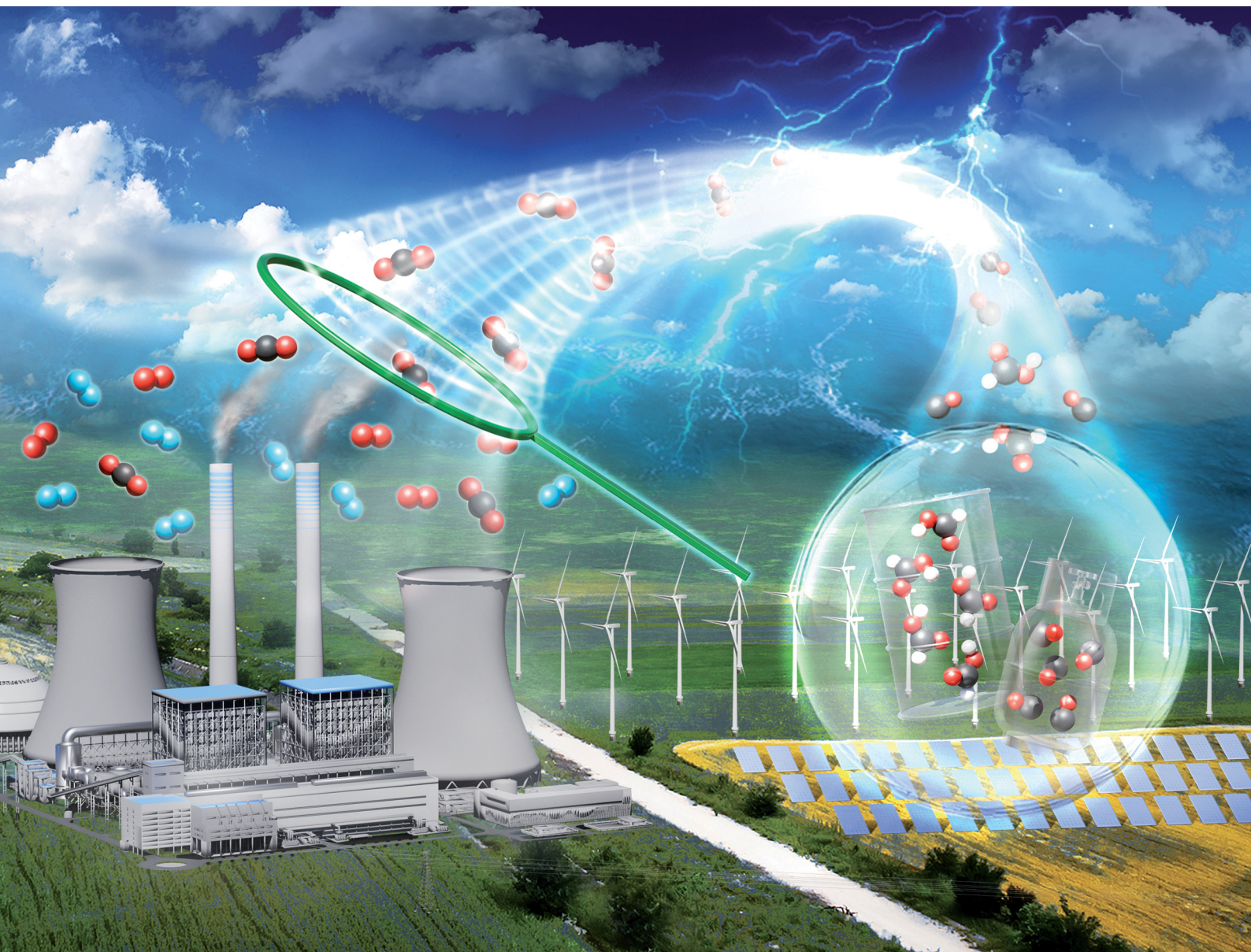


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## REVIEW ARTICLE

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Electrochemical valorization of captured CO<sub>2</sub>: recent  
advances and future perspectives



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# Electrochemical valorization of captured CO<sub>2</sub>: recent advances and future perspectives†

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The excessive emission of CO<sub>2</sub> has led to severe climate change, prompting global concern. Capturing CO<sub>2</sub> and converting it through electrochemistry into value-added products represent promising approaches to mitigating CO<sub>2</sub> emissions and closing the carbon cycle. Traditionally, these two processes have been performed independently, involving multiple steps, high energy consumption, and low efficiency. Recently, the electrochemical conversion of captured CO<sub>2</sub>, which integrates the capture and conversion processes (also referred to as electrochemically reactive CO<sub>2</sub> capture), has garnered increasing attention. This integrated approach bypasses the energy-intensive steps involved in the traditional independent process, including CO<sub>2</sub> release, purification, compression, transportation, and storage. In this review, we discuss recent advances in the electrochemical conversion of captured CO<sub>2</sub>, focusing on four key aspects. First, we introduce various capture media, emphasizing the thermodynamic aspects of carbon capture and their implications for integration with electrochemical conversion. Second, we discuss product control mediated by the selection of different catalysts, highlighting the connections between the conversion of captured CO<sub>2</sub> and gas-fed CO<sub>2</sub>. Third, we examine the effect of reactor systems and operational conditions on the electrochemical conversion of captured CO<sub>2</sub>, shedding light on performance optimization. Finally, we explore real integration systems for CO<sub>2</sub> capture and electrochemical conversion, revealing the potential of this new technology for practical applications. Overall, we provide insights into the existing challenges, potential solutions, and thoughts on opportunities and future directions in the emerging field of electrochemical conversion of captured CO<sub>2</sub>.

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## 1. Introduction

The excessive emission of CO<sub>2</sub>, the primary anthropogenic greenhouse gas, has caused severe climate change, presenting one of the most urgent global challenges.<sup>1,2</sup> The amount of CO<sub>2</sub> released into the atmosphere due to human-related activities is massive, with emissions of ~35 Gt CO<sub>2</sub> just in 2021.<sup>3</sup> For this

reason, atmospheric CO<sub>2</sub> levels have surged from 280 ppm before the Industrial Revolution to 420 ppm.<sup>4</sup> Consequently, global temperatures have risen by ~1 °C compared to pre-industrial times, with projections indicating a potential increase exceeding 2 °C by the end of this century if CO<sub>2</sub> emissions remain unchecked.<sup>4,5</sup> Climate change has already resulted in severe events on earth, including glacier retreats, sea level elevation, extreme weather events, and ecosystem degradation.

Carbon capture, utilization, and storage (CCUS) technologies have been developed rapidly over the past decades to mitigate CO<sub>2</sub> emissions and reduce atmospheric CO<sub>2</sub> concentration.<sup>6,7</sup> CCUS typically involves multiple steps, including CO<sub>2</sub> capture from flue gas by amine or other alkaline solutions/materials, release of the captured CO<sub>2</sub> by temperature or pressure swings, followed by CO<sub>2</sub> purification, compression, and transportation before it is finally stored or utilized.<sup>8</sup> The long-term storage of CO<sub>2</sub> is mainly implemented by mineral carbonation, along with oceanic and underground geological storage.<sup>9</sup> However, CO<sub>2</sub> can also be utilized directly in food preservation and production, as well as in industrial

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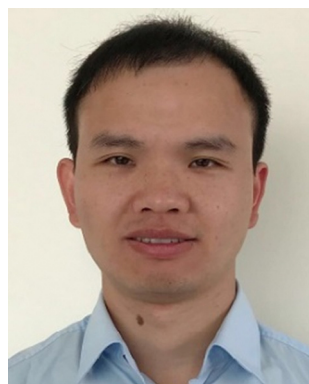
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processes,<sup>10</sup> or indirectly by conversion into various value-added products and fuels through thermochemical,<sup>11,12</sup> photochemical,<sup>13–15</sup> biochemical,<sup>16</sup> and electrochemical techniques.<sup>17</sup> Among these techniques, electrochemical conversion of CO<sub>2</sub> stands out due to several advantages such as mild reaction conditions, environmental friendliness, use of renewable electricity, and controllable reaction rate and product selectivity.<sup>18</sup> In particular, gas diffusion electrodes and flow cell configurations have been effectively utilized to boost the productivity of electrochemical CO<sub>2</sub> reduction at industrial-relevant current densities (>200 mA cm<sup>-2</sup>).<sup>19,20</sup>

To date, the CO<sub>2</sub> capture from diluted sources (0.04–15%) and the follow-up electrochemical conversion have been operated in three distinct routes, *i.e.*, (1) independent, (2) coupled, and (3) integrated (Fig. 1).<sup>21,22</sup> Route 1 involves multiple decoupled processes, where CO<sub>2</sub> capture occurs independently of electrochemical CO<sub>2</sub> conversion. Route 2 entails CO<sub>2</sub> capture and release stages, immediately followed by the electrochemical valorization of the released CO<sub>2</sub>. Route 3 exhibits complete integration between the capture and electrochemical conversion of CO<sub>2</sub>, bypassing the CO<sub>2</sub> stripping step required in Routes 1 and 2. For all three routes, producing value-added



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*and was appointed Professor in 2010. His research expertise spans electrochemistry, polymer brushes, responsive polymers, smart hybrid materials, and composites incorporating carbon substrates such as graphene. In recent years, he has leveraged his combined expertise in these fields to tackle the scientifically complex and socially important challenge of converting carbon dioxide, a key greenhouse gas, into valuable building blocks for the chemical industry and energy sector.*

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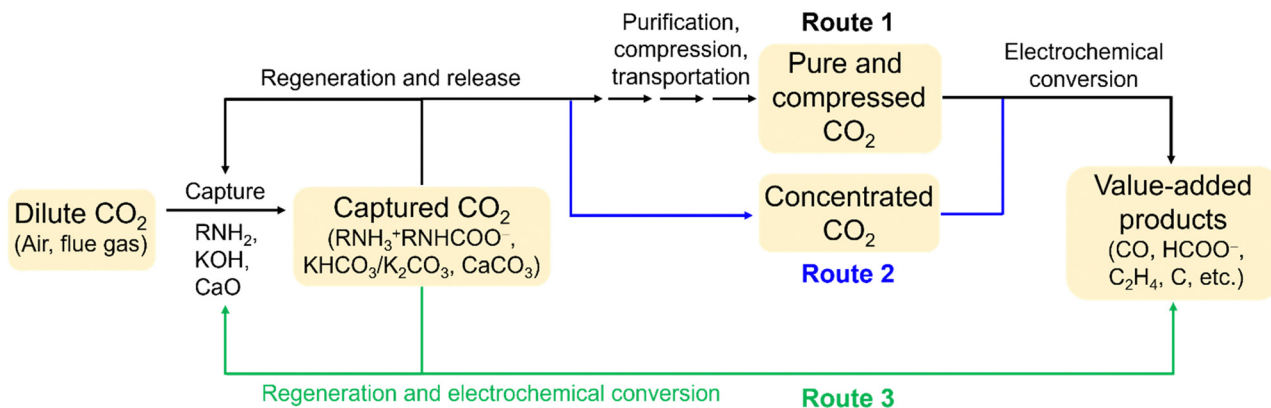


Fig. 1 Three routes for CO<sub>2</sub> capture and electrochemical conversion: (1) independent, (2) coupled, and (3) integrated.

chemicals and fuels helps offset capture expenses, rendering commercial deployment economically more feasible.

### 1.1. Route 1 (independent)

The independent systems inherently incur energy penalties and costs associated with CO<sub>2</sub> release, purification, compression, and transportation. In particular, the CO<sub>2</sub> desorption step can be energy-intensive if thermal regeneration at high temperatures is required. Nevertheless, Route 1 configuration can emerge as a viable scenario, considering the potential incompatibility in operating conditions between capture technologies that utilize temperature or pressure swings and the electrochemical conversion of CO<sub>2</sub> under ambient conditions. This configuration offers flexibility for independently optimizing the capture and conversion stages. However, it is important to note that standalone electrochemical systems using gas-fed CO<sub>2</sub> often face a significant challenge due to the typically low single-pass CO<sub>2</sub> conversion efficiency (<20%).<sup>23–25</sup> Consequently, this leads to low product concentration and significantly escalates downstream separation/purification costs.<sup>26,27</sup>

### 1.2. Route 2 (coupled)

An advantage of the coupled CO<sub>2</sub> capture and conversion system is that it bypasses the CO<sub>2</sub> purification, compression, and transportation steps, thereby reducing the complexity and energy consumption of the overall process. Here, the CO<sub>2</sub> for the downstream conversion is directly supplied by the upstream CO<sub>2</sub> capture unit, which usually releases CO<sub>2</sub> by electrochemically driven redox couples or pH swings.<sup>28,29</sup> Note that the coupled cascade system still involves independent CO<sub>2</sub> capture and conversion, as well as the energy-intensive CO<sub>2</sub> release step. Accordingly, the problem of low single-pass conversion efficiency for CO<sub>2</sub> exists. In addition, by enhancing the overlap between the capture and conversion steps, fewer degrees of freedom are available for optimizing the electrocatalysts toward higher activity and selectivity for a targeted CO<sub>2</sub> reduction product.

### 1.3. Route 3 (integrated/reactive capture)

Compared with Route 2, these systems offer the advantage of reducing the total energy requirements for capture and

conversion by eliminating CO<sub>2</sub> release and many other follow-up steps, which typically incur a significant energy penalty. By directly converting the captured CO<sub>2</sub> at the electrode surface, the regeneration of the capture media and the production of valuable products occur simultaneously. In this sense, Route 3 integrates the two processes of CO<sub>2</sub> capture and follow-up electrochemical conversion and has also been coined electrochemically reactive capture of CO<sub>2</sub>.<sup>30–32</sup>

As a result, Route 3 represents a more straightforward and sustainable approach for CCUS than the other two routes, at least at first glance. This unique advantage has stimulated increasing activities in the study of direct electrochemical valorization of captured CO<sub>2</sub> in the past several years. For instance, several reaction media, such as amine/carbamate solution, hydroxide/carbonate/bicarbonate solution, and molten oxide/carbonate, have proven effective in mediating CO<sub>2</sub> capture and subsequent electrochemical conversion. This offers the opportunity to directly transform CO<sub>2</sub> from flue gas or the air into valuable products such as carbon monoxide, formate, methane, and ethylene. Despite the significant advances and great prospects, several critical challenges still need to be addressed to advance such an emerging technology for large-scale applications.

These challenges lie in the unclear mechanism and low efficiency of the conversion of captured CO<sub>2</sub>, poor integration of CO<sub>2</sub> capture and conversion processes, and others. In this context, a timely and thorough review article summarizing the progress and discussing the challenges in this emerging field would benefit the community.

In this review, we summarize the recent advances in the strategy of reactive CO<sub>2</sub> capture, with a specific focus on the electrochemical conversion of captured CO<sub>2</sub>. Techno-economic analyses comparing the three different routes for CO<sub>2</sub> capture and conversion can be found in recent reviews and are thus not covered in this paper.<sup>30,33</sup> Moreover, readers with interests in related topics such as electrochemical CO<sub>2</sub> capture<sup>34,35</sup> and electrochemical CO<sub>2</sub> conversion<sup>36</sup> are referred to the respective reviews.

This review is structured around four aspects of the technology: capture media, electrocatalysts, system optimization, and practical considerations for continuous operation (Fig. 2). We



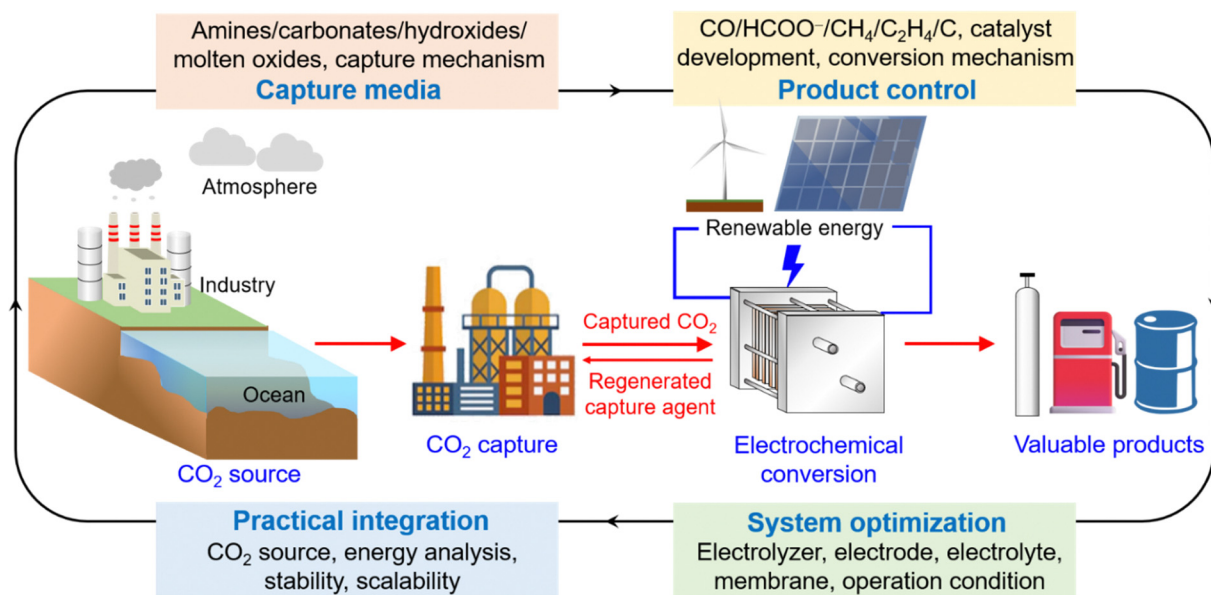


Fig. 2 Themes covered in this review on the electrochemical conversion of captured CO<sub>2</sub>.

start by introducing various types of capture media, emphasizing the thermodynamic aspects of carbon capture and their implications for integrated Route 3 processes. We move on to examine different electrocatalyst compositions and morphologies, discussing their influence on product distribution from the conversion of captured CO<sub>2</sub> and its relationship with the conversion of gas-fed CO<sub>2</sub>. Next, we explore the effects of reactor systems and operational conditions on the electrochemical conversion of captured CO<sub>2</sub>, aiming to dissect the key factors determining the conversion performance. Finally, we present examples of integrated CO<sub>2</sub> capture and conversion processes. Furthermore, we offer insights into the challenges and potential solutions and present our perspectives on the opportunities and future directions for integrating CO<sub>2</sub> capture and electrochemical conversion. This exploration uncovers promising avenues for practical applications of this emerging field in achieving more sustainable CO<sub>2</sub> capture and conversion, potentially contributing to mitigating global climate change.

## 2. Properties of capture media

The electrochemical conversion of captured CO<sub>2</sub> from diluted sources marks a significant advancement in the field of CCUS. Historically, CO<sub>2</sub> capture and subsequent electrochemical valorization were treated as separate research domains. The electrochemical valorization has primarily focused on novel electrocatalyst development, electrolyte selection, cell configuration engineering, and using gas-fed concentrated CO<sub>2</sub> without considering the carbon source (Routes 1 and 2 in Fig. 1). However, the emergence of highly efficient electrochemical systems for CO<sub>2</sub> reduction over the past decade has reshaped the field.<sup>37,38</sup> Consequently, the CO<sub>2</sub> capture step and the

conversion of resulting captured CO<sub>2</sub> have begun to be integrated to optimize the system (Route 3 in Fig. 1). This section explores the various capture media wherein the captured CO<sub>2</sub> can be utilized for electrochemical conversion, encompassing aqueous amines, alkaline solutions, and molten oxides. In this section, our focus is directed toward the underlying mechanisms of carbon capture and the thermodynamic aspects of chemical CO<sub>2</sub> sorption.

### 2.1. Amine solutions

The fundamental process of CO<sub>2</sub> removal from a gas stream leveraging its reversible binding with amines was discovered in 1930.<sup>39</sup> Initially utilized to separate CO<sub>2</sub> from natural gas and hydrogen, such a chemical reactivity has since been employed in amine scrubbing for post-combustion capture of CO<sub>2</sub> on small-scale gas and coal-fired plants.<sup>40</sup> Currently, amine scrubbing is the most cost-effective and widely used technology for CO<sub>2</sub> capture from industrial flue gases in power plants, oil refineries, cement production, and other applications. This is due to the high absorption rate and large CO<sub>2</sub> capacity of amines. For example, NRG Energy Inc. and JX Nippon Oil & Gas Exploration Corp. have launched a post-combustion carbon capture project called Petra Nova, which aims to remove over 90% of the CO<sub>2</sub> from the flue gas of a coal-fired power plant in Texas, USA using an amine solution.<sup>41</sup> However, it is important to note that the high temperatures in flue gas environments can lead to amine losses due to thermal degradation and evaporation. Furthermore, the presence of poisoning gases such as SO<sub>x</sub> and NO<sub>x</sub> can decrease the yield of captured CO<sub>2</sub>. While amine scrubbing is often hailed as the most cost-effective post-combustion CO<sub>2</sub> capture technology, it remains relatively expensive in terms of scalability. Therefore, ongoing research endeavors aim to enhance amine scrubbing processes, address their limitations, and optimize efficiency.





