Nagy, G. Extended investigation of electrochemical CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>. *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 CO<sub>2</sub> 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 CO<sub>2</sub> at coinage metal nanodendrites in aqueous ethanolamine. *Chem. Eur. J.* **27**, 1346–1355 (2021).
36. Li, Y. C. et al. CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>. *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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> capture and conversion to methyl formate using methanol. *ACS Sustain. Chem. Eng.* **7**, 12270–12280 (2019).
44. Lee, G. et al. Electrochemical upgrade of CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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. CO<sub>2</sub> chemistry: task-specific ionic liquids for CO<sub>2</sub> capture/activation and subsequent conversion. *RSC Adv.* **1**, 545–567 (2011).
52. Bates, E. D., Mayton, R. D., Ntai, I. & Davis, J. H. CO<sub>2</sub> capture by a task-specific ionic liquid. *J. Am. Chem. Soc.* **124**, 926–927 (2002).
53. Luo, X. et al. Significant improvements in CO<sub>2</sub> 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 CO<sub>2</sub> in imidazolium-based ionic liquid solutions. *ACS Catal.* **7**, 7285–7295 (2017).
55. Zeng, Y., Zou, R. & Zhao, Y. Covalent organic frameworks for CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>. *ACS Appl. Mater. Interfaces* **5**, 1005–1012 (2020).
59. Lin, S. et al. Covalent organic frameworks comprising cobalt porphyrins for catalytic CO<sub>2</sub> 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).

## Acknowledgements

This material is based on work performed by the Liquid Sunlight Alliance, which is supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, and Fuels from Sunlight Hub under award no. DE-SC0021266. We also acknowledge the support from SoCalGas on the analysis of CO<sub>2</sub> capture processes under award no. 5660060287. This research received funding from the Netherlands Organization for Scientific Research (NWO) under project no. 733.000.008 in the framework of the Solar to Products programme co-funded by Shell Global Solutions International B.V., and from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement no. 852115).

**Author contributions**

C.X., H.A.A. and D.A.V. conceptualized and organized different levels of coupling between electrochemical CO<sub>2</sub> conversion with CO<sub>2</sub> capture in the manuscript. I.S. and A.G. contributed to writing and editing of the various approaches for coupling CO<sub>2</sub> capture with CO<sub>2</sub> 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.

**Additional information**

**Correspondence** should be addressed to Harry A. Atwater, David A. Vermaas or Chengxiang Xiang.

**Peer review information** *Nature Catalysis* thanks Caroline Saouma and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.

**Reprints and permissions information** is available at [www.nature.com/reprints](http://www.nature.com/reprints).

**Publisher's note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© Springer Nature Limited 2021