The capture of CO<sub>2</sub> using amine-based technologies involves two primary steps: absorption of CO<sub>2</sub> and CO<sub>2</sub>-stripping for amine regeneration. The process is initiated by directing a CO<sub>2</sub>-diluted gas stream at or near ambient temperature through the amine solution. During this phase, CO<sub>2</sub> is captured *via* a thermodynamically favorable reaction with the amine, yielding carbamate and ammonium ions (eqn (1)). Amines generally display high values of absorption enthalpies ( $\Delta H_{\text{abs}}$ ), ranging from  $-90$  to  $-60$  kJ mol<sup>-1</sup> when flue gas (12–15% CO<sub>2</sub> concentration) is employed.<sup>42</sup> Subsequently, the amine undergoes regeneration through stripping with water vapor at temperatures ranging from 100–120 °C, which shifts the equilibrium in eqn (1) toward the reactants. Following this, water is condensed from the stripper vapor, leaving behind pure CO<sub>2</sub>. The main energy demand in the process comes from stripping CO<sub>2</sub> from the CO<sub>2</sub>-rich amine stream, which requires 115–140 kJ mol-CO<sub>2</sub><sup>-1</sup>. This step consumes more energy than is released during the absorption phase because it produces a higher-purity CO<sub>2</sub> stream than the original flue gas. Thus, the critical thermodynamic parameters governing the amine scrubbing process revolve around the chemical interaction between the amine and CO<sub>2</sub>.



Different strategies have been employed to balance the efficiency of the chemical absorption step and the total energy consumption for the amine regeneration. Predictably, enhancing the chemical interaction between CO<sub>2</sub> and the amine to improve absorption rates leads to increased energy input required to break the C–N bond of the carbamate group during amine regeneration, which is translated to the use of higher temperatures during the stripping step. For instance, primary and secondary amines display a very high heat of absorption since they can quickly generate chemically stable carbamates during their reaction with CO<sub>2</sub>.<sup>43</sup> However, their regeneration energy requirement is high. In contrast, tertiary amines have a low heat of absorption and need less regeneration energy for solvent recovery, as bicarbonate, instead of carbamate, is formed for CO<sub>2</sub> capture with tertiary amines.

The most commonly used amine-based capture medium is a 30 wt% aqueous monoethanolamine solution, valued for its high CO<sub>2</sub> absorption rate, large absorption volume, and low cost.<sup>44</sup> Other frequently employed amines include diethanolamine and methyldiethanolamine, which are examples of secondary and tertiary amines, respectively. Although these aqueous amine solutions are widely used for CO<sub>2</sub> absorption, they have drawbacks, such as amine loss and thermal decomposition. A reported strategy to overcome such issues is mixing monoethanolamine with other secondary or tertiary amines with low energy consumption for regeneration.<sup>45</sup> This results in a mixture in the absorber unit that simultaneously displays high absorption capacity, high absorption rate, and low regeneration energy consumption. For instance, a 2:1 mixture of monoethanolamine and diethylenetriamine has been reported to increase CO<sub>2</sub> absorption capacity by 53% and removal

efficiency by 31% with respect to the commonly used 30 wt% monoethanolamine aqueous solution.<sup>46</sup>

Since 2010, amine scrubbing has been successfully applied to capture CO<sub>2</sub> from natural gas, hydrogen, and other gases with low oxygen content.<sup>40</sup> For instance, aqueous monoethanolamine solution can capture CO<sub>2</sub> from flue gas of coal-fired plants.<sup>47</sup> Unfortunately, it has displayed oxidative and thermal degradation under these conditions. When the oxygen content in the gas stream is in the range of 15%, a more concentrated amine solution (30 wt%) is required to increase the rate of CO<sub>2</sub> capture, which is inhibited by the oxidation of the amine in the presence of oxygen. Additionally, thermal degradation has been minimized by operating at lower temperatures (100 °C).<sup>48</sup>

Stern *et al.* proposed in 2013 an alternative process that uses an electrochemical swing based on Cu<sup>2+</sup>/Cu to strip CO<sub>2</sub> from the carbamate adduct and regenerate the amine.<sup>49</sup> The electrochemically mediated amine regeneration (EMAR) cycle leverages the high stability of the Cu<sup>2+</sup>–amine complexes compared to the carbamate, thus favoring the dissociation of CO<sub>2</sub> from the latter. Formation constants of cupric amine complexes exhibit values of 10<sup>18</sup> for polyamines such as ethylenediamine, while binding constants between amines and CO<sub>2</sub> typically fall in the order of  $\sim 10^3$ .<sup>50</sup>

Currently, the EMAR technology has potential for large-scale applications in systems following Route 2 in Fig. 1. One of its most notable advantages is its ability to achieve high amine utilization, reducing the capital costs for auxiliary equipment due to lower circulation rates.<sup>51</sup> Additionally, the EMAR technology requires less energy input since the capture and strip of CO<sub>2</sub> are performed at room temperature. Since the process requires only electrical energy, decentralized devices can be developed at point sources to capture and convert CO<sub>2</sub> as needed.

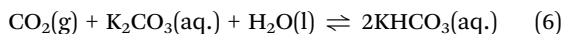
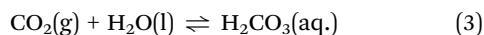
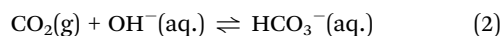
## 2.2. Aqueous alkaline solutions

CO<sub>2</sub> capture in many industrial processes has been successfully performed using inorganic salt solutions of various weak acids.<sup>52</sup> The most commonly employed salts are sodium and potassium carbonate, which, due to their alkaline pH (typically 9–11), absorb acid gases such as CO<sub>2</sub>. For instance, the traditional Benfield process, which has been in use since the 1950s, was developed as an alternative to amine scrubbing and uses hot K<sub>2</sub>CO<sub>3</sub> solutions to absorb CO<sub>2</sub> from a synthesis gas under relatively high CO<sub>2</sub> partial pressures and high temperatures.<sup>53</sup>

The capture of CO<sub>2</sub> using aqueous K<sub>2</sub>CO<sub>3</sub> solutions depends on the established equilibria when CO<sub>2</sub> dissolves in water and how these equilibria are affected by pH changes. In open systems, increasing the pH raises the total concentration of dissolved carbon, while lowering the pH causes CO<sub>2</sub> to be released, thereby decreasing CO<sub>2</sub> absorption. When CO<sub>2</sub> passes through aqueous K<sub>2</sub>CO<sub>3</sub>, it can react *via* two pathways. First, bicarbonate ions can be directly formed from the reaction of CO<sub>2</sub> with hydroxide ions (eqn (2)). Alternatively, CO<sub>2</sub> can be hydrated by water to produce carbonic acid (eqn (3)), which then deprotonates to form bicarbonate (eqn (4)). In either case, the resulting decrease in pH is buffered by the equilibrium



between the carbonate and bicarbonate species (eqn (5)). Overall,  $\text{K}_2\text{CO}_3$  in water captures  $\text{CO}_2$  as potassium bicarbonate (eqn (6)), with a  $\Delta H_{\text{abs}}$  value of approximately  $-40 \text{ kJ mol}^{-1}$ .<sup>35</sup>



Either eqn (2) or (3) represents the process's rate-limiting step, depending on pH, as the deprotonation/protonation reactions in aqueous systems (eqn (4) and (5)) are considered barrierless. Accordingly, in solutions with  $\text{pH} > 9$ , the generally faster reaction between  $\text{CO}_2$  and hydroxide ions dominates. In contrast, in solutions with  $\text{pH} < 7$ , the slower  $\text{CO}_2$  hydration reaction becomes more prominent. For  $\text{K}_2\text{CO}_3$  solutions, where the pH is usually  $> 9$ , the reaction with hydroxide ions predominates and serves as the rate-determining step.

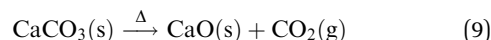
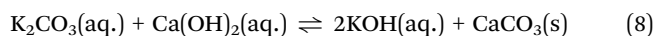
The release of  $\text{CO}_2$  from  $\text{KHCO}_3$ , along with the regeneration of  $\text{K}_2\text{CO}_3$  (reverse of eqn (6)), takes place through a pressure swing between the absorption and desorption units, eliminating the need for an additional temperature swing. This engineering approach enables absorption and regeneration at the same elevated temperature ( $\sim 100^\circ\text{C}$ ), improving absorption kinetics and reducing energy consumption by nearly half.<sup>53</sup>

Aqueous  $\text{K}_2\text{CO}_3$  solutions offer several advantages over traditional amine-based absorption liquids, including lower toxicity and nonvolatility, which minimize absorbent losses and decrease solvent replacement costs. Most importantly, carbonates exhibit resistance to absorbent degradation and are relatively inexpensive compared to many amines. A practical challenge associated with the carbonate absorption medium is that the precipitation of bicarbonate salts limits the use of highly concentrated solutions. However, recent research has shown that purposeful precipitation of bicarbonate salts can facilitate high-pressure stripping processes, reducing the regeneration energy requirement and liquid circulation rates.<sup>54</sup> For example, an Australian company, KC8 Capture Technologies, uses a  $\text{K}_2\text{CO}_3$  solution to capture 90–95% of  $\text{CO}_2$  emissions from flue gas, forming  $\text{KHCO}_3$ , which can then precipitate and be subjected to  $\text{CO}_2$  release and  $\text{K}_2\text{CO}_3$  regeneration.<sup>55</sup> The regeneration energy requirement of the technology is 88–110  $\text{kJ mol}^{-1}\text{CO}_2$ , which is lower than that typically needed for amine-based processes. Another challenge for the carbonate absorption medium is its slow kinetics for  $\text{CO}_2$  absorption, which can be improved by adding activators or promoters such as amines<sup>53,56</sup> and enzymes.<sup>57,58</sup>

Analogous to carbonate solutions, aqueous hydroxide solutions can also be used to capture  $\text{CO}_2$ , but in this case, carbonate salts are produced as described in eqn (7). The produced carbonate can continue to capture  $\text{CO}_2$  to form bicarbonate.



Initially proposed in 1999 as a solution for direct air capture (DAC), the high absorption rate of this process results from the large thermodynamic driving force of the reaction between dissolved  $\text{CO}_2$  and hydroxide ions ( $-\Delta H_{\text{abs}} = 90\text{--}100 \text{ kJ mol}^{-1}$ ).<sup>59</sup> Although the original process was limited by reduced capture capability due to the low solubility of the used  $\text{Ca}(\text{OH})_2$ , most recent implementations of this technology use  $\text{KOH}$ , which has a solubility in water over two orders of magnitude greater than that of  $\text{Ca}(\text{OH})_2$ .<sup>60</sup> Once  $\text{K}_2\text{CO}_3$  is formed in the absorption chamber (eqn (7)), the next step is the precipitation of calcium carbonate and the regeneration of reusable  $\text{KOH}$  in solution (eqn (8)). The calcium carbonate is then subjected to a calcination process at  $\sim 900^\circ\text{C}$  to liberate  $\text{CO}_2$  and generate  $\text{CaO}$  (eqn (9)), which generates the calcium hydroxide required in the precipitation chamber by reaction with water. Industrial applications of this technology for DAC have shown promising results by achieving a capture rate of  $1 \text{ Mt CO}_2 \text{ year}^{-1}$  (Carbon Engineering ULC).<sup>61</sup> However, this plant needs high-grade heat ( $230 \text{ kJ mol}^{-1}\text{CO}_2$ ), which is supplied by burning natural gas.



### 2.3. Molten metal oxides

Capture of  $\text{CO}_2$  using alkali and alkaline-earth metal oxides has been employed in large-scale processes for over 150 years. Its first application involved purifying hydrogen by removing  $\text{CO}_2$  with  $\text{CaO}$  in a gasification process. However, it was not until 1999 that Shimizu *et al.* introduced the carbonate looping process, which paved the way for  $\text{CO}_2$  capture by metal oxides at medium to high temperatures ( $> 200^\circ\text{C}$ ).<sup>62</sup> In this process,  $\text{CaO}$  reacts with post-combustion  $\text{CO}_2$  to form  $\text{CaCO}_3$  (eqn (10)), followed by its thermal decomposition to  $\text{CaO}$  and the release of pure  $\text{CO}_2$ . Compared to liquid amine scrubbing, the higher operating temperatures of metal oxides provide the advantage of incurring lower energy penalties when the carbon capture process is implemented into power plants or other high-temperature processes.<sup>63</sup>

The most used metal oxide sorbents utilize alkaline-earth metals such as calcium and magnesium to capture  $\text{CO}_2$  by forming the corresponding carbonates (eqn (10) and (11)). Although the carbonation reactions for  $\text{CaO}$  and  $\text{MgO}$  are exergonic, relatively high operating temperatures are required for the  $\text{CO}_2$  capture step to achieve adequate  $\text{CO}_2$  capture rates. This ensures that the carbonation reaction is primarily controlled by thermodynamics, leading to high process efficiencies. For example, continuous  $\text{CO}_2$  capture from ambient air has been demonstrated using  $\text{CaO}$  particles at temperatures ranging from  $365$  to  $400^\circ\text{C}$ , achieving a  $\text{CO}_2$  removal efficiency of 99.9% after five consecutive cycles.<sup>64</sup>



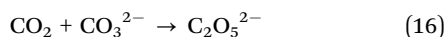
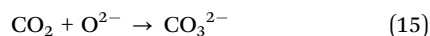
Using oxides of alkali metals such as  $\text{Li}$ ,  $\text{Na}$ , and  $\text{K}$  as sorbents is not often considered for large-scale  $\text{CO}_2$  capture



applications. The formed carbonates (eqn (12)–(14)) typically require temperatures exceeding 1200 °C to release the absorbed CO<sub>2</sub> and regenerate the metal oxides. However, these mono-valent oxides have played an important role in altering the CO<sub>2</sub> sorption mechanisms of CaO and MgO.<sup>65</sup> When used as promoters, the alkali metal oxides readily transform into their carbonate forms in the presence of CO<sub>2</sub> with  $\Delta H_{\text{abs}}$  of approximately  $-300 \text{ kJ mol}^{-1}$ .<sup>65</sup> The melting points of Li<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, and K<sub>2</sub>CO<sub>3</sub> are relatively low, ranging from 730–900 °C, and eutectic mixtures of the three components possess melting points as low as  $\sim 400$  °C. Taking advantage of these low melting points, a strategy has been devised to enhance the rate and extent of CO<sub>2</sub> uptake by CaO and MgO-based sorbents. This involves coating sorbents with binary or ternary molten alkali carbonates, which enhances CO<sub>2</sub> transport within the sorbent.



Huang *et al.* reported the remarkable effects of alkali carbonate molten salts on the performance of CaO particles for CO<sub>2</sub> capture.<sup>66</sup> The (Li–K)<sub>2</sub>CO<sub>3</sub> molten salt coating was found not only to promote CO<sub>2</sub> uptake but also to facilitate CO<sub>2</sub> desorption from CaO. Particularly at low temperatures of 500 and 600 °C, the CO<sub>2</sub> capture capacity increased significantly from 1.19 and 3.26 mmol g<sup>−1</sup> to 6.93 and 10.38 mmol g<sup>−1</sup>, respectively, using 7.5 mol % (Li–K)<sub>2</sub>CO<sub>3</sub>. The coating of alkali carbonate molten salts is believed to prevent the formation of a rigid CaCO<sub>3</sub> layer on the surface of the CaO particles. This facilitates the ongoing reaction of dissolved CO<sub>2</sub> with O<sup>2−</sup>, originating from CaO, in the liquid molten salts, resulting in the formation of CO<sub>3</sub><sup>2−</sup> (eqn (15)). The (Li–K)<sub>2</sub>CO<sub>3</sub> molten salt is particularly effective in enhancing CO<sub>2</sub> uptake due to the high O<sup>2−</sup> migration, which ensures the continuous counter diffusion of CO<sub>3</sub><sup>2−</sup> and O<sup>2−</sup>.<sup>67</sup> Furthermore, CO<sub>2</sub> can be captured by the reaction with the continuously delivered CO<sub>3</sub><sup>2−</sup> to form dicarbonate ions (eqn (16)).



In 2015, Harada *et al.* disclosed that coating MgO particles with molten alkali metal nitrates could significantly improve the CO<sub>2</sub> uptake,<sup>68</sup> which increased from  $<1 \text{ mmol g}^{-1}$  for uncoated MgO to  $10.2 \text{ mmol g}^{-1}$  at 300 °C with the coating. They also demonstrated the molten alkali metal nitrates prevented the formation of a rigid carbonate layer on the surface of MgO, which would otherwise be impermeable to CO<sub>2</sub>. The high concentration of oxide ions in the molten salt restricted the generation of this rigid layer and facilitated the generation of carbonate ions (eqn (11)).<sup>69</sup> This resulted in the rapid formation of MgCO<sub>3</sub> and eased the regeneration of particles at moderate temperatures.

## 2.4 Electrochemical reactions of captured CO<sub>2</sub>

The physicochemical properties of each capture medium will affect the thermodynamics of the electrochemical conversion of the corresponding CO<sub>2</sub>-adduct to any of the possible products. As depicted in Fig. 3, the electrocatalytic conversion of the captured CO<sub>2</sub> is an energetically uphill pathway, with the initial energy level determined by the CO<sub>2</sub> absorption enthalpy of the capture medium employed. For instance, the electrochemical conversion of bicarbonate, derived from the CO<sub>2</sub> capture with aqueous carbonate solutions (eqn (6)), is less endothermic than the direct conversion of the carbamate obtained from the reaction between CO<sub>2</sub> and aqueous amines (eqn (1)). This is translated to a higher energy input for the electrochemical conversion of the carbamate as the result of the stronger interaction between CO<sub>2</sub> and the capture medium.

The electronic and steric properties of the CO<sub>2</sub>-adduct are also crucial in determining the kinetics of the electrochemical conversion of captured CO<sub>2</sub>. The energies of intermediates involved in the pathways leading to the reduced products are influenced by the chemical structure of the captured CO<sub>2</sub> species, thereby affecting the reaction kinetics. Moreover, the chemical composition and morphology of the catalyst can alter the binding energies of such reaction intermediates, consequently impacting reaction rates and favoring specific products. Thus, there is a complex interplay between the nature of the captured CO<sub>2</sub> species and the electrocatalyst, collectively determining the kinetics for generating the products.

For instance, carbamates can be directly converted at the cathode, producing CO or other carbon-based products while regenerating the amine for another capture cycle (eqn (17)). The efficiency of the electrochemical conversion of CO<sub>2</sub> captured as carbamate can be affected by several factors. First, the energy required to break the C–N bond in the carbamate group increases with stronger binding interactions between CO<sub>2</sub> and the amine, which raises the overpotential of the electrocatalytic reaction. Moreover, the selectivity toward carbonaceous

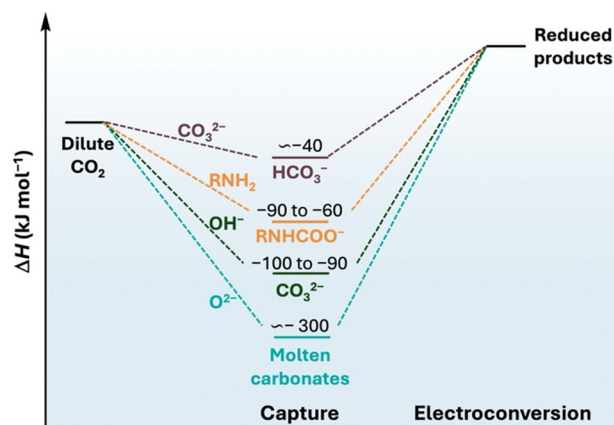
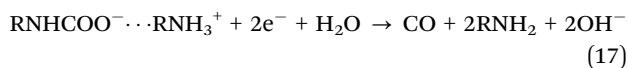


Fig. 3 Schematic representation of the energetics for the electrochemical conversion of captured CO<sub>2</sub>. Enthalpy changes in CO<sub>2</sub> absorption are shown for each capture medium. For ease of representation, energy levels are not to scale.

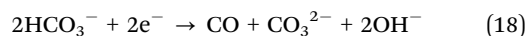




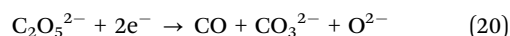
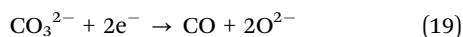
products can be adjusted by changing the concentration of the amine solutions to improve the mass transport of the amine-CO<sub>2</sub> adduct to the electrode, thereby suppressing the undesired hydrogen evolution reaction (HER). Also, considering that the electrochemical conversion of carbamate follows an inner-sphere electron transfer mechanism,<sup>70</sup> the distance between the carbamate and the electrode surface is crucial in determining the kinetics of the electrocatalytic reaction. Consequently, the structure of the amine will significantly influence the efficiency of carbamate conversion.



In the case of CO<sub>2</sub> capture using hydroxide or carbonate solutions, bicarbonate is the final product (eqn (2) and (6)). The bicarbonate solution can undergo electrochemical reduction to obtain CO or other products while regenerating the initial carbonate ions (eqn (18)). A challenging aspect of bicarbonate reduction systems is resolving the electrochemically active species, considering the dynamic acid-base equilibria that define the relative concentrations of CO<sub>2</sub>, bicarbonate, and carbonate at the electrode surface (eqn (2)–(5)).



The CO<sub>2</sub> capture by molten oxide generates molten carbonate (eqn (15)), which can be reduced at elevated temperatures (400–900 °C) at the cathode to form CO or other products while regenerating the oxide (eqn (19)). Similarly, dicarbonate ions can be directly reduced at the cathode, regenerating the carbonate and oxide ions (eqn (20)). These electrochemical transformations are unique since they are carried out at much higher temperatures than the conversion of carbamate or bicarbonate solutions. It has been shown that adjusting the temperature can effectively control the selectivity of the electrocatalytic reactions.<sup>71</sup>



The electrocatalytic conversion of CO<sub>2</sub> captured by various capture media, as described above, facilitates the conversion of CO<sub>2</sub> from diluted sources into value-added products. Producing carbonaceous products other than carbon monoxide, such as formate, ethylene, and carbon materials, entails more complex reaction pathways. The next section will explore these topics in detail.

### 3. Catalyst-mediated product control for converting captured CO<sub>2</sub>

The electrocatalyst is crucial in converting captured CO<sub>2</sub>, affecting the type and distribution of products, and the conversion efficiency. Recent progress in the electrochemical valorization of captured CO<sub>2</sub> has made it possible to produce various products, including CO, HCOO<sup>−</sup>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>5</sub>OH, and carbon materials, as summarized in Table 1.

These products are important chemicals, fuels, or materials with many industrial applications. Carbon monoxide is a key component of syngas, which is extensively used to synthesize long-chain hydrocarbons through the Fischer-Tropsch process.<sup>114</sup> In addition, CO is widely utilized in synthesizing various carbonyl compounds *via* carbonylation reactions.<sup>18</sup> Formate and formic acid are used in leather and textile manufacturing, serve as preservatives in livestock feed, and act as efficient H<sub>2</sub> carriers in fuel cells.<sup>115</sup> Methane, the primary component of natural gas, serves as a gas fuel for electricity generation, heating buildings, transportation, and industrial processes. Ethylene is an important building block for industrial chemical production, particularly in the manufacture of polyethylene, the most widely used plastic worldwide.<sup>116</sup> Ethanol is commonly used as a solvent, disinfectant, precursor, liqueur, and liquid fuel. Carbon materials, with varying morphology and physiochemical properties, are extensively utilized in applications such as adsorption, separation, and catalysis.<sup>117</sup>

#### 3.1. Mechanism of conversion of captured CO<sub>2</sub>

There are two possible pathways for the electrochemical valorization of captured CO<sub>2</sub>, each influencing catalyst selection. (a) An indirect pathway, where the captured CO<sub>2</sub> is first converted back to CO<sub>2</sub> at the electrode-electrolyte interface and then undergoes electrochemical reduction (Fig. 4a); (b) a direct pathway, where the captured CO<sub>2</sub> is directly reduced at the electrode (Fig. 4b).

In the indirect conversion, the captured CO<sub>2</sub> (such as bicarbonate or carbamate) dissociates, producing CO<sub>2</sub> *in situ* at the electrode-electrolyte interface (Fig. 4a). This dissociation process is typically triggered by either temperature or proton flux changes within the electrolyzer. Currently, most reported instances of electrochemical conversion of captured CO<sub>2</sub> in aqueous solutions follow this indirect pathway (Table 1).<sup>72–74</sup> Because of the *in situ* CO<sub>2</sub> generation, the catalyst selection closely aligns with conventional electrochemical CO<sub>2</sub> conversion, *i.e.*, Ag and single-atom catalysts (SACs) facilitate CO production, Bi and Sn catalyze formate formation, while Cu-based catalysts are suitable for producing hydrocarbons and alcohols. The key aspect of the indirect pathway hinges on balancing the rate of *in situ* CO<sub>2</sub> release with the rate of CO<sub>2</sub> reduction at the electrode surface to achieve the conversion of the captured CO<sub>2</sub> with high activity and selectivity. This requires precise design of the catalyst structures and properties, as well as optimization of the electrolyzer, electrolyte, and other operating conditions.

The second pathway is the direct conversion, which bypasses the formation of CO<sub>2</sub> before the reduction process (Fig. 4b). Here, the captured CO<sub>2</sub> (such as bicarbonate or carbamate) serves as the primary reactant, setting this approach apart from conventional electrochemical CO<sub>2</sub> conversion. One significant advantage of focusing on (bi)carbonate and carbamate instead of CO<sub>2</sub> is achieving much higher reactant concentrations. So far, only a few documented examples have utilized the direct pathway in aqueous bicarbonate and carbamate, primarily under high-temperature



Table 1 Recent progress of catalyst-mediated product control in the electrochemical conversion of captured CO<sub>2</sub> (since 2019)

| Cathode materials                          | Captured CO <sub>2</sub>                                                                               | Electrolyzer                            | Pathway  | Products                                                                                                                                                              | FE (%) | $ j $ (mA cm <sup>-2</sup> ) <sup>a</sup> | $T$ (°C) <sup>b</sup> | Ref. |
|--------------------------------------------|--------------------------------------------------------------------------------------------------------|-----------------------------------------|----------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------|-------------------------------------------|-----------------------|------|
| Ag nanoparticles (NPs) on Ag film          | K <sub>2</sub> CO <sub>3</sub>                                                                         | MEA with BPM                            | Indirect | CO                                                                                                                                                                    | 28     | 100                                       | R.T.                  | 72   |
| Ag NPs                                     | K <sub>2</sub> CO <sub>3</sub>                                                                         | MEA with cation exchange membrane (CEM) | Indirect | CO                                                                                                                                                                    | 46     | 200                                       | R.T.                  | 73   |
| Ag NPs                                     | K <sub>2</sub> CO <sub>3</sub>                                                                         | MEA with CEM                            | Indirect | CO                                                                                                                                                                    | 42     | 200                                       | R.T.                  | 74   |
| Ag NPs-coated porous carbon                | KHCO <sub>3</sub>                                                                                      | MEA with BPM                            | Indirect | CO                                                                                                                                                                    | 37     | 100                                       | R.T.                  | 75   |
| Ag NPs                                     | KHCO <sub>3</sub>                                                                                      | MEA with BPM                            | Indirect | CO                                                                                                                                                                    | 82     | 100                                       | R.T.                  | 76   |
| Ag NPs                                     | KHCO <sub>3</sub>                                                                                      | MEA with BPM                            | Indirect | CO                                                                                                                                                                    | ~65    | 200                                       | R.T.                  | 77   |
| Ag NPs                                     | KHCO <sub>3</sub>                                                                                      | MEA with CEM                            | Indirect | CO                                                                                                                                                                    | 99     | 51.5                                      | R.T.                  | 78   |
| Ag (free-standing porous electrode)        | KHCO <sub>3</sub>                                                                                      | MEA with BPM                            | Indirect | CO                                                                                                                                                                    | 59     | 100                                       | R.T.                  | 79   |
| Ag foam                                    | KHCO <sub>3</sub>                                                                                      | MEA with CEM                            | Indirect | CO                                                                                                                                                                    | 40     | 100                                       | R.T.                  | 80   |
| Ag foam                                    | KHCO <sub>3</sub> + DTAB <sup>c</sup>                                                                  | MEA with BPM                            | Indirect | CO                                                                                                                                                                    | 80     | 100                                       | R.T.                  | 81   |
| Ag (electrodeposited)                      | KHCO <sub>3</sub> + DTAB <sup>c</sup>                                                                  | MEA with BPM                            | Indirect | CO                                                                                                                                                                    | 85     | 100                                       | 50                    | 82   |
| Ag (Br-modified)                           | NH <sub>4</sub> HCO <sub>3</sub>                                                                       | H cell                                  | Indirect | CO                                                                                                                                                                    | 77.8   | 18 <sup>d</sup>                           | R.T.                  | 83   |
| Ag/C                                       | Captured CO <sub>2</sub> from the air using KOH solution                                               | MEA with BPM                            | Indirect | CO                                                                                                                                                                    | 13     | 50                                        | R.T.                  | 84   |
| Ag NPs on a Ag film                        | CO <sub>2</sub> -captured monoethanolamine                                                             | Flow cell                               | Direct   | CO                                                                                                                                                                    | 72     | 50                                        | 60                    | 85   |
| Ag (Cl-modified)                           | CO <sub>2</sub> -captured 2-amino-2-methyl-1-propanol (AMP)                                            | H cell                                  | Indirect | CO                                                                                                                                                                    | 91     | 6                                         | R.T.                  | 86   |
| Au (foil)                                  | CO <sub>2</sub> -captured AMP                                                                          | Flow cell                               | Indirect | CO                                                                                                                                                                    | 45     | 10                                        | 75                    | 87   |
| Ni SAC                                     | CO <sub>2</sub> -captured monoethanolamine                                                             | MEA with BPM                            | Indirect | CO                                                                                                                                                                    | 64.9   | 50                                        | R.T.                  | 88   |
| Ni SAC                                     | KHCO <sub>3</sub>                                                                                      | MEA with BPM                            | Indirect | CO                                                                                                                                                                    | 67.2   | 100                                       | R.T.                  | 89   |
| Ni SAC                                     | KHCO <sub>3</sub>                                                                                      | MEA with BPM                            | Indirect | CO                                                                                                                                                                    | 93     | 200                                       | R.T.                  | 90   |
| CoPc@CNT                                   | KHCO <sub>3</sub>                                                                                      | MEA with CEM                            | Indirect | CO                                                                                                                                                                    | 96.2   | 300                                       | R.T.                  | 91   |
| FeNi alloy (foam)                          | Na <sub>2</sub> CO <sub>3</sub> -K <sub>2</sub> CO <sub>3</sub>                                        | Undivided cell                          | Direct   | CO                                                                                                                                                                    | 90.5   | 100                                       | 800                   | 92   |
| Bi-coated carbon                           | KHCO <sub>3</sub>                                                                                      | MEA with BPM                            | Indirect | HCOO <sup>-</sup>                                                                                                                                                     | 64     | 100                                       | R.T.                  | 93   |
| Bi electrodeposited on carbon              | NH <sub>4</sub> HCO <sub>3</sub>                                                                       | MEA with AEM                            | Indirect | HCOO <sup>-</sup>                                                                                                                                                     | 75     | 100                                       | 40                    | 94   |
| SnO <sub>2</sub> /C                        | Captured CO <sub>2</sub> from air using KOH solution                                                   | MEA with BPM                            | Indirect | HCOO <sup>-</sup>                                                                                                                                                     | 16     | 50                                        | R.T.                  | 84   |
| Sn (rotating disc electrode)               | KHCO <sub>3</sub>                                                                                      | H cell                                  | Indirect | HCOO <sup>-</sup>                                                                                                                                                     | 66     | ~3 <sup>d</sup>                           | R.T.                  | 95   |
| Sn (foil)                                  | KHCO <sub>3</sub>                                                                                      | H cell                                  | Indirect | HCOO <sup>-</sup>                                                                                                                                                     | 18     | 6                                         | R.T.                  | 96   |
| Sn (foil)                                  | KHCO <sub>3</sub>                                                                                      | Undivided cell                          | Direct   | HCOO <sup>-</sup>                                                                                                                                                     | 83     | 146 <sup>d</sup>                          | 100                   | 97   |
| Pb (foil)                                  | KHCO <sub>3</sub>                                                                                      | Flow cell                               | Indirect | HCOO <sup>-</sup>                                                                                                                                                     | 50     | 25                                        | 75                    | 87   |
| Cu (foil)                                  | CO <sub>2</sub> -captured AMP                                                                          | MEA with BPM                            | Indirect | CH <sub>4</sub>                                                                                                                                                       | 27     | 400                                       | R.T.                  | 98   |
| Cu (mesh)                                  | KHCO <sub>3</sub>                                                                                      | MEA with BPM                            | Indirect | CH <sub>4</sub>                                                                                                                                                       | 27     | 500                                       | R.T.                  | 99   |
| Fe                                         | Li <sub>2</sub> CO <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> -K <sub>2</sub> CO <sub>3</sub> -LiOH | Undivided cell                          | Direct   | CH <sub>4</sub>                                                                                                                                                       | 63.3   | 15                                        | 575                   | 100  |
| Fe sheet                                   | Li <sub>1.427</sub> Na <sub>0.359</sub> K <sub>0.214</sub> CO <sub>3</sub> ~ 0.15LiOH                  | Undivided cell                          | Direct   | CH <sub>4</sub>                                                                                                                                                       | 42.7   | 400                                       | 650                   | 101  |
| Cu/Ag (bilayer)                            | KHCO <sub>3</sub>                                                                                      | MEA with BPM                            | Indirect | C <sub>2</sub> H <sub>4</sub> (CH <sub>3</sub> COO <sup>-</sup> , C <sub>2</sub> H <sub>4</sub> , C <sub>2</sub> H <sub>5</sub> OH, C <sub>3</sub> H <sub>7</sub> OH) | 41.6   | 100                                       | R.T.                  | 102  |
| Cu/CoPc-carbon nanotube (CNT)              | K <sub>2</sub> CO <sub>3</sub>                                                                         | MEA with CEM and interposer             | Indirect | C <sub>2</sub> H <sub>4</sub>                                                                                                                                         | 34     | 300                                       | R.T.                  | 103  |
| Cu/Ag (NPs)                                | K <sub>2</sub> CO <sub>3</sub>                                                                         | MEA with BPM                            | Indirect | C <sub>2</sub> H <sub>4</sub>                                                                                                                                         | 9      | 150                                       | R.T.                  | 104  |
| Ag-Cu(OH) <sub>2</sub> nanowire on Cu foam | K <sub>2</sub> CO <sub>3</sub> /KHCO <sub>3</sub>                                                      | MEA with BPM                            | Indirect | C <sub>2</sub> H <sub>4</sub>                                                                                                                                         | 12     | 100                                       | R.T.                  | 105  |
| Cu/Zn (Muntz brass sheet; 3:2 alloy)       | Li <sub>2</sub> CO <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub>                                       | Undivided cell                          | Direct   | carbon nano-scaffold                                                                                                                                                  | 85     | 200                                       | 670                   | 106  |
| Sn (liquid cathode)                        | Li <sub>2</sub> CO <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> -K <sub>2</sub> CO <sub>3</sub>       | Undivided cell                          | Direct   | Sn-C spheres (Sn@C)                                                                                                                                                   | 84     | N.A. <sup>e</sup>                         | 550                   | 107  |
| SnO <sub>2</sub>                           | CaCO <sub>3</sub> -CaCl <sub>2</sub> -NaCl                                                             | Undivided cell                          | Direct   | Sn@CNT                                                                                                                                                                | 85.1   | N.A.                                      | 800                   | 108  |
| Steel (galvanized)                         | CO <sub>2</sub> -captured Li <sub>1.5</sub> Na <sub>1.3</sub> BO <sub>3</sub>                          | Undivided cell                          | Direct   | CNT                                                                                                                                                                   | 55     | 120                                       | 600                   | 109  |
| Steel (galvanized)                         | Li <sub>2</sub> CO <sub>3</sub>                                                                        | Undivided cell                          | Direct   | Carbon platelets                                                                                                                                                      | N.A.   | 200                                       | 730                   | 110  |
| Ni                                         | Li <sub>2</sub> CO <sub>3</sub> -K <sub>2</sub> CO <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub>       | Undivided cell                          | Direct   | Graphite                                                                                                                                                              | N.A.   | 5-100                                     | 650-750               | 111  |
| Ni                                         | LiCl-Li <sub>2</sub> CO <sub>3</sub> -LiBO <sub>2</sub>                                                | Undivided cell                          | Direct   | Carbon nanofibers                                                                                                                                                     | 93.8   | 35                                        | 550                   | 112  |
| Ni                                         | Li <sub>2</sub> CO <sub>3</sub>                                                                        | Undivided cell                          | Direct   | Carbon nano-onion                                                                                                                                                     | N.A.   | 150                                       | 750                   | 113  |

<sup>a</sup>  $|j|$ : current density. <sup>b</sup>  $T$ : temperature. <sup>c</sup> DTAB: dodecyltrimethylammonium bromide. <sup>d</sup> Calculated based on data from references. <sup>e</sup> N.A.: not available.



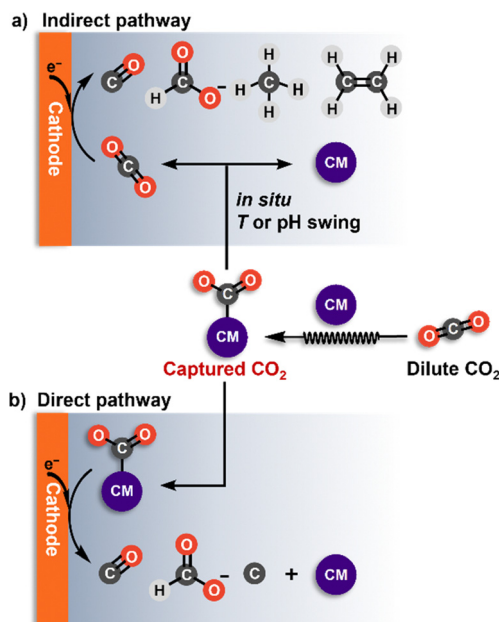


Fig. 4 Illustration of the two pathways of electrochemically reactive  $\text{CO}_2$  capture: (a) Indirect with the captured  $\text{CO}_2$  converted back to  $\text{CO}_2$  at the electrode–electrolyte interface before its electrochemical reduction; (b) direct with the captured  $\text{CO}_2$  as a reactant in the electrochemical step. CM: capture medium.

conditions.<sup>85,97,118</sup> Similarly, in molten salts, the captured  $\text{CO}_2$  (as  $\text{CO}_3^{2-}$ ) can be directly converted, using the high temperature to overcome the energy barrier for reduction.

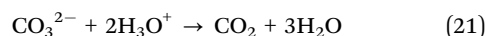
The direct conversion of bicarbonate or carbamate, particularly to  $\text{C}_{2+}$  products, presents a formidable challenge, with few studies reported. It has been observed that the direct pathway for carbonate conversion does not involve CO intermediates.<sup>118</sup> As a result, this pathway cannot generate  $\text{C}_{2+}$  products, as these are primarily formed through CO–CO coupling. To effectively catalyze the conversion of bicarbonate or carbamate, the catalysts need to have a strong affinity for the reactant. Since heterogeneous electron transfer is an inner-sphere reaction, the proximity between the reactant and the electrode surface is crucial for the electrolysis reaction. Unlike charge-neutral  $\text{CO}_2$  molecules, bicarbonates and carbamates are anions that tend to migrate toward the anode, resulting in low concentrations at the cathode interface. Therefore, a positively charged catalyst surface may aid in attracting the anionic reactant through electrostatic interactions. Thus, careful tuning of the electronic configuration and the morphology of electrocatalysts, along with surface modification, is essential to promote efficient reactant adsorption. Additionally, a more comprehensive understanding of the mechanistic pathway for the direct conversion of bicarbonate or carbamate is needed to investigate the potential for C–C coupling in this system.

### 3.2. Production of CO

In the electrochemical conversion of captured  $\text{CO}_2$  into CO, silver nanomaterials are extensively utilized as catalysts, similar to their prominent role in the electrochemical reduction of

$\text{CO}_2$ .<sup>72,75,119</sup> Li *et al.* employed Ag as the electrocatalysts for the electroreduction of a carbonate electrolyte, achieving a CO faradaic efficiency ( $\text{FE}_{\text{CO}}$ ) that decreased from 28% to 12% as the current density increased from 100 to 300  $\text{mA cm}^{-2}$ .<sup>72</sup> In this process, the carbonate reacts with protons from the bipolar membrane (BPM) to generate  $\text{CO}_2$  *in situ* near the electrode surface (eqn (21)), following the indirect pathway depicted in Fig. 4a. In another work, Li *et al.* discovered that pure Ag foil was ineffective in catalyzing the direct reduction of  $\text{NH}_4\text{HCO}_3$ , while a Br-modified Ag electrode exhibited higher efficiency with a significant  $\text{FE}_{\text{CO}}$  of 77.8% and a current density of 13.8  $\text{mA cm}^{-2}$  at  $-0.6$  V vs. RHE.<sup>83,120</sup> They hypothesized that the Br modification could increase the number of active sites on the Ag surface, promoting the release of  $\text{CO}_2$  from  $\text{NH}_4\text{HCO}_3$  and its subsequent reduction.

Mezza *et al.* conducted a systematic study on the effect of Ag mass loading on the performance of bicarbonate electrolysis to CO (eqn (18)) through the indirect pathway. Their findings showed that as the Ag loading rose from 116 to 565  $\mu\text{g cm}^{-2}$ ,  $\text{FE}_{\text{CO}}$  improved from 55% to 77%, while the partial current density of CO rose from 6 to 13  $\text{mA cm}^{-2}$ . Further increases in the Ag loading did not lead to additional improvement because a balance was reached between the availability of active sites and the electrode permeability.<sup>121</sup> It is important to note that there is a trade-off between selectivity and activity of CO production under these conditions. The decrease in  $\text{FE}_{\text{CO}}$  at higher current densities is due to an imbalance between the utilization rate of the *in situ* generated  $\text{CO}_2$  and the local  $\text{CO}_2$  concentration on the catalyst surfaces.

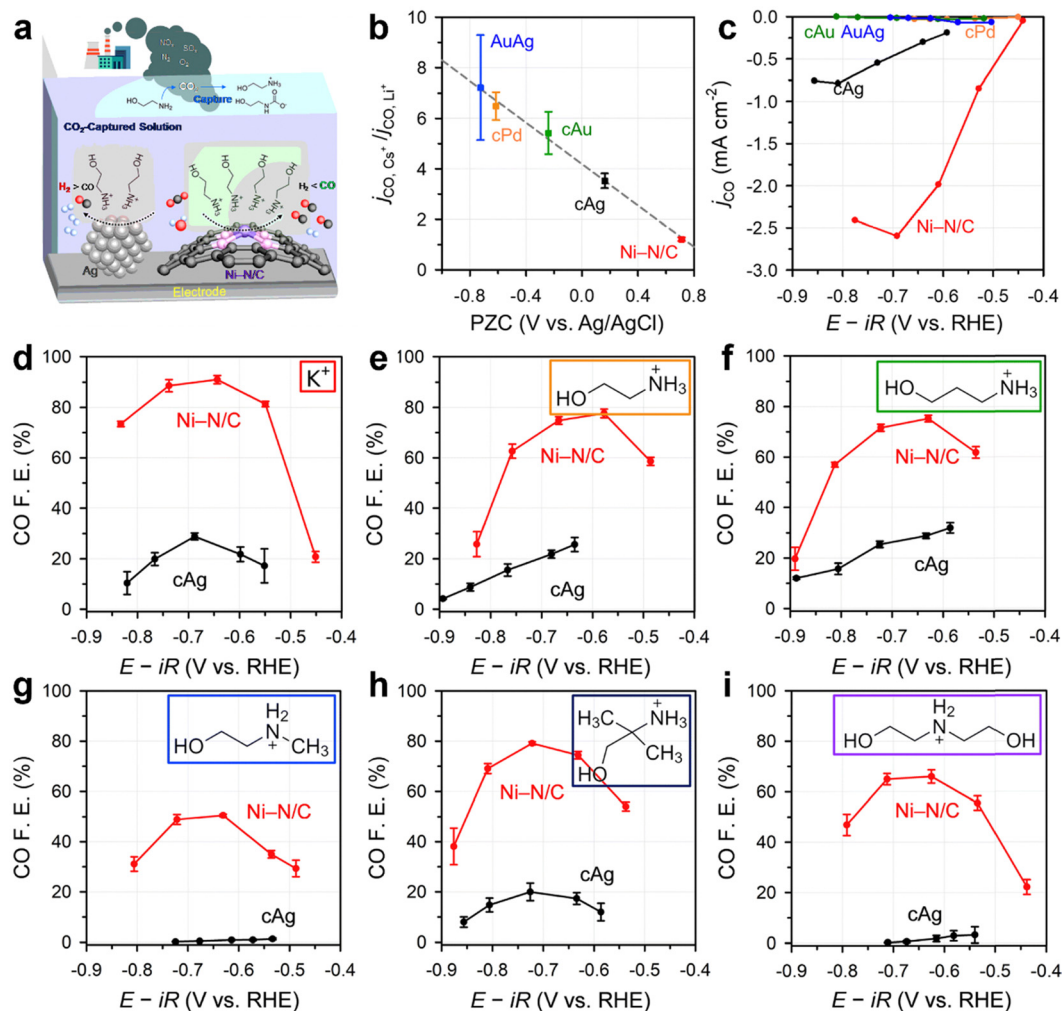


Lee *et al.* proposed a direct pathway for using carbamate electrolyte as the reactant in electrochemical conversion (Fig. 4b). They achieved an impressive  $\text{FE}_{\text{CO}}$  of 72% at 50  $\text{mA cm}^{-2}$  in a flow cell using a Ag electrocatalyst as the cathode in an electrolyte consisting of 30 wt% monoethanolamine with 2 M KCl at 60 °C (eqn (17)).<sup>85</sup>

SACs have emerged as promising candidates for the electrolytic conversion of captured  $\text{CO}_2$ , due to their exceptional selectivity for CO, high activity, and maximum atom efficiency. Kim *et al.* demonstrated that a Ni–N/C SAC exhibited more selective production of CO (78.3%) compared to commercially available Ag (cAg) catalysts (38.3%) in  $\text{CO}_2$ -captured monoethanolamine (Fig. 5a).<sup>88</sup> They ascribed this enhanced performance to the much higher potential of zero charge (PZC) of Ni–N/C compared to cAg, as a positively shifted PZC can increase the surface cation charge density at the same applied potential in the reduction reaction. This, in turn, stabilizes the  $\text{CO}_2^-$  intermediate and enhances the  $\text{CO}_2$  reduction activity. This relationship was further confirmed by studying the cation sensitivity using additional catalysts (AuAg alloy, cPd, and cAu catalysts; Fig. 5b and c). Ni–N/C could maintain a  $\text{FE}_{\text{CO}}$  of up to 50% as the cation size increased from  $\text{K}^+$  to diethanolammonium (Fig. 5d–i), showing selective CO production in different







**Fig. 5** (a) Schematic illustration of the superior performance of Ni-N/C catalysts compared with Ag in electrochemical conversion of captured CO<sub>2</sub> to CO. (b) and (c) Relationship between cation sensitivity of the catalysts and CO production performance: (b) normalized partial current density,  $j_{\text{CO}}$ , at  $-1.7$  V vs. NHE with respect to the PZC of the catalysts in  $0.05$  M carbonate electrolytes; (c)  $j_{\text{CO}}$  of the catalysts for the electrolysis of CO<sub>2</sub>-absorbing  $5$  M monoethanolamine solution. FE<sub>CO</sub> of Ni-N/C and cAg for electrolysis in CO<sub>2</sub>-absorbing (d)  $1$  M KHCO<sub>3</sub>, (e)  $1$  M monoethanolamine, (f)  $1$  M 3-amino-1-propanol, (g)  $1$  M 2-(methylamino)ethanol, (h)  $1$  M 2-amino-2-methyl-1-propanol, and (i)  $1$  M diethanolamine Ar-saturated solutions. Reproduced with permission from ref. 88.

CO<sub>2</sub>-captured media. In contrast, the FE<sub>CO</sub> of cAg dropped to almost zero as the bulkiness of the amine increased.

In addition, Yue *et al.* used a Ni SAC derived from a metal-organic framework (MOF) to boost the electrolytic bicarbonate conversion to CO, achieving a FE<sub>CO</sub> of  $67.2\%$  at  $100$  mA cm<sup>-2</sup>.<sup>89</sup> The abundant mesopores in the Ni SAC promoted the transport of the *in situ* released CO<sub>2</sub> reactant. Cu electrodes have also demonstrated potential in the electrocatalytic conversion of carbamate into CO. Zhang and Kraatz showed that Cu electrodes significantly enhanced FE<sub>CO</sub> to  $58\%$  compared to glassy carbon electrodes ( $2.3\%$ ) when using ethylenediamine as the capture media at  $-0.76$  V vs. RHE.<sup>122</sup> This differs substantially from numerous reports that typically show Cu-based materials catalyzing the conversion of gas-fed CO<sub>2</sub> to C<sub>2+</sub> products.<sup>123,124</sup> Furthermore, the current density rose notably from  $0.63$  to  $18.4$  mA cm<sup>-2</sup>. While the morphology and crystalline properties

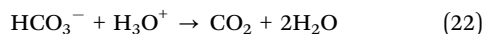
of the Cu electrodes used were not specified, these factors are likely crucial in CO production.

### 3.3. Production of HCOO<sup>-</sup>

Hori and Suzuki were the first to report the electrocatalytic reduction of bicarbonate into formate at a mercury electrode at relatively low current densities ( $<1$  mA cm<sup>-2</sup>).<sup>125</sup> They suggested that the electrolytic reduction of HCO<sub>3</sub><sup>-</sup> is a very slow process due to the slow dissociation of HCO<sub>3</sub><sup>-</sup> to CO<sub>2</sub> (reverse of eqn (2)). Min and Kanan employed a Pd electrocatalyst that achieved a formate faradaic efficiency (FE<sub>formate</sub>) of  $\sim 54\%$  at  $6.0$  mA cm<sup>-2</sup> in aqueous bicarbonate solutions without requiring any CO<sub>2</sub> input.<sup>126</sup> They hypothesized that bicarbonate first decomposed into CO<sub>2</sub>, followed by the subsequent reduction of CO<sub>2</sub> to formate (Fig. 4a, indirect pathway). In a flow cell equipped with a BPM, Bi catalysts demonstrated high efficiency



in converting  $\text{HCO}_3^-$  to formate, achieving a  $\text{FE}_{\text{formate}}$  of 64% at  $100 \text{ mA cm}^{-2}$  in a  $3 \text{ M KHCO}_3$  electrolyte.<sup>93</sup> In this process, the proton flux facilitated by the BPM converted  $\text{HCO}_3^-$  to  $\text{CO}_2$  (eqn (22)), which was subsequently reduced to formate on the Bi surface. Similarly, electrodeposited Bi on a carbon paper substrate exhibited excellent performance in an ammonium bicarbonate ( $\text{NH}_4\text{HCO}_3$ )-fed electrolyzer, using *in situ*  $\text{CO}_2$  as the primary reactant at slightly elevated temperature ( $\sim 40^\circ\text{C}$ ).<sup>94</sup> Because  $\text{NH}_4\text{HCO}_3$  ( $36^\circ\text{C}$ ) has a much lower decomposition temperature than ethanolamine- $\text{CO}_2$  ( $120^\circ\text{C}$ ) and  $\text{KHCO}_3$  ( $150^\circ\text{C}$ ), it can provide larger amounts of  $\text{CO}_2$  to the Bi electrode, resulting in higher current densities at a smaller energy input.



Pei *et al.* demonstrated that a dynamic  $\text{Sn}^{\delta+}/\text{Sn}$  interface significantly enhanced the direct reduction of bicarbonate to formate, achieving an optimal partial current density of  $121 \text{ mA cm}^{-2}$  for formate with a FE of 83% achieved in a  $3 \text{ M KHCO}_3$  solution at  $100^\circ\text{C}$ .<sup>97</sup> Their study indicated that formate was generated directly from bicarbonate, rather than from  $\text{CO}_2$  produced by the dissociation of bicarbonate at high temperatures (Fig. 4b, direct pathway).

Ma *et al.* revealed that carbonate intermediates adsorbed onto a Cu electrode during the electrochemical  $\text{CO}_2$  reduction in a  $\text{KHCO}_3$  electrolyte over a potential range from  $-1.0$  to  $0.2 \text{ V vs. RHE}$  (Fig. 6a).<sup>118</sup> At potentials of  $-0.4 \text{ V vs. RHE}$  and more negative, these intermediates were reduced to formate. Although the  $\text{FE}_{\text{formate}}$  was quite low (0.61%), this finding demonstrated the potential for directly reducing carbonates using a modified Cu electrode. Pulse electrolysis experiments conducted under a  $\text{N}_2$  atmosphere with  $0.05 \text{ M K}_2\text{CO}_3$  aqueous solution as the electrolyte corroborated the direct electroreduction of carbonate at the Cu surface (Fig. 6b).<sup>118</sup> *In situ* Raman spectroscopy at the applied potential of  $-0.05 \text{ V vs. RHE}$ , confirmed the formation of a  $^*\text{CO}_3^{2-}$  intermediate (where \* indicates it is bound to the surface). Upon switching the potential to  $-0.50 \text{ V vs. RHE}$ , the surface-bound carbonate was reduced to formate, as detected by high-performance liquid chromatography. Isotope labeling confirmed that the carbonate was the carbon source of the produced formate. In contrast,

constant potential electrolysis at  $-0.50 \text{ V vs. RHE}$  under the same reaction conditions yielded no formate.

The carbonate reduction mechanism was modeled using density functional theory (DFT) calculations according to the two pathways shown in Fig. 6. The results indicated for the direct pathway that carbonate absorption at Cu sites is favorable at  $-0.05 \text{ V vs. RHE}$  (Fig. 6b; first step of red lines). However, at this potential, the protonation of  $^*\text{CO}_3^{2-}$  to form  $^*\text{HCO}_3^-$  is unfavorable (Fig. 6b; red lines). Upon switching the potential to  $-0.50 \text{ V vs. RHE}$ , the formation of  $^*\text{HCO}_3^-$  becomes feasible, along with the subsequent reaction steps leading to formate production (Fig. 6b; black lines). Notably, carbonate with  $\Delta G_{\text{ads}} = 0.68 \text{ eV}$  cannot be adsorbed at  $-0.50 \text{ V vs. RHE}$  (Fig. 6b; gray lines) due to increased repulsion between  $\text{CO}_3^{2-}$  and the negatively charged electrode. This explains the lack of formate production during constant potential electrolysis experiments.

For the indirect pathway, which involves the release of  $\text{CO}_2$  before electrochemical reduction (Fig. 6a), the calculations show that a  $^*\text{CO}_3^{2-}$  intermediate forms through the reaction of  $\text{CO}_2$  with a residual  $^*\text{O}$  atom on the Cu surface. As expected, this reaction pathway toward formate production becomes energetically favorable at  $-0.50 \text{ V vs. RHE}$  (Fig. 6a; black lines). Note that this pathway is stoichiometric in reactants and cannot continue once the  $^*\text{O}$  atoms are consumed. Overall, the experimental and computational findings demonstrate that carbonate can be directly reduced at electrode surfaces, providing a possible method to activate the otherwise inert  $\text{CO}_2$ -adduct.

### 3.4. Production of $\text{CH}_4$

Methane is a highly desirable product due to its superior heat value of  $55.5 \text{ MJ kg}^{-1}$ , significantly greater than that of  $\text{CO}$  ( $10.2 \text{ MJ kg}^{-1}$ ) and methanol ( $22.7 \text{ MJ kg}^{-1}$ ).<sup>127</sup> Lees *et al.* reported that a Cu catalyst modified with cetyltrimethylammonium bromide (CTAB) facilitated  $\text{CH}_4$  formation at a partial current density of  $120 \pm 10 \text{ mA cm}^{-2}$  and with a yield of  $34 \pm 7\%$  during bicarbonate electrolysis, where the *in situ* generated  $\text{CO}_2$  served as the actual reactant.<sup>98</sup> A one-dimensional continuum model of the cathode compartment suggested that  $\text{H}^+$  from the BPM in the bicarbonate electrochemical reactor would

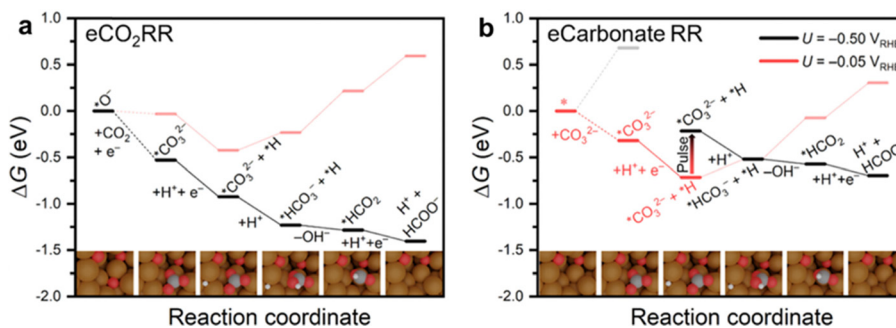


Fig. 6 Energy profiles of (a)  $\text{CO}_2$  reduction by  $\text{CO}_2$  adsorption on an  $^*\text{O}$  site at Cu and further reduction to formate at an applied potential of  $-0.5 \text{ V vs. RHE}$ , and (b)  $\text{CO}_3^{2-}$  reduction to formate at applied potentials of  $-0.05 \text{ V vs. RHE}$  (red),  $-0.50 \text{ V vs. RHE}$  (black), and with the potential pulsed from  $-0.05$  to  $-0.50 \text{ V vs. RHE}$ . Reproduced with permission from ref. 118.



neutralize hydroxide generated at the cathode surface, favoring  $\text{CH}_4$  over multicarbon products.

In the electrochemical conversion of captured  $\text{CO}_2$ ,  $\text{CH}_4$  is predominantly generated at elevated temperatures, with molten salts as the capture medium.<sup>100</sup> When molten carbonate salts are used, the type and distribution of products are largely determined by the properties of these salts, as well as the electrolysis conditions, including temperature and applied potential. In this setup, cathode materials are essential as they act as electron-transfer agents, which can greatly influence the overpotential and efficiency of the reactions. For effective electrolysis in molten salts, the cathode material must fulfill two criteria: (1) resistant to corrosion by the highly alkaline molten salts during high-temperature electrolysis. (2) Unable to alloy with Li, Na, or K at high temperatures in molten salts, as this would compromise the electrode structure.<sup>100</sup>

Wu *et al.* reported on the electrolysis of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  employing Fe and Ni electrodes as the cathode and anode, respectively, in an alkali carbonate/LiOH electrolyte at 600 °C.<sup>128</sup> The electrolysis products comprised 64.9%  $\text{CH}_4$ , 34.8%  $\text{H}_2$ , and 0.3%  $\text{C}_{2+}$ . Bai *et al.* systematically compared the overpotential and  $\text{CH}_4$  yield of different cathode materials, including Fe, stainless steel (SS304), Ti, and cupronickel sheets, in molten  $\text{Li}_{1.427}\text{Na}_{0.359}\text{K}_{0.214}\text{CO}_3 \sim 0.15\text{LiOH}$  at 650 °C.<sup>101</sup> Their study found that Fe, cupronickel, and SS304 exhibited similar cathodic overpotentials, all higher than that of Ti. Notably, the highest  $\text{CH}_4$  yield (33.3%) was achieved with the cupronickel cathode, exceeding the yield from the standard Fe cathode (25.4%) despite its higher activity. This enhanced  $\text{CH}_4$  production from the cupronickel cathode is likely due to the synergistic electronic effects of Cu and Ni atoms, which improve the adsorption of reaction intermediates for  $\text{CH}_4$  production during electrolysis.

### 3.5. Production of $\text{C}_{2+}$

The electrochemical conversion of captured  $\text{CO}_2$  into  $\text{C}_{2+}$  products offers greater potential in terms of market size and value compared to  $\text{C}_1$  products. However, this area of research has not been as extensively explored. Lee *et al.* applied Cu/Ag bilayer electrodes with engineered bilayer cation- and anion-conducting ionomers to convert bicarbonate into  $\text{C}_{2+}$  products such as acetate, ethylene, ethanol, and propanol.<sup>102</sup> The *in situ* generated  $\text{CO}_2$  was first converted to CO on the Ag layer (Fig. 4a, indirect pathway), which was then efficiently transformed into  $\text{C}_{2+}$  products on the Cu layer, due to the locally concentrated CO. They achieved a maximum FE of  $41.6 \pm 0.4\%$  for  $\text{C}_{2+}$  products at a current density of 100  $\text{mA cm}^{-2}$ . Prajapati *et al.* developed a fully integrated system for  $\text{CO}_2$  capture and reduction using Cu mesh catalysts, achieving a steady-state  $\text{CO}_2$  reduction FE of 57% and a high FE of 40% for  $\text{C}_2\text{H}_4$  at a current density of 200  $\text{mA cm}^{-2}$  (see Section 5.2).<sup>129</sup>

Recently, Song *et al.* demonstrated the direct conversion of carbonate solutions to  $\text{C}_2\text{H}_4$  using a customized Cu–Ag catalyst in a BPM-MEA (membrane electrode assembly) setup. Although the carbonate electrolysis resulted in a relatively low FE of  $\sim 10\%$  for  $\text{C}_2\text{H}_4$  production, the Cu–Ag electrode configuration

effectively achieved nearly zero  $\text{CO}_2$  concentration in the outlet stream. Increasing the operating temperature to 50 °C further enhanced  $\text{C}_2\text{H}_4$  production, with a higher partial current density of 18–20  $\text{mA cm}^{-2}$  compared with 10  $\text{mA cm}^{-2}$  at room temperature.<sup>104</sup>

### 3.6. Production of carbon materials

In addition to the common products from  $\text{CO}_2$  reduction, valuable carbon materials, such as graphene and nanotubes, can be obtained in the electrochemical conversion of molten carbonate salt. The cathode's function as a substrate for carbon deposition affects the nucleation and growth of these carbon materials.<sup>130</sup> For example, a Zn galvanized steel cathode surface was shown to yield a high proportion of carbon nanofibers ( $>80\%$ ), a result not achievable with a 316 stainless steel cathode.<sup>131</sup>

Hu *et al.* successfully produced graphene using stainless steel as the cathode material in molten salt electrolysis.<sup>132</sup> They proposed that active Fe atoms on the cathode surface catalyze carbon growth, leading to the formation of  $\text{Fe}_3\text{C}$  as a key intermediate product. Subsequently, active Fe atoms are inserted into the interlayer of the graphene sheets, enabling continuous layer-by-layer growth through micro-explosion reactions in the interlayer space caused by the intense generation of CO. Moreover, different cathode materials were found to influence the structure of the carbon products, with Cu rods resulting in ball-structured graphene and Ni cathodes catalyzing the formation of flat graphene sheets.

Pint *et al.* demonstrated the electrochemical synthesis of carbon nanotubes from the capture and conversion of ambient  $\text{CO}_2$  using Fe as the cathode and further revealed a correlation between the thickness of the Fe metal layer and the diameter of the carbon nanotubes.<sup>133</sup> This highlights the importance of active metal atoms on the cathode as nucleation sites that catalyze the growth of carbon films.

### 3.7. Designing catalysts with $\text{CO}_2$ capture capability

Recently, a growing body of research has focused on using catalysts capable of capturing  $\text{CO}_2$ . In these studies, the capture and conversion of  $\text{CO}_2$  are integrated within the catalyst itself, eliminating the need to rely on the electrolyte. For example, Liu *et al.* demonstrated this by depositing amine-linked covalent organic frameworks (COFs) onto a flat Ag electrode.<sup>134</sup> They created a molecularly defined interface for the electrochemical reduction of  $\text{CO}_2$  to CO, achieving significantly higher efficiency and selectivity than a bare Ag electrode. This improved performance was attributed to the synergistic interaction between the COFs and the Ag electrode interface. The porous nature of the COFs facilitated  $\text{CO}_2$  diffusion to the electrode surface, while the amine functional groups near the electrode surface boosted the  $\text{CO}_2$  conversion efficiency by promoting the formation of a carbamate intermediate. Similar effects were observed in another study, where Liu *et al.* coated Ag nanoparticles with a thin 2 nm layer of 4-aminobutylphosphonic acid confined in poly(vinylpyrrolidone).<sup>135</sup>





Yan *et al.* used redox-active 2-amino-5-mercapto-1,3,4-thiadiazole (AMT) functionalized gold nanoparticles to achieve electrochemical carbon capture and conversion from flue gas.<sup>136</sup> The AMT ligand not only acts as a selective capture agent to concentrate CO<sub>2</sub> near the active site but also serves as a protective layer to inhibit O<sub>2</sub> reduction. As a result, a maximum FE<sub>CO</sub> of 80.2% at −0.45 V vs. RHE in an H-type cell and 66.0% at a voltage of 2.7 V in a full cell was achieved in simulated flue gas (15% CO<sub>2</sub>, 4% O<sub>2</sub>, balanced with N<sub>2</sub>). Notably, a microporous conductive Bi-based MOF (BiHHTP, HHTP = 2,3,6,7,10,11-hexahydroxytriphenylene) was recently reported to efficiently capture CO<sub>2</sub> from dilute sources under high humidity and catalyze the electroreduction of the adsorbed CO<sub>2</sub> into formic acid with a high current density of 80 mA cm<sup>−2</sup> and a FE of 90% at a low cell voltage of 2.6 V.<sup>137</sup> This high performance was attributed to the CO<sub>2</sub> capture capability of the micropores on BiHHTP and the lower Gibbs free energy of formation for the key intermediate \*OCHO on the exposed Bi sites.

Generally, amine-based molecules<sup>135,138,139</sup> and porous framework materials<sup>140–142</sup> are employed as agents for capturing CO<sub>2</sub>. The immobilization of amine groups onto the catalysts will enable the catalysts to concentrate CO<sub>2</sub> molecules near the active sites, thereby enhancing the electrochemical conversion of CO<sub>2</sub>. Furthermore, functional groups such as amines help stabilize key intermediates during CO<sub>2</sub> reduction, improving selectivity for specific products. Using catalysts with CO<sub>2</sub> capture capabilities is particularly valuable when dealing with flue gas, as it significantly suppresses the competing reduction of O<sub>2</sub>.

## 4. Reactor and system optimization

Besides the capture medium and the catalyst, several other factors influence the outcome of the electrochemical conversion of captured CO<sub>2</sub>, including the electrolyzer design, electrode configuration, ion exchange membranes, electrolyte with additives, and reaction conditions. This section will explore these aspects in detail.

### 4.1. Batch cell versus flow reactor

The electrochemical conversion of captured CO<sub>2</sub> can be conducted in a batch or flow process.<sup>143</sup> The conversion of molten carbonate has typically been carried out in an undivided cell equipped with heating elements under batch conditions, as high temperature is required for this process (Fig. 7a). At elevated temperatures, the electrolysis of molten carbonate can typically achieve a current density of 100–200 mA cm<sup>−2</sup> and a FE of 60–90% for carbonaceous products.<sup>108,144</sup> However, for the conversion of captured CO<sub>2</sub> in aqueous solution (such as bicarbonate and carbamate) at room temperature, both batch (*e.g.*, H-cell) and flow (*e.g.*, MEA) reactors have been used. Nonetheless, the reaction process and outcomes vary significantly depending on the type of reactor employed.

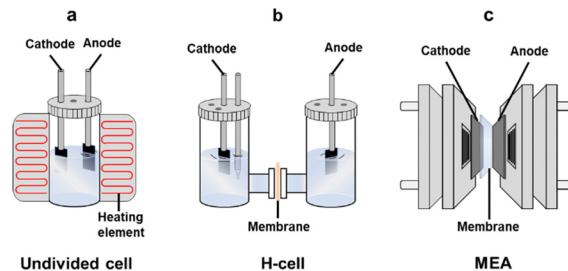


Fig. 7 Three types of reactors used for the electrochemical conversion of captured CO<sub>2</sub>: (a) an undivided cell for molten carbonate electrolysis at high temperatures, (b) an H-cell, and (c) an MEA for electrolysis of aqueous bicarbonate and carbamate solutions at room temperature.

In an H-cell, the potential can be easily adjusted to control the product distribution, but this setup typically achieves low current density and FE (Fig. 7b). For instance, Hu *et al.* carried out electrolysis of a KHCO<sub>3</sub> solution in an H-type cell using a hybrid catalyst composed of cobalt porphyrin and carbon nanotubes, achieving a current density of a few mA cm<sup>−2</sup> and FE<sub>CO</sub> of 18%.<sup>145</sup> This performance is much lower than that of gas-fed CO<sub>2</sub> conversion using the same H-cell with the same catalyst and is also significantly poorer than that achieved in an MEA setup. Similarly, Chen *et al.* conducted the electrochemical reduction of carbamate formed through CO<sub>2</sub> capture by 30% monoethanolamine solution in an H-cell using various smooth or porous metal electrodes, such as In, Sn, Bi, Pb, Pd, Ag, Cu, and Zn.<sup>146</sup> The highest FE<sub>CO</sub> and FE<sub>HCOO−</sub> reported were 39% and 45%, respectively, with current densities below 50 mA cm<sup>−2</sup>. These studies indicate that the electrochemical conversion performance of aqueous bicarbonate and carbamate solutions in an H-cell reactor is relatively low. This is due to the very low concentration of *in situ* liberated CO<sub>2</sub>, produced only from the dissociation of RNHCOO<sup>−</sup> or HCO<sub>3</sub><sup>−</sup> (reverse of eqn (1) and (2)), and the mass transport limitation of the liberated CO<sub>2</sub> in the H-cell.<sup>125</sup> The liberated CO<sub>2</sub> must diffuse through the reaction layer to be reduced at the electrode surface.<sup>146</sup>

The current density and FE can be significantly enhanced when converting captured CO<sub>2</sub> in flow reactors, such as MEA electrolyzers (Fig. 7c). This enhancement is due to the specific configuration within the MEA electrolyzers, which includes the CO<sub>2</sub>-captured electrolyte, catalyst layer, and membrane. Besides the dissociation of RNHCOO<sup>−</sup> or HCO<sub>3</sub><sup>−</sup>, a much higher concentration of CO<sub>2</sub> can be generated near the catalyst layer due to the reaction of RNHCOO<sup>−</sup> or HCO<sub>3</sub><sup>−</sup> with H<sup>+</sup> produced from the heterolytic dissociation of water at the BMP. As a result, most studies on captured CO<sub>2</sub> conversion have been conducted using MEA electrolyzers, achieving significantly higher FE up to 90% and larger current density up to 200 mA cm<sup>−2</sup> in some cases (Table 1).<sup>90,91,98</sup> These performance metrics are comparable to those achieved with gas-fed CO<sub>2</sub> conversion and are suitable for meeting the requirements of industrial applications.<sup>147,148</sup>

In summary, conducting the conversion of aqueous bicarbonate/carbamate solutions in an H-cell offers high flexibility and quick startup, but it often results in low overall efficiency.



In contrast, MEA electrolyzers operate with higher efficiency, leading to increased production rates, which makes them more advantageous for large-scale applications. The next section will further explore how the key components of MEA electrolyzers impact the performance of the electrochemical conversion of bicarbonate/carbamate solutions.

#### 4.2. Electrode configuration

In the electrochemical conversion of gas-fed  $\text{CO}_2$ , gas diffusion electrodes (GDEs) are required to achieve a large current density.<sup>149</sup> Increasing the hydrophobicity of GDEs can enhance performance, suppress the flooding of the electrodes, and thus maintain stability for  $\text{CO}_2$  electrolysis over a longer period.<sup>150,151</sup> However, the electrodes for the electrolysis of captured  $\text{CO}_2$  differ significantly from those typically employed for gaseous  $\text{CO}_2$  electrolysis because the source of  $\text{CO}_2$  is different. In general, a certain level of hydrophilicity is needed for these electrodes to ensure adequate contact between the catalyst on the electrode and the  $\text{CO}_2$ -captured solution, whether to facilitate the direct conversion of the  $\text{CO}_2$ -captured solution or reduction of the *in situ* generated  $\text{CO}_2$ .

Lees *et al.* systematically investigated the impact of electrode structure on the electrolysis of bicarbonate solutions using a Ag catalyst.<sup>76</sup> They found that adding hydrophobic polytetrafluoroethylene (PTFE), a microporous layer (MPL), or both, negatively affected bicarbonate electrolysis, significantly reducing  $\text{FE}_{\text{CO}}$ . The hydrophobic PTFE and MPL hinder the transport of solvated  $\text{HCO}_3^-$  ions through the GDE, thereby decreasing the rate of *in situ*  $\text{CO}_2$  generation at the electrode *via* the reaction of  $\text{HCO}_3^-$  with  $\text{H}^+$  from the bipolar membrane (eqn (22)). They also examined the effect of Nafion loading in the catalyst layer and observed that  $\text{FE}_{\text{CO}}$  initially increased to a plateau of  $\sim 58\%$  and then decreased as the Nafion loading increased at a current density of  $100 \text{ mA cm}^{-2}$ . The optimal Nafion loading was found to be 4.0 wt%. This behavior is likely due to variations in the catalyst layer morphology; lower Nafion loading leads to poor adhesion of the Ag catalyst to the electrode, while higher loading leads to a densified catalyst layer that blocks the pores of the gas diffusion layer. Similar behavior has been observed in the electrochemical conversion of gas-fed  $\text{CO}_2$ .<sup>152</sup> By removing the hydrophobic components of the GDE and optimizing the catalyst coverage, optimal performance for bicarbonate electrolysis was achieved, with a  $\text{FE}_{\text{CO}}$  of 82% at  $100 \text{ mA cm}^{-2}$ .

Based on this understanding, the same group developed a free-standing porous Ag electrode, which demonstrated higher hydrophilicity than the commonly used GDE and could be more easily integrated into commercial electrolyzers.<sup>79</sup> As a result, the free-standing Ag electrode achieved a respectable  $\text{FE}_{\text{CO}}$  of 59% at  $100 \text{ mA cm}^{-2}$  under ambient pressure for converting 3 M  $\text{KHCO}_3$ .

Later, Lee *et al.* successfully modeled the generation, diffusion, and consumption of chemical species, identifying an optimal electrode architecture for the electrochemical conversion of carbonate solution to  $\text{C}_{2+}$  products over a Cu catalyst.<sup>103</sup> Their modeling results showed that the spacing distance

between the cation exchange layer (CEL) and the catalyst layer (CL) influenced the concentrations of  $\text{CO}_3^{2-}$ ,  $\text{H}^+$ , *in situ* generated  $\text{CO}_2(\text{g})$ , and  $\text{CO}_2(\text{aq.})$  in the carbonate solution (Fig. 8). When the CEL and the CL were closely spaced, the local pH at the CEL decreased to no more than 10, as the diffusion of  $\text{CO}_3^{2-}$  and  $\text{OH}^-$  could easily neutralize the  $\text{H}^+$  coming from the CEL. This prevented the *in situ* generation of  $\text{CO}_2(\text{g})$  or products during electrolysis. However, when the spacing distance between the CEL and the CL was in the range of 100–300  $\mu\text{m}$ , optimal conditions for converting carbonate to  $\text{C}_{2+}$  products could be achieved, with a low pH ( $< 4$ ) at the CEL, promoting the *in situ* generation of a high concentration of  $\text{CO}_2(\text{g})$  ( $> 4 \text{ vol}\%$ ) at the CL. Despite this, the pH remained  $> 13$  at the CL, as  $\text{OH}^-$  was continuously produced by the conversion of the *in situ* generated  $\text{CO}_2(\text{g})$  from carbonate. The high local pH favored the C–C coupling to form  $\text{C}_{2+}$  products over  $\text{C}_1$  products. Finally, increasing the spacing distance to  $> 540 \mu\text{m}$  decreased the concentration of  $\text{CO}_2(\text{g})$  and hindered the carbonate conversion due to the increased likelihood of  $\text{CO}_2$  being recaptured over the extended layer distance.

Based on this modeling, the authors used a porous hydrophilic mixed cellulose ester as an interposer to create a well-defined spacing between the CEL and the CL. The electrolysis of carbonate solutions at  $250 \text{ mA cm}^{-2}$  over a Cu catalyst using an interposer thickness of 130–270  $\mu\text{m}$  increased  $\text{FE}_{\text{C}_{2+}}$  to 40%. This was three times larger than with an interposer thickness of 60  $\mu\text{m}$  ( $\text{FE}_{\text{C}_{2+}} = 14\%$ ) and nearly twice as high as observed in the 540  $\mu\text{m}$  case ( $\text{FE}_{\text{C}_{2+}} = 25\%$ ). These results highlight the critical role of electrode configuration design in enhancing the selective electrochemical conversion of carbonate solution to  $\text{C}_{2+}$  products.

#### 4.3. Ion exchange membrane

Ion exchange membranes serve as separators and regulate ion transport between the cathodic and anodic chambers of the electrolyzer. The choice of ion exchange membrane has a significant impact on the electrolysis process (Fig. 9). BPMs are widely used in the electrochemical conversion of bicarbonate solutions because  $\text{HCO}_3^-$  can react with the  $\text{H}^+$  produced by the BPM to generate *in situ*  $\text{CO}_2$  at the BPM–electrode interface (eqn (22)). The *in situ* generated  $\text{CO}_2$  subsequently receives electrons from the electrode and undergoes reduction to produce various value-added products such as CO, formate, and  $\text{C}_2\text{H}_4$ . Using BPMs for bicarbonate conversion offers several benefits, including rapid water dissociation, minimized crossover of generated products, and extended operational lifespan.<sup>153</sup> However, employing BPMs requires an additional potential of 0.83 V for  $\text{H}^+$  generation *via* water dissociation under standard conditions, resulting in a large overpotential, increased energy consumption, and reduced energy efficiency.

Replacing the BPM with an anion exchange membrane (AEM) or a cation exchange membrane (CEM) can lower the cell voltage but may negatively impact the conversion efficiency. Li *et al.* found that an electrolysis cell with a BPM showed a higher  $\text{FE}_{\text{formate}}$  (+35%) for  $\text{KHCO}_3$  conversion than a corresponding AEM cell, which was attributed to the higher local  $\text{CO}_2$



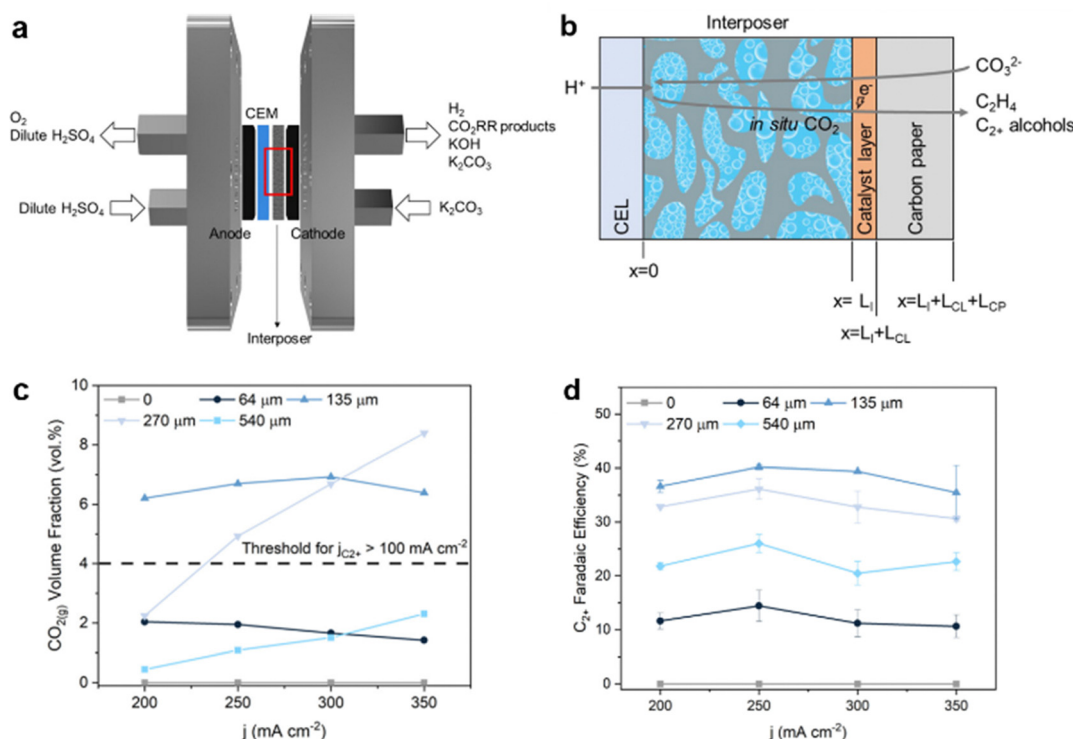


Fig. 8 (a) MEA electrolyzer for aqueous carbonate conversion, where the cathode and anode are separated by an interposer. (b) Schematic of the cathode configuration, including the cation-exchange layer (CEL), the interposer, catalyst layer, and carbon paper. (c) CO<sub>2</sub>(g) volume fraction for different spacing ( $L_i$ ) conditions, *i.e.*, 0, 64, 135, and 540 μm at current densities of 200, 250, 300, and 350 mA cm<sup>-2</sup> in 1.5 M K<sub>2</sub>CO<sub>3</sub> electrolyte. (d) FE of C<sub>2</sub>+ products in carbonate electrolysis using a Cu electrocatalyst in 1.5 M K<sub>2</sub>CO<sub>3</sub> electrolyte with various interposer thicknesses from 0–540 μm. Reproduced with permission from ref. 103.

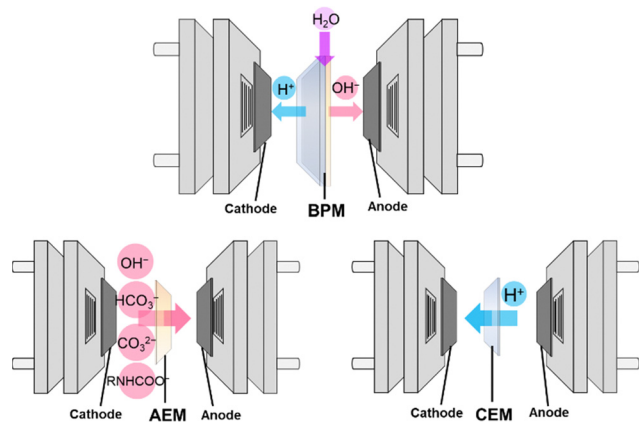


Fig. 9 Schematic illustration of three typical types of ion exchange membranes used in electrochemical conversion of captured CO<sub>2</sub>.

concentration at the electrode in the BPM system.<sup>93</sup> In the AEM cell, CO<sub>2</sub> was formed only through the bicarbonate dissociation equilibrium (reverse of eqn (2)). However, the trend reversed when using a different bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>) solution, where replacing the BPM with the AEM resulted in an increased FE<sub>formate</sub>.<sup>94</sup> This was explained by the favorable microenvironment created by NH<sub>4</sub><sup>+</sup>, which would suppress the HER at the electrode–membrane interface. It is important to note that

formate crossover could be observed in the AEM cell, as AEMs are designed for anion exchange.<sup>154</sup>

Utilizing a CEM can also create an acidic environment at the cathode–membrane interface, as protons are generated from water oxidation (*i.e.*, the oxygen evolution reaction (OER)) or the acidic electrolyte in the anodic chamber permeating through the membrane.<sup>103</sup> These protons can react with the captured CO<sub>2</sub> (in the form of bicarbonate or carbamate) to produce high local concentrations of free CO<sub>2</sub> near the catalyst layer, thereby enhancing the electrolysis efficiency. To ensure effective proton transport through the CEM, it is crucial to maintain a neutral or acidic electrolyte in the anodic chamber. However, this condition makes the OER more challenging, requiring a larger overpotential.<sup>155</sup> To address this issue, Zhang *et al.* conducted the hydrogen oxidation reaction at the anode instead of the conventional OER during electrolysis of 3 M KHCO<sub>3</sub> and used a CEM in place of the BPM. This approach allowed them to produce CO at a high partial current density of 220 mA cm<sup>-2</sup> at a cell voltage of only 2.3 V.<sup>80</sup>

#### 4.4. Electrolyte with additives

As highlighted in the preceding section, the distance between the reactant and the electrode has a crucial impact on the reaction outcomes. Consequently, using a CO<sub>2</sub>-captured amine solution as the electrolyte presents efficiency challenges, unlike





converting the bicarbonate solution. This disparity arises because the bulky carbamate ( $\text{RNHCOO}^-$ ) and ammonium ( $\text{RNH}_3^+$ ) ions impede mass transport at the electrochemical double layer (EDL).

To address this issue, Khurram *et al.* investigated the introduction of various electrolyte salts, including  $\text{LiPF}_6$ ,  $\text{LiClO}_4$ ,  $\text{NaClO}_4$ ,  $\text{KClO}_4$ , and  $\text{TBAClO}_4$ , into  $\text{CO}_2$ -captured amine solutions in dimethyl sulfoxide.<sup>156</sup> They observed that while the anions had a minor impact, the cations significantly influenced the speciation of amine- $\text{CO}_2$  adducts. Specifically, pairing the  $\text{K}^+$  cation with  $\text{RNHCOO}^-$  could enhance the rates of electrochemical reactions due to improved  $\text{K}^+$  transfer from the bulk solution to the reaction site. Therefore, the judicious selection of strong electrolyte salt that facilitates rapid cation transfer is essential for achieving high efficiency in converting amine-captured  $\text{CO}_2$ .

Later, Lee *et al.* demonstrated that introducing alkali metal ions into the aqueous  $\text{CO}_2$ -captured amine solution could significantly improve the electrochemical conversion of the amine- $\text{CO}_2$  adduct (carbamate).<sup>85</sup> They proposed that the alkali cations (*e.g.*,  $\text{K}^+$ ) modified the EDL to facilitate the heterogeneous electron transfer from the catalyst to the carbamate (Fig. 10a). Using this approach, efficient conversion of the carbamate to CO was achieved with a Ag catalyst, resulting in a  $\text{FE}_{\text{CO}} = 72\%$  at  $50 \text{ mA cm}^{-2}$ .

Surfactants exert a large influence on the efficiency of gas-fed  $\text{CO}_2$  conversion,<sup>157,158</sup> as well as the electrochemical conversion of captured  $\text{CO}_2$ . Chen *et al.* reported that adding the

cationic surfactant, CTAB, suppressed the competing HER, thereby greatly enhancing the conversion of carbamate derived from the  $\text{CO}_2$  capture by monoethanolamine (Fig. 10b).<sup>146</sup> This enhancement was evident in the increase of  $\text{FE}_{\text{formate}}$  from 2.4% to 45.4% over an In electrode. In contrast, other surfactants, such as sodium dodecylsulfate (anionic) and TritonX-100 (non-ionic), showed a negligible effect, indicating that the performance of the carbamate conversion depends on the type of surfactant added. Ahmad *et al.* found that adding CTAB to the  $\text{CO}_2$ -captured 2-amino-2-methyl-1-propanol solution increased the  $\text{FE}_{\text{CO}}$  over a Cl-modified polycrystalline Ag electrode due to a more compact EDL.<sup>86</sup> Similarly, for the conversion of a bicarbonate solution, Lees *et al.* observed that the presence of just 3 mM CTAB increased the  $\text{CO}_2$  reduction current density from 11 to  $162 \text{ mA cm}^{-2}$  and the  $\text{FE}_{\text{CH}_4}$  from 0 to 27% at an applied current density of  $400 \text{ mA cm}^{-2}$ .<sup>98</sup> This performance improvement was attributed to reduced oxide coverage on the Cu electrode during electrolysis when CTAB was added.

#### 4.5. Operation parameters

The concentration of the captured  $\text{CO}_2$  significantly impacts the electrochemical performance of the system. For bicarbonate conversion, higher concentrations lead to higher FE of carbonaceous products.<sup>93</sup> Increasing the bicarbonate concentration accelerates the rate at which  $\text{HCO}_3^-$  dissociates and reacts with  $\text{H}^+$  from the membrane to liberate  $\text{CO}_2$ . Thus, a high

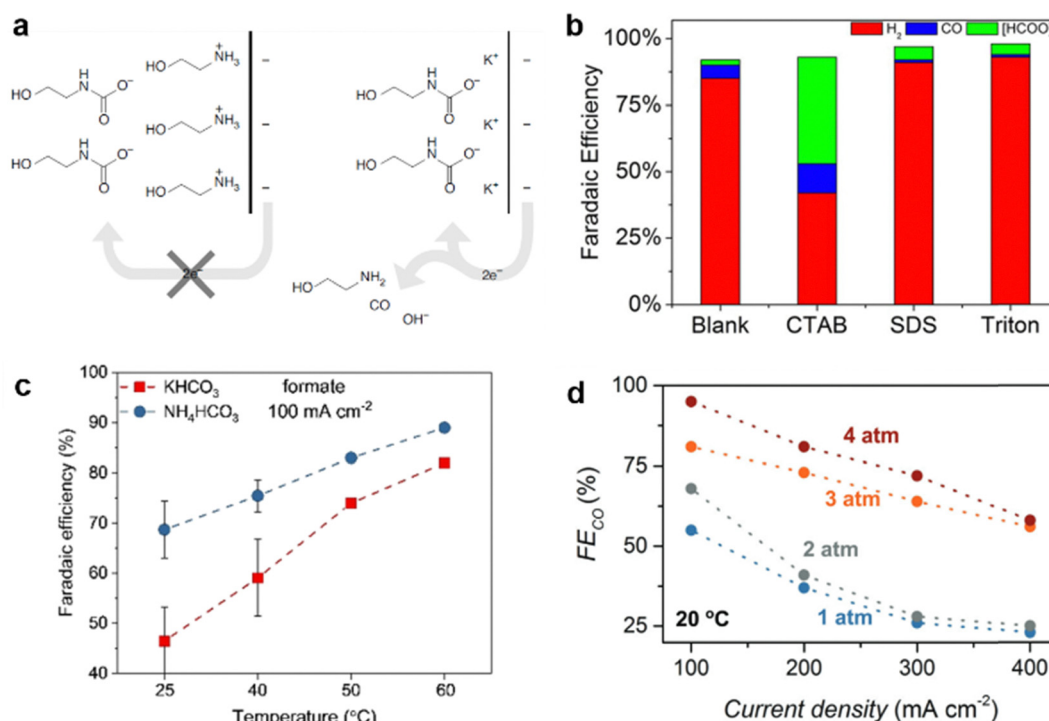


Fig. 10 Effect of (a) strong electrolyte KCl (reproduced with permission from ref. 85), (b) surfactant (reproduced with permission from ref. 146), (c) temperature (reproduced with permission from ref. 94), and (d) pressure (reproduced with permission from ref. 79) on the conversion of aqueous carbamate or bicarbonate solution.



concentration (3 M, near saturation) is typically used for bicarbonate conversion.

Temperature can influence the performance of bicarbonate conversion in several ways. First, increasing the temperature of the electrolyte is expected to promote  $\text{CO}_2$  generation by shifting the bicarbonate equilibrium toward  $\text{CO}_2$  (reverse of eqn (2)). Moreover, a temperature rise causes an increase in pH due to the formation of  $\text{OH}^-$ , which suppresses the HER. Raising the temperature also enhances mass transport, thereby accelerating the electrochemical process. This effect has been observed in numerous studies, resulting in improved FE for forming carbonaceous products (Fig. 10c).<sup>79,94</sup> Similarly, the effect of the temperature was exploited in the conversion of  $\text{CO}_2$ -captured amine (carbamate) solutions. Pérez-Gallent *et al.* reported that the reaction rate of the conversion of  $\text{CO}_2$ -captured 2-amino-2-methyl-1-propanol in a propylene carbonate solution was significantly enhanced when the temperature was raised from 15 to 75 °C.<sup>87</sup> The increase in reaction rate was attributed to the much faster liberation of  $\text{CO}_2$  at elevated temperatures, which was eight times higher at 75 °C than at 15 °C.

The effect of temperature becomes more complex in the electrochemical conversion of molten carbonate salts. Deng *et al.* reported that the electrolysis of  $\text{CaCO}_3$ -containing molten  $\text{LiCl-KCl}$  over a Ni electrode produced carbon materials with various shapes and morphologies.<sup>159</sup> At 450 °C, micron-sized hollow carbon spheres and ultrathin carbon sheets were the major products, depending on the applied cell voltage. As the temperature increased to 550 and 650 °C, a range of other carbon materials, such as quasi-spherical carbon particles, coral-like carbon, and carbon nanofibers, were formed. In a subsequent study, it was demonstrated that raising the operational temperature led to an increase in current density or a reduction in cell voltage for the conversion of  $\text{CaCO}_3$  in the  $\text{LiCl-KCl}$  melt.<sup>160</sup> These conditions facilitated the dissolution of both the reactant  $\text{CaCO}_3$  and the product  $\text{CaO}$  in the melt, thereby preventing the accumulation of solid  $\text{CaO}$  on the electrode. As a result, the process exhibited greater durability and energy efficiency. The energy consumption for producing 1 kg of carbon was calculated to be 16.3 kW h  $\text{kg}^{-1}$  at 650 °C, compared with 31.4 kW h  $\text{kg}^{-1}$  at 450 °C.

Zhang *et al.* demonstrated that pressure, in addition to temperature, affects the performance of bicarbonate conversion (Fig. 10d).<sup>79</sup> When the inlet pressure of the electrolyzer was increased from 1 to 4 atm,  $\text{FE}_{\text{CO}}$  increased from 55% to 95%, and the cathodic energy efficiency from 22% to 34% at a current density of 100  $\text{mA cm}^{-2}$ . At 4 atm pressure, an impressive current density of 400  $\text{mA cm}^{-2}$  for bicarbonate conversion with  $\text{FE}_{\text{CO}} > 55\%$  could be achieved. This performance enhancement was attributed to the kinetically improved supply of  $\text{CO}_2$  to the catalyst at elevated pressures.

The authors also explored how the electrolyte flow rate influenced the performance of bicarbonate conversion. They increased the flow rate from 30 to 100  $\text{mL min}^{-1}$ , which led to an increase in *in situ* generated  $\text{CO}_2$  and, consequently, a higher  $\text{FE}_{\text{CO}}$ . This effect was attributed to the enhanced convective mass transport of  $\text{HCO}_3^-$ . Building on this finding, they

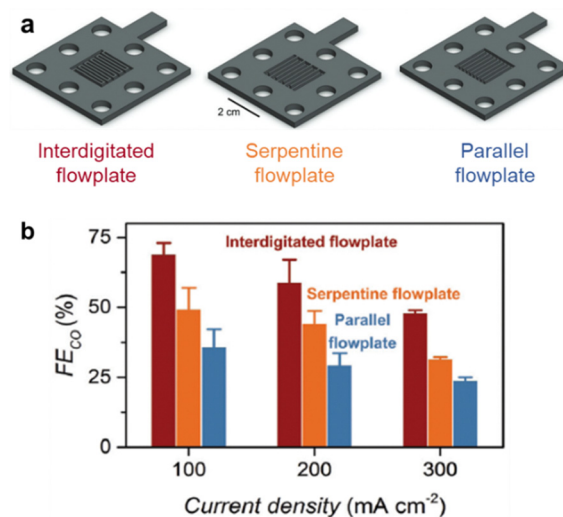


Fig. 11 (a) Interdigitated, serpentine, and parallel cathodic flow plate designs used in bicarbonate electrolysis. (b)  $\text{FE}_{\text{CO}}$  as a function of current density for interdigitated, serpentine, and parallel flow plates tested in a bicarbonate electrolyzer equipped with porous silver electrodes. Reproduced with permission from ref. 79.

modified the flow plate geometry to further enhance convective mass transport. Three types of flow plates were tested, *i.e.* interdigitated, serpentine, and parallel (Fig. 11). Convection was the primary mode of mass transport in the interdigitated flow plate, while diffusion was dominant in the parallel and serpentine flow plates. As a result, the electrolyzer with the interdigitated flow pattern exhibited higher  $\text{FE}_{\text{CO}}$  ( $\approx 69\%$  at 100  $\text{mA cm}^{-2}$ ) compared to the other two. These results demonstrate that enhancing the convective mass transport can increase  $\text{FE}_{\text{CO}}$  significantly for converting captured  $\text{CO}_2$ .

## 5. Practical integration of $\text{CO}_2$ capture and conversion

In this section, we present practical examples that fully integrate the two processes of  $\text{CO}_2$  capture and electrochemical conversion (Fig. 1, Route 3). We begin by examining technologies based on different  $\text{CO}_2$  sources, including air,<sup>161,162</sup> flue gas,<sup>163,164</sup> and ocean water,<sup>165,166</sup> as these sources significantly influence the outcome of the integration due to differences in  $\text{CO}_2$  concentration and purity.

### 5.1. Conversion of captured $\text{CO}_2$ from various sources

**5.1.1. Air.**  $\text{CO}_2$  in the atmosphere can be captured and utilized through DAC technologies. In the earth's atmosphere,  $\text{CO}_2$  constitutes  $\sim 400$  ppm. Although this concentration has devastating climate impacts, it is relatively low in absolute terms, imposing an entropy penalty on DAC technologies. The minimum energy required to separate a stream of air with a  $\text{CO}_2$  concentration of 400 ppm into one stream with 200 ppm  $\text{CO}_2$  and another with 99%  $\text{CO}_2$ , all at the same temperature and pressure, is about 20  $\text{kJ mol}^{-1}$ .<sup>35</sup> However, the efficiency of real-world DAC technologies is likely to be limited to



$\sim 5\%$ .<sup>167</sup> Therefore, the energy requirement to achieve a 99% concentration of captured  $\text{CO}_2$  that can be effectively converted electrochemically is  $\sim 400 \text{ kJ mol-CO}_2^{-1}$ .

If conventional energy sources such as coal were used to power a DAC system with 5% efficiency, there would be no net  $\text{CO}_2$  capture, as producing the required 400 kJ to capture one mol of  $\text{CO}_2$  would generate 2.5 moles of  $\text{CO}_2$ . This is also true for natural gas, the least carbon-intensive fossil fuel, which emits one mol of  $\text{CO}_2$  while generating 396 kJ of energy. Therefore,  $\text{CO}_2$ -free power sources such as nuclear, wind, solar, and hydro must drive air capture systems. For example, the energy requirement of  $400 \text{ kJ mol-CO}_2^{-1}$  is equivalent to  $\sim 2500 \text{ kW h t-CO}_2^{-1}$ , which could be provided by a large 3 MW wind turbine operating for 1 h.

Integrating the  $\text{CO}_2$  capture and electrochemical conversion processes is challenging because the rate of capture is usually much lower than the achievable rate of conversion. A study exemplifying this issue involved absorbing atmospheric  $\text{CO}_2$  over 8.5 h using an alkaline solution (1 M KOH), resulting in the formation of a bicarbonate/carbonate mixture (Fig. 12).<sup>84</sup> This solution was then used as the catholyte in a zero-gap flow electrolyzer to produce industrially significant carbon products. At a current density of  $50 \text{ mA cm}^{-2}$ , a  $\text{FE}_{\text{formate}}$  of 16% (using  $\text{SnO}_2/\text{C}$  as the electrocatalyst) and  $\text{FE}_{\text{CO}}$  of 13% (using  $\text{Ag}/\text{C}$ ) were achieved. To improve electrochemical performance, it would be necessary to capture higher concentrations of  $\text{CO}_2$  by increasing the base concentration and/or extending the absorption period. From an economic perspective, this

would reduce the attractiveness of integrating the two technologies.

Recently, Almajed *et al.* evaluated the feasibility of directly integrating DAC with (bi)carbonate electrolysis using KOH and  $\text{K}_2\text{CO}_3$  solutions as the capture media (Fig. 13a).<sup>168</sup> They found that the presence of  $\text{CO}_3^{2-}$  alongside  $\text{HCO}_3^-$  in the effluent from the air contactor significantly reduced electrolysis performance due to incomplete  $\text{CO}_2$  capture, ultimately decreasing the  $\text{CO}_2$  capture fraction from 78% to  $\leq 1\%$ . As a result, they estimated that air contractors would need to be 5–14 times larger than those typically required for DAC to produce suitable effluents for (bi)carbonate electrolysis, leading to unfavorable process economics. Furthermore, they demonstrated that regenerating the capture media after the electrolysis was insufficient for effective  $\text{CO}_2$  recapture. This incompatibility between DAC and (bi)carbonate electrolysis was attributed to the mismatched pH values between the air contactor outlet/electrolyzer inlet and the air contactor inlet/electrolyzer outlet. To resolve this issue, the authors suggested acidifying the air contactor effluent and basifying the electrolyzer effluent by incorporating an electrodialysis unit or directly feeding acidic/basic streams to the respective effluents (Fig. 13b). However, this approach would inevitably increase both capital and operational costs.

The third example concerns molten metal oxides, such as  $\text{Li}_2\text{O}$ , which have shown potential for directly sequestering  $\text{CO}_2$  from the air at elevated temperatures, resulting in the formation of carbonate salts.<sup>131</sup> These carbonates can then undergo electrochemical reduction, producing solid carbon

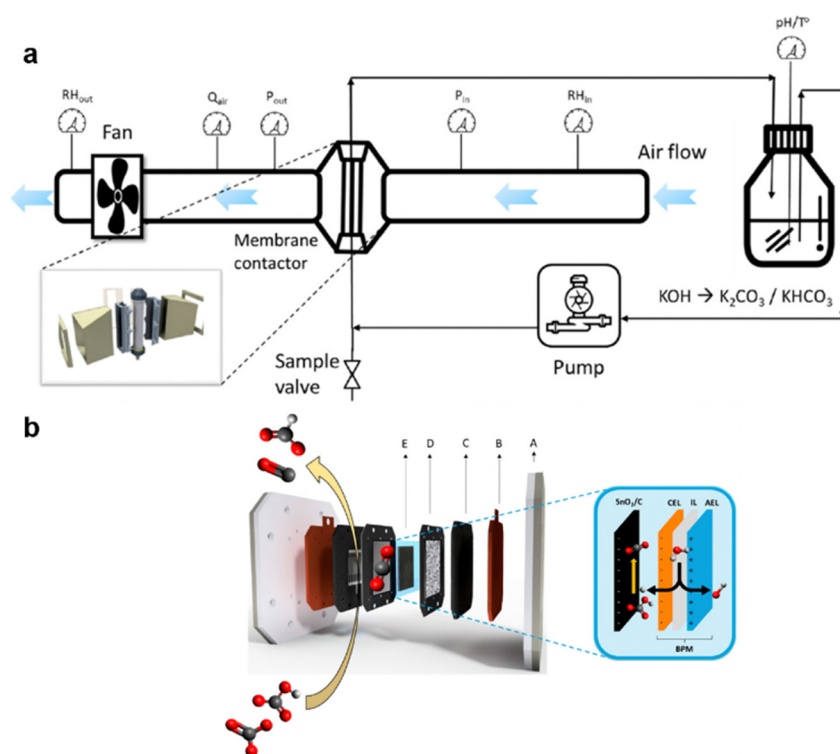
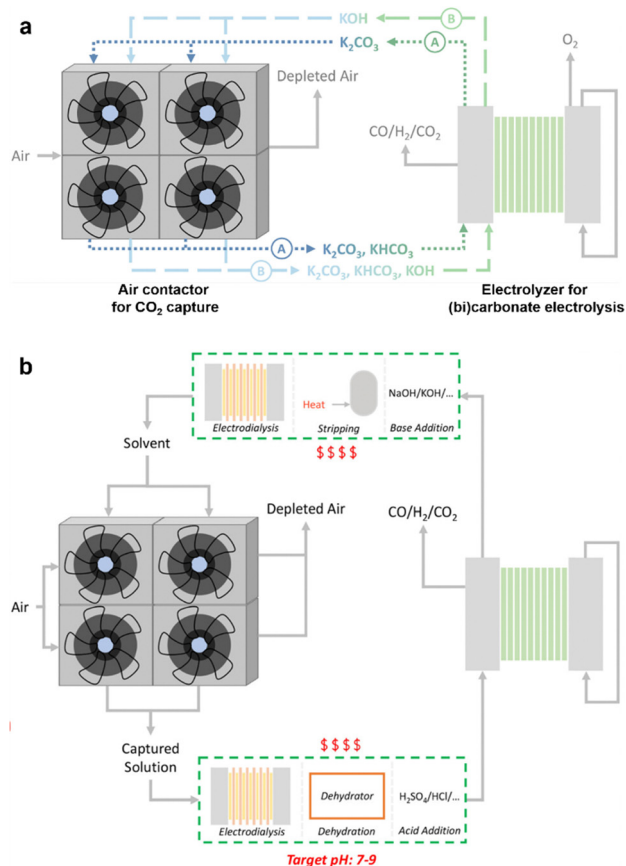


Fig. 12 Integration of atmospheric  $\text{CO}_2$  capture and the subsequent electrochemical conversion of the captured  $\text{CO}_2$ : (a) diagram of the  $\text{CO}_2$  capture setup and (b) the electrolytic cell for converting captured  $\text{CO}_2$ . Reproduced with permission from ref. 84.







**Fig. 13** Schematic of the integration route proposed in the literature, with the air contactors on the left and the electrolyzer stacks on the right. (a) The two pathways for CO<sub>2</sub> capture from the air are (A) K<sub>2</sub>CO<sub>3</sub>-based and (B) KOH-based. (b) Potential solutions to address the different pH requirements of the capture and conversion processes are shown inside the green dashed boxes at the top and bottom. Reproduced with permission from ref. 168.

on and attached to the cathode and oxygen at the anode. This process has been demonstrated on a laboratory scale to successfully convert ambient air into carbon and oxygen, producing, e.g., 10 g h<sup>-1</sup> of carbon nanofibers at 100 A.

These examples highlight the feasibility of integrating electrochemical conversion with CO<sub>2</sub> capture from the air. However, the efficiency of the integration is currently not satisfactory due to the slow CO<sub>2</sub> capture. One approach to overcome this limitation is to use a significantly larger amount of capture agent while vigorously feeding air into the solution under stirring. Alternatively, existing methods could be suitable for small, decentralized units with minimal time constraints. Integrating electrochemical conversion with DAC technology provides the flexibility to be deployed anywhere, making it ideal for reducing emissions from dispersed sources when combined with renewable energy for power generation. Nevertheless, the widespread implementation of DAC infrastructure presents challenges, including substantial investment and land use. Furthermore, DAC technology is relatively new and less mature, which may pose hurdles regarding scalability and cost-effectiveness, at least in the short term.

**5.1.2. Flue gas.** Flue gas refers to emissions from industrial operations, power generation, and combustion processes. The CO<sub>2</sub> content in flue gases is 2–3 orders of magnitude higher than in the atmosphere, depending on the fuel sources, such as coal (12–15% CO<sub>2</sub>) and natural gas (3–4% CO<sub>2</sub>). Consequently, the minimum energy input required to concentrate CO<sub>2</sub> in flue gas to a highly concentrated stream is reduced by a factor of three with respect to DAC systems. Therefore, extracting CO<sub>2</sub> from flue gas is more efficient than from the atmosphere, making it a promising approach for reducing CO<sub>2</sub> emissions.

In most cases, the capture agents and methodologies developed for DAC can also be applied to flue gas and *vice versa*. This is similarly true for the integrated CO<sub>2</sub> capture and conversion approach. However, significant amounts of gas impurities in flue gas, such as NO<sub>x</sub> and SO<sub>x</sub>, can cause considerable inefficiencies and increase cost, as they may interfere with both the capture and the conversion processes. For example, removing SO<sub>2</sub> from flue gas by converting it into CaSO<sub>3</sub> requires a substantial energy input of 380 kJ mol<sup>-1</sup>.<sup>169</sup> Removing NO<sub>x</sub> involves its selective reduction to N<sub>2</sub> over a supported vanadia catalyst using ammonia as a reductant. Although this chemical reaction is exergonic, ~500 kJ of energy is required per mol of NO<sub>x</sub> removed in commercial systems.<sup>169</sup>

Most studies on the electrochemical conversion of flue gas neglect these impurities by using simulated flue gas, which consists of a variable mixture of CO<sub>2</sub> and usually N<sub>2</sub>. In general, the risk of interference from acidic impurities like SO<sub>2</sub> and NO<sub>2</sub> is minimal when CO<sub>2</sub> is captured using alkaline (bi)carbonate solutions, as these can neutralize such impurities.<sup>36,170,171</sup> Among the NO<sub>x</sub> gases, the relatively inert NO is usually the predominant component, requiring oxidation to NO<sub>2</sub> using, e.g., hydrogen peroxide for effective removal.<sup>170</sup> Unfortunately, even small amounts of impurities can negatively impact catalyst performance and, consequently, the conversion process. Therefore, several studies on gas-fed CO<sub>2</sub> have thoroughly investigated this issue, with findings highly relevant for integrated processes, especially those involving *in situ* generated CO<sub>2</sub>.

Ko *et al.* examined the influence of NO<sub>x</sub> on Cu, Ag, and Sn catalysts by introducing 8300 ppm NO into a CO<sub>2</sub> stream.<sup>172</sup> For Ag and Sn catalysts, NO reduction reactions reduced FE by 35%. Similarly, introducing 10 000 ppm SO<sub>x</sub> led to a decrease in FE by 25–40% when targeting CO or formate.<sup>173</sup> In both cases, the catalytic efficiency was restored upon reintroducing a pure CO<sub>2</sub> stream into the reactor. For the Cu catalyst, a significant shift in selectivity toward formate was observed, along with a decrease in the production of C<sub>2+</sub> products, highlighting Cu's high sensitivity to SO<sub>2</sub> impurities.<sup>173</sup>

Removing these impurities beforehand may be necessary, although it often requires a combination of specialized and expensive technologies for each impurity. A more effective approach would be to develop catalysts that can tolerate these impurities. This was demonstrated in a study,<sup>174</sup> where stability experiments were conducted with the presence of ~200 ppm SO<sub>2</sub> or NO in the feed gas stream using Bi<sub>2</sub>O<sub>3</sub> (producing formate) and Ag (producing CO) as catalysts. Encouragingly,



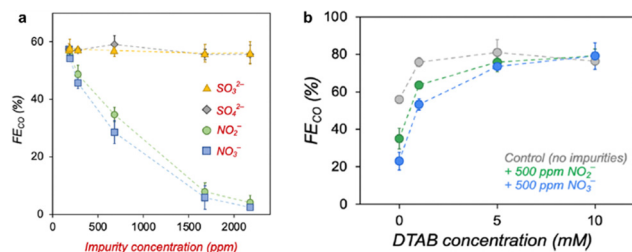


Fig. 14  $FE_{CO}$  for electrolysis of 3 M  $KHCO_3$  solution at  $100 \text{ mA cm}^{-2}$  using a porous silver foam cathode with (a) 0–2000 ppm of flue gas impurities and (b) as a function of DTAB concentration. Reproduced with permission from ref. 81.

the results showed consistent performance and high FE ( $>90\%$ ) for both catalysts toward the target products over 20 h.

Zhang *et al.* evaluated the effects of nitrogen and sulfur contaminants ( $NH_4^+$ ,  $NO_3^-$ ,  $SO_4^{2-}$ , and  $SO_3^{2-}$ ) on the catalytic performance of a porous silver electrode for the conversion of 3 M bicarbonate.<sup>79</sup> At concentrations of 100 ppm for these ions, there was no significant effect on  $FE_{CO}$  or  $FE_{H_2}$ , except for  $NO_3^-$ , which reduced  $FE_{CO}$  from 56% to 28%. At 500 ppm  $NO_3^-$ , no CO or  $H_2$  was produced due to the competitive reduction of  $NO_3^-$ . Later, Pimlott *et al.* conducted a detailed study on the impact of nitrogen- and sulfur-containing impurities at varying concentrations.<sup>81</sup> They observed that adding anions such as  $SO_4^{2-}$  and  $SO_3^{2-}$  (originating from  $SO_x$  impurities) in 3 M  $KHCO_3$ , had no impact on product formation (Fig. 14a). In contrast, dissolved  $NO_2^-$  and  $NO_3^-$  ions (originating from  $NO_x$  impurities) at a concentration of 2000 ppm in the same electrolyte reduced  $FE_{CO}$  by up to 55% at a current density of  $100 \text{ mA cm}^{-2}$ . This decrease in  $FE_{CO}$  was attributed to the relatively more positive electrochemical potentials at which  $NO_x$  anions are reduced compared to  $CO_2$ , rather than catalyst degradation. Switching to a fresh  $KHCO_3$  solution restored performance, indicating minimal long-term impact from  $NO_3^-$ . This demonstrates that direct bicarbonate conversion is more tolerant to impurities than gaseous  $CO_2$  conversion.

An alternative strategy to minimize the impact of  $NO_x$  impurities is to remove  $NO_2^-$  and  $NO_3^-$  from the bicarbonate solutions before they reach the electrolyzer, using methods such as reverse osmosis, ion exchange, distillation, or bionitrification.<sup>175</sup> However, these processes can be cumbersome. To address this, Pimlott *et al.* demonstrated that adding surfactants like 10 mM dodecyltrimethylammonium bromide (DTAB) to the bicarbonate solution suppressed the reduction of aqueous  $NO_x$  impurities and increased the  $FE_{CO}$  from 56% to 80% at  $100 \text{ mA cm}^{-2}$ , even slightly higher than without impurities (Fig. 14b).<sup>81</sup> This improvement occurs because the surfactant's alkyl chains suppress the HER and increase the local  $CO_2$  concentration by displacing ions near the catalyst surface.<sup>157,176</sup> From this perspective, adding surfactants to the electrolyte solution could be a cost-effective way to mitigate the poisonous effects of anionic contaminants during the conversion of captured  $CO_2$ .

Understanding the effect of oxygen on the electrochemical conversion process is crucial, given that it is often present in

flue gas streams at concentrations of several percent. A recent study examined an electrolyzer supplied with either  $CO_2$  or bicarbonate.<sup>177</sup> When 10%  $O_2$  was introduced into the  $CO_2$  stream entering a gas-fed electrolyzer, CO selectivity decreased by over 90%. In contrast, the presence of  $O_2$  in the bicarbonate solution did not affect the performance of a liquid-fed electrolyzer. Regardless of the  $O_2$  concentration in the gas streams (ranging from 0–100%), the conversion of bicarbonate solutions consistently produced CO at a Ag/C electrode with a  $FE_{CO}$  of  $\sim 65\%$  at a current density of  $100 \text{ mA cm}^{-2}$ . This indifference to  $O_2$  is a very encouraging result for integrated  $CO_2$  capture and electrochemical conversion. Nonetheless, a potential strategy to mitigate the adverse effects of  $O_2$ , even for the feed-stream approach, is to operate the electrolyzer at a high total current density to ensure all  $O_2$  at the electrode is reduced. Although this approach entails higher electricity usage, the associated costs appear negligible for low  $O_2$ -containing feed streams ( $\leq 3\%$   $O_2$ ) at  $300 \text{ mA cm}^{-2}$ .<sup>174</sup>

Many industrial factories already have infrastructure for capturing and processing flue gas, which facilitates the integration of  $CO_2$  capture with conversion. However, this does not change the fact that implementing  $CO_2$  conversion technologies in industrial settings requires significant initial investments in infrastructure and equipment. Another limitation of flue gas capture is that it is confined to areas with substantial industrial activity, making it ineffective for addressing  $CO_2$  emissions from dispersed sources such as transportation, buildings, or agriculture.

**5.1.3. Ocean.** The ocean acts as a major reservoir for carbon, absorbing  $CO_2$  from the atmosphere through oceanic carbon sequestration. Dissolved  $CO_2$  levels in surface ocean waters vary depending on factors such as temperature, pressure, and biological activity, with an average concentration of  $\sim 50$  times greater than in the air. Ocean capture can be achieved using natural seawater or through alkalinity enhancement, where seawater is treated with alkaline substances to increase its capacity to absorb  $CO_2$ .<sup>165,178</sup>

The potential for integrating ocean capture with electrochemical conversion is immense. Although studies to date have focused on the release/capture of  $CO_2$  or the coupled capture/conversion approach (Fig. 1, Route 2), we will describe one such study as a source of inspiration for future integration efforts. Digdaya *et al.* reported a reactor operated using ocean water with a bipolar membrane electro dialysis (BPMED) cell followed by vapor-fed  $CO_2$  reduction.<sup>165</sup> The BPMED cell utilized a one-electron reversible redox couple ( $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ ) at the electrodes instead of the conventional water-splitting reaction. This demonstrated efficient capture of  $CO_2$  (released upon acidifying the bicarbonate-containing ocean water) at an electrochemical energy consumption of  $155.4 \text{ kJ mol}^{-1}$  or  $0.98 \text{ kWh kg}^{-1}$  of  $CO_2$ , with a  $CO_2$  capture efficiency of 71%.

Once  $CO_2$  was released and led to the vapor-fed electrochemical reduction, various fuels and chemicals, such as CO,  $CH_4$ , ethylene, and ethanol, could be produced with a total FE of up to 73% at current densities of  $58 \text{ mA cm}^{-2}$  when using a Cu electrocatalyst. Similarly, CO could be selectively obtained with



a FE of up to 95% at a current density of  $11.2 \text{ mA cm}^{-2}$  using a Ag electrocatalyst. It is important to note that the energy required for  $\text{CO}_2$  capture constitutes only a small fraction of the total capture and conversion energy. For example, converting  $\text{CO}_2$  to  $\text{CH}_4$  would require  $13.9 \text{ kWh kg}^{-1}$  of  $\text{CO}_2$ . To date, this process has been executed coupled, with the  $\text{CO}_2$  being released from the bicarbonate-containing ocean water and directed to the vapor-fed electrode. However, there is nothing preventing the integration of these steps, as bicarbonate can be electrochemically converted to products directly or indirectly (Table 1).

## 5.2. Continuous operation of $\text{CO}_2$ capture and conversion

With a comprehensive understanding of  $\text{CO}_2$  capture processes and the conversion of captured  $\text{CO}_2$ , the natural progression is to integrate these processes to streamline operations and enhance overall efficiency. Below, we highlight three studies that have carefully considered aligning the two processes for continuous operation. While the first two examples utilize simulated flue gas, the third employs pure  $\text{CO}_2$ .

Wang and Luo discussed both a coupled and an integrated system designed for  $\text{CO}_2$  capture, electrocatalytic reduction, and purification of gaseous products.<sup>23</sup> An alkaline solution was generated *via* a BPMED cell to capture  $\text{CO}_2$  from the simulated flue gas ( $\text{N}_2:\text{CO}_2 = 5:1$ ). The absorbed  $\text{CO}_2$  was then released by acidifying the absorbent solution with the acidic solution generated from the BPMED cell. The liberated  $\text{CO}_2$  was electrocatalytically reduced into CO at a Ag GDE using a flow-cell setup. However, due to low single-pass efficiency, the CO concentration reached only  $\sim 10\%$  at  $200 \text{ mA cm}^{-2}$  and  $\sim 15\%$  at  $300 \text{ mA cm}^{-2}$ . Nevertheless, any unreacted  $\text{CO}_2$  could be absorbed by the alkaline solution produced by the BPMED cell, resulting in a pure stream of syngas. The authors also explored an integrated process, bypassing the  $\text{CO}_2$  release process, by examining the performance of a Ag electrode directly in  $1 \text{ M KHCO}_3$  (Fig. 1, Route 3). In this scenario, a  $\text{FE}_{\text{CO}}$  of 40% was achieved at a current density of  $50 \text{ mA cm}^{-2}$ . Unfortunately, the current density could not be further increased, as this led to the continuous decline in CO production, accompanied by a gradual increase in  $\text{H}_2$  from the HER.<sup>88,94</sup> Thus, the integrated approach will require significant optimization before it can be scaled up and operated stably.

Prajapati *et al.* integrated  $\text{CO}_2$  capture and electrochemical conversion using a continuous flow system (Fig. 15).<sup>129</sup> To capture  $\text{CO}_2$ , they employed a migration-assisted moisture-gradient (MAMG) process, where gaseous  $\text{CO}_2$  was absorbed as  $\text{HCO}_3^-$  in a  $\text{CO}_2$ -binding organic liquid. The captured  $\text{CO}_2$  was then led through an anion exchange membrane under an electric field to an aqueous solution, where it was converted to dissolved  $\text{CO}_2$ . For  $\text{CO}_2$  reduction, they devised an electrochemical cell setup using a Cu mesh electrode, enabling the extraction of  $\text{CO}_2$ -free products such as CO,  $\text{CH}_4$ , and  $\text{C}_2\text{H}_4$ . In practice, they operated the MAMG  $\text{CO}_2$  capture unit at a current of 600 mA and the  $\text{CO}_2$  reduction unit at a current density of  $200 \text{ mA cm}^{-2}$ , which achieved a 40% FE for  $\text{C}_2\text{H}_4$  from a simulated flue gas feed and could be operated stably for

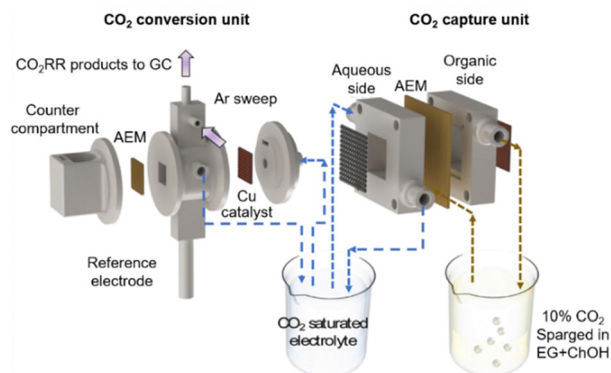


Fig. 15 Illustration of the integrated system featuring MAMG  $\text{CO}_2$  capture and electrochemical conversion. Reproduced with permission from ref. 129.

24 h. To effectively integrate the  $\text{CO}_2$  capture and  $\text{CO}_2$  reduction processes without diminishing the overall efficiency or necessitating downstream purification or recycling of  $\text{CO}_2$ , the rate of  $\text{CO}_2$  capture must match the rate of  $\text{CO}_2$  reduction.

Bai *et al.* developed a molten-salt-based electrolyzer capable of continuously capturing and converting  $\text{CO}_2$  with 100% efficiency into  $\text{CH}_4$  and CO, along with  $\text{H}_2$  from the HER (Fig. 16).<sup>101</sup> Notably, the  $\text{CO}_2$  fed into the reactor was completely captured by the molten salt electrolyte by carefully optimizing the feeding rate. The highest  $\text{CH}_4$  selectivity (33%) was achieved at  $400 \text{ mA cm}^{-2}$  using a commercial  $\text{CuNi}_{18}$  sheet as the cathode and a corrosion-resistant Ni sheet as the anode in a molten  $\text{Li}_{1.427}\text{Na}_{0.359}\text{K}_{0.214}\text{CO}_3 \sim 0.15\text{LiOH}$  electrolyte at  $650^\circ\text{C}$  (reactor dimensions: diameter = 2 cm, length = 4 cm). Pure  $\text{CO}_2$  was supplied to the reactor at a flow rate of  $20 \text{ mL min}^{-1}$ . Unlike previous molten-salt single cells based on the one-pot method, this reactor operated without the need for membranes and with a conversion efficiency of 100% for a single pass, eliminating the need to separate unreacted  $\text{CO}_2$  from the gaseous products. Unfortunately, the operation of this system lasted for only 3.6 h, and a gradual increase in the electrolysis voltage was observed, showing its unsatisfactory stability. In general, molten salt systems require substantial energy input to maintain operations at high temperatures. In addition, for molten salt systems that generate carbonaceous

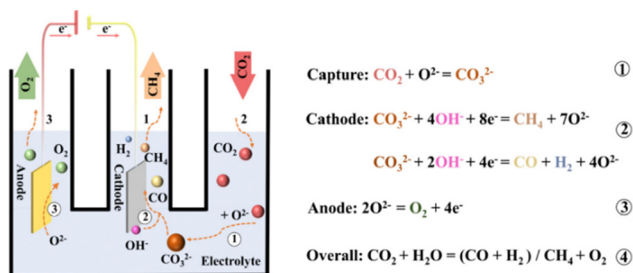


Fig. 16 Schematic illustration of a reactor for reactive  $\text{CO}_2$  capture, featuring a commercial  $\text{CuNi}_{18}$  sheet as the cathode and a corrosion-resistant Ni sheet as the anode in molten  $\text{Li}_{1.427}\text{Na}_{0.359}\text{K}_{0.214}\text{CO}_3 \sim 0.15\text{LiOH}$ . Reproduced with permission from ref. 101.





products,<sup>131,132</sup> regular pauses in production are necessary to remove carbon deposits accumulated on the cathode.

Although examples of the practical integration of CO<sub>2</sub> capture with subsequent conversion are limited, they have demonstrated the feasibility and potential of this technology. One approach involves running the two processes sequentially, with the conversion starting only after the capture is complete. The cycle can then restart after the conversion and regeneration of the capture agent. Alternatively, the conversion of captured CO<sub>2</sub> can be conducted concurrently with the capture process, which appears promising if the capture can be performed efficiently, as in the case of CO<sub>2</sub> from flue gas. However, if this is not the case, this approach may result in overall low conversion efficiency and selectivity issues due to the low steady-state concentration of the captured CO<sub>2</sub>.

### 5.3. Energy cost analysis

An important aspect of the practical integration of CO<sub>2</sub> capture and conversion is the analysis of the energy costs of the entire process, from capturing CO<sub>2</sub> from dilute sources to generating the desired product. This analysis is crucial for assessing the feasibility of the technology from both technical and economic perspectives. Since CO is the most reported product from the electrolysis of both gas-fed CO<sub>2</sub> and captured CO<sub>2</sub> systems, we first compare the energy consumption for producing CO between independent and integrated CO<sub>2</sub> capture and electrochemical conversion (Table 2). In the analysis, we considered three key steps that incur the main energy costs in the entire chain of CO<sub>2</sub> capture and conversion, *i.e.*, CO<sub>2</sub> capture/release, electrolysis, and product separation. The energy consumption analysis used experimentally reported data, including faradaic efficiencies, full-cell potentials, and CO<sub>2</sub> utilization efficiencies. As a result, the calculated energy values inherently carry some degree of uncertainty due to the variability and limitations of the experimental conditions and measurements (see the ESI† for details).

The independent CO<sub>2</sub> capture and electrochemical conversion strategy (Fig. 1, Route 1) requires a substantial energy investment to release CO<sub>2</sub> from the capture media. For DAC technologies using potassium hydroxide solutions, the energy required to release CO<sub>2</sub> from the subsequently formed CaCO<sub>3</sub> is 178.3 kJ mol<sup>-1</sup>.<sup>183</sup> Furthermore, in alkaline CO<sub>2</sub>-fed electrolyzers, CO<sub>2</sub> gas can be lost due to its reaction with OH<sup>-</sup> ions generated during the reduction reaction. Therefore, the CO<sub>2</sub> utilization efficiency, defined as the percentage of input carbon converted to a targeted product, is typically no greater than 20% for electrolyzers that generate CO.<sup>179,180</sup> In other words, to obtain one mol of CO product, 5 moles of CO<sub>2</sub> need to be captured, thus leading to an energy consumption of 892 kJ mol-CO<sup>-1</sup> for this CO<sub>2</sub> regeneration step. As expected, the energy required for the CO<sub>2</sub> capture and release steps with CO<sub>2</sub>-fed electrolyzers increases as the CO<sub>2</sub> utilization efficiency decreases. For the electrolysis step, gas-fed CO<sub>2</sub> electrolyzers, whether in flow cell or MEA configurations, require relatively low energy costs, ranging from 480 to 633 kJ mol-CO<sup>-1</sup>. This is due to the high level of optimization of the electrocatalysts for

Table 2 Comparison of the energy requirements between integrated (Route 3) and independent (Route 1) pathways for the production of CO, HCOO<sup>-</sup>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>4</sub><sup>a</sup>

|         | System                        | Product                       | CO <sub>2</sub> utilization (%) | CO <sub>2</sub> regeneration <sup>b</sup> | FE (%) | Electrolysis EE (%) <sup>c</sup> | Electrolysis <sup>b</sup> | Outlet CO <sub>2</sub> (%) | Product purity (vol%) | Product separation <sup>bd</sup> | Total energy <sup>b</sup> | CCU EE (%) | Ref. |
|---------|-------------------------------|-------------------------------|---------------------------------|-------------------------------------------|--------|----------------------------------|---------------------------|----------------------------|-----------------------|----------------------------------|---------------------------|------------|------|
| Route 1 | CO <sub>2</sub>               | CO                            | 20                              | 892                                       | 77     | 41                               | 633                       | 50                         | 26                    | 1250                             | 2775                      | 9          | 179  |
|         | CO <sub>2</sub>               | CO                            | 17                              | 1049                                      | 99     | 54                               | 480                       | 36                         | 32                    | 1050                             | 2579                      | 10         | 180  |
| Route 3 | HCO <sub>3</sub> <sup>-</sup> | CO                            | 60                              | 0                                         | 70     | 25                               | 1014                      | 25                         | 54                    | 200                              | 1214                      | 21         | 90   |
|         | CO <sub>3</sub> <sup>2-</sup> | CO                            | 100                             | 0                                         | 25     | 35                               | 734                       | 0                          | 25                    | 0                                | 734                       | 35         | 72   |
|         | Carbamate                     | CO                            | 90                              | 0                                         | 72     | 40                               | 634                       | 0                          | 72                    | 0                                | 634                       | 41         | 85   |
| Route 1 | CO <sub>2</sub>               | HCOO <sup>-</sup>             | 9                               | 1981                                      | 96     | 29                               | 917                       | N.A.                       | N.A.                  | 265                              | 3163                      | 9          | 181  |
| Route 3 | HCO <sub>3</sub> <sup>-</sup> | HCOO <sup>-</sup>             | 70                              | 0                                         | 85     | 40                               | 499                       | 0                          | 0.8 M                 | 265                              | 764                       | 26         | 94   |
| Route 1 | CO <sub>2</sub>               | CH <sub>4</sub>               | 1                               | 13715                                     | 62     | 16                               | 5495                      | 99                         | 1                     | 38000                            | 57210                     | 1          | 182  |
| Route 3 | HCO <sub>3</sub> <sup>-</sup> | CH <sub>4</sub>               | 25                              | 0                                         | 27     | 4                                | 20584                     | 75                         | 7                     | 1500                             | 22084                     | 4          | 98   |
|         | Molten salt                   | CH <sub>4</sub>               | 100                             | 0                                         | 43     | 21                               | 36989 <sup>e</sup>        | 0                          | 16                    | 0                                | 36989                     | 3          | 101  |
| Route 1 | CO <sub>2</sub>               | C <sub>2</sub> H <sub>4</sub> | 5                               | 3566                                      | 70     | 34                               | 3974                      | 77                         | 3                     | 15400                            | 22940                     | 6          | 19   |
| Route 3 | CO <sub>3</sub> <sup>2-</sup> | C <sub>2</sub> H <sub>4</sub> | 100                             | 0                                         | 34     | 10                               | 13971                     | 0                          | 8                     | 0                                | 13971                     | 10         | 103  |

<sup>a</sup> See the ESI for details on the calculation procedure. <sup>b</sup> Unit: kJ mol-product<sup>-1</sup>. <sup>c</sup> EE: Energy efficiency. <sup>d</sup> Separation energy of unreacted CO<sub>2</sub> from reaction products. <sup>e</sup> Electrolysis energy without thermal considerations is 4881 kJ mol-product<sup>-1</sup>; an extra 32 108 kJ mol<sup>-1</sup> has been added due to the process being conducted at 650 °C (see the ESI).



the CO<sub>2</sub>-to-CO conversion, resulting in systems displaying high FEs, large current densities, and low cell voltages.

After electrolysis, the outlet gas stream consists of CO, unreacted CO<sub>2</sub>, and H<sub>2</sub> byproduct, which requires separation before obtaining pure CO. Greenblatt *et al.* outlined general approaches to separating product mixtures resulting from CO<sub>2</sub> valorization.<sup>184</sup> The unreacted CO<sub>2</sub> and unwanted H<sub>2</sub> gases can be separated through, *e.g.*, pressure/temperature-based swings, adsorption/desorption, and membrane separation. Since the CO<sub>2</sub> utilization efficiency is low, the percentage of unreacted CO<sub>2</sub> at the outlet gas stream can be as high as 50%, and the purity of CO is estimated to be 26%.<sup>179</sup> Such a low CO purity leads to high energy consumption for the separation step, estimated at 1250 kJ mol-CO<sup>-1</sup>. In total, the energy consumption from cradle to grave is 2775 kJ mol-CO<sup>-1</sup>. Given that the theoretical energy consumption for converting gas-fed CO<sub>2</sub> to CO is 257 kJ mol-CO<sup>-1</sup>,<sup>38</sup> the global carbon capture and utilization (CCU) energy efficiency for the entire chain is 9%.

In the case of the electrochemically reactive capture of CO<sub>2</sub> (Fig. 1, Route 3), the absence of energy costs associated with the CO<sub>2</sub> capture/release step is a significant advantage, highlighting the potential of this technology in reducing energy consumption. The primary energy cost in the integrated pathway is the electrochemical conversion of the captured CO<sub>2</sub> solution. For instance, in the electrochemical conversion of a bicarbonate solution to CO,<sup>90</sup> the energy consumption for this step is 1014 kJ mol-CO<sup>-1</sup>, which is higher than for the electrolysis of gas-fed CO<sub>2</sub>. However, the CO<sub>2</sub> utilization efficiency for converting bicarbonate is 60%, significantly higher than that of gas-fed CO<sub>2</sub> electrolyzers. Since some *in situ* generated CO<sub>2</sub> exits the electrolyzer without being converted to CO, the concentration of CO in the outlet gas stream is 54%, thus requiring 200 kJ mol-CO<sup>-1</sup> to separate the small amount of unconverted CO<sub>2</sub>. The total energy consumption for the entire process, from CO<sub>2</sub> capture in dilute sources to CO production *via* a bicarbonate system, amounts to 1214 kJ mol-CO<sup>-1</sup>, which is significantly lower than for the independent CCU process. Moreover, the global CCU energy efficiency of the integrated pathway is 21%, twice as high as that of the independent CCU process.

In the case of carbonate and carbamate solutions, the *in situ* generated CO<sub>2</sub> can be quantitatively converted to CO, as almost no CO<sub>2</sub> is detected in the outlet gas stream.<sup>72,85</sup> This suggests that the CO<sub>2</sub> utilization efficiency for both cases is nearly 100%. In this scenario, the total energy consumption for converting carbonate or carbamate solutions can be estimated at 734 and 634 kJ mol-CO<sup>-1</sup>, respectively. These values are approximately four times lower than those for independent systems, highlighting their potential for practical applications (Table 2). The global CCU energy efficiencies are calculated to be 35% for the carbonate system and 41% for the carbamate system, significantly higher than those achieved with CO<sub>2</sub>-fed electrolyzers. Notably, if the targeted product is syngas (a combination of CO and H<sub>2</sub>), the separation energy can be considered zero since no unreacted CO<sub>2</sub> is present in the outlet gas stream.

The estimation of the separation energy for the CO product focused exclusively on the energy required to remove unreacted

CO<sub>2</sub>, without accounting for the separation of the H<sub>2</sub> byproduct. This approach is based on several considerations. First, CO<sub>2</sub> removal is the most energy-intensive step,<sup>185</sup> while extracting H<sub>2</sub> from syngas after CO<sub>2</sub> removal requires significantly less energy. For example, the energy cost for CO<sub>2</sub> separation can vary widely, ranging from 100–900 kJ mol<sup>-1</sup> of CO<sub>2</sub>, depending on the separation method used. For the energy calculations, a fixed value of 500 kJ mol<sup>-1</sup> of CO<sub>2</sub> was assumed for separating unreacted CO<sub>2</sub> from the gaseous output.<sup>72</sup> In contrast, the energy required for H<sub>2</sub> removal from syngas (with a ratio of ~1:3 CO:H<sub>2</sub>) is about 85 kJ mol-H<sub>2</sub><sup>-1</sup>.<sup>186</sup> Secondly, the H<sub>2</sub> concentration in the gas stream is typically much lower than that of unreacted CO<sub>2</sub> or the primary product, CO. As a result, the energy cost for H<sub>2</sub> separation generally accounts for a small fraction of the overall energy consumption for various CO<sub>2</sub> capture and conversion methods.

For instance, in cases where FE<sub>CO</sub> ≥ 70%, the estimated energy cost for H<sub>2</sub> separation is ≤ 34 kJ mol-CO<sup>-1</sup>, representing < 2% of the total energy consumption for both Route 1 scenarios and under 5% for the two Route 3 scenarios (*e.g.*, bicarbonate and carbamate conversion). In the context of carbonate conversion, where FE<sub>CO</sub> is only 25% (*i.e.*, CO/H<sub>2</sub> = 1:3), the estimated energy cost for H<sub>2</sub> separation rises to 255 kJ mol-CO<sup>-1</sup>. Even with this increased cost, the total energy consumption for Route 3 (*e.g.*, carbonate conversion, 989 kJ mol-CO<sup>-1</sup>) remains lower than that for the two Route 1 scenarios (2775 and 2559 kJ mol-CO<sup>-1</sup>, respectively). It is important to note that the energy cost for H<sub>2</sub> separation heavily depends on the gas stream composition and the required purity levels of CO and H<sub>2</sub>. Consequently, the cost will vary based on the specific components of the gas stream. These factors introduce complexity and result in uncertainties that are challenging to quantify. Given the relatively minor contribution of H<sub>2</sub> separation and its associated complexities, these energy costs are not included in Table 2.

Among the different types of captured CO<sub>2</sub> (*i.e.*, bicarbonate/carbonate/carbamate), the energy consumption for converting carbamate to CO/syngas is the lowest, which aligns with the weaker binding energy of amines with CO<sub>2</sub> compared to hydroxide solutions. Therefore, from an energy consumption standpoint, integrating CO<sub>2</sub> capture by amine with the electrolysis of the resulting carbamate to produce CO/syngas is the most advantageous option.

Similar conclusions can be drawn for the generation of HCOO<sup>-</sup> as the product. In the case of CO<sub>2</sub>-fed electrolyzers, due to the low CO<sub>2</sub> utilization efficiency (9%), 1981 kJ mol-formate<sup>-1</sup> of energy is required for the CO<sub>2</sub> capture and release steps.<sup>181</sup> Additionally, considering the electrolysis and purification steps, the total energy consumption amounts to 3163 kJ mol-formate<sup>-1</sup>, corresponding to a global CCU energy efficiency of 9%. In contrast, the direct electrochemical upgrading of a bicarbonate solution in the integrated process requires only 764 kJ mol-formate<sup>-1</sup>, leading to a global CCU energy efficiency of 26%.<sup>94</sup> These efficiency values demonstrate the promising potential of the integrated strategy in producing an important chemical such as HCOO<sup>-</sup>.



A key difference between the systems producing CO and those generating  $\text{HCOO}^-$  lies in the purification methods to separate  $\text{HCOO}^-$  from the liquid electrolyte solution. For one thing, the formate after electrolysis usually has a low concentration (0.8 M) in the electrolyte, which brings difficulty for separation (Table 2). For another, since  $\text{HCOO}^-$  is a charged product that can combine with electrolyte cations to form salts, an additional acidification step is required to obtain the more valuable formic acid. The resulting formic acid in water can then be separated by azeotropic distillation or extraction, which requires  $265 \text{ kJ mol}^{-1} \text{ formate}^{-1}$ .<sup>187</sup>

In producing highly reduced products such as  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$ ,  $\text{CO}_2$ -fed electrolyzers typically exhibit low  $\text{CO}_2$  utilization efficiency. For example, electrolyzers converting  $\text{CO}_2$  into  $\text{CH}_4$  have demonstrated efficiencies of  $\sim 1\%$ ,<sup>182</sup> while those producing  $\text{C}_2\text{H}_4$  achieve  $\sim 5\%$ .<sup>19</sup> These low efficiencies result in high energy costs associated with the  $\text{CO}_2$  capture and release steps. Moreover, for both independent and integrated pathways, the energy costs of the electrolysis step are significantly higher compared to electrolyzers that generate CO or  $\text{HCOO}^-$ . This is due to the greater number of electrons required to convert  $\text{CO}_2$  into  $\text{CH}_4$  (8 electrons) or  $\text{C}_2\text{H}_4$  (12 electrons), as opposed to the 2 electrons needed for producing CO or  $\text{HCOO}^-$ , substantially increasing the energy consumption of the electrolysis. For instance, in the direct electrochemical conversion of a bicarbonate solution to  $\text{CH}_4$ ,<sup>98</sup> the energy required for the electrolysis step can be calculated to amount to  $20\,584 \text{ kJ mol}^{-1} \text{ CH}_4^{-1}$ . However, when considering the  $\text{CO}_2$  capture/release and product purification steps, the direct conversion of bicarbonate into  $\text{CH}_4$  has a lower total energy consumption ( $22\,084 \text{ kJ mol}^{-1} \text{ CH}_4^{-1}$ ) compared to  $\text{CO}_2$ -fed electrolyzers ( $57\,210 \text{ kJ mol}^{-1} \text{ CH}_4^{-1}$ ). The higher concentration of  $\text{CO}_2$  in the electrolyzer outlet makes the independent pathway more energetically expensive, as more energy is required to separate the unreacted  $\text{CO}_2$  from  $\text{CH}_4$  than in the integrated approach.

An energy analysis of  $\text{CH}_4$  production using molten salts indicates that even in an electrolysis step carried out at  $650^\circ\text{C}$ , the integrated strategy is energetically more favorable.<sup>101</sup> With molten salts, the  $\text{CO}_2$  utilization efficiency is exceedingly high, and the energy consumption for the electrolysis step is relatively low ( $4881 \text{ kJ mol}^{-1} \text{ CH}_4^{-1}$ ). However, additional energy is required to heat the electrolyzer to  $650^\circ\text{C}$ , amounting to  $32\,108 \text{ kJ mol}^{-1} \text{ CH}_4^{-1}$ . This brings the total energy cost to  $36\,989 \text{ kJ mol}^{-1} \text{ CH}_4^{-1}$ , which is still lower than the total energy costs for producing  $\text{CH}_4$  using a  $\text{CO}_2$ -fed electrolyzer ( $57\,210 \text{ kJ mol}^{-1} \text{ CH}_4^{-1}$ ).

Based on the energy consumption analysis shown in Table 2, we conclude that the integrated  $\text{CO}_2$  capture and electrochemical conversion strategy (Fig. 1, Route 3) is more energy-efficient than independent processes (Fig. 1, Route 1), regardless of the products formed. This makes the integrated approach potentially more economical. The analysis also suggests that CO or syngas would be the most feasible initial targets, followed by  $\text{HCOO}^-$ , as the total energy consumption for producing CO and  $\text{HCOO}^-$  from dilute  $\text{CO}_2$  sources *via* electrochemically reactive carbon capture is lower than for other products such as  $\text{CH}_4$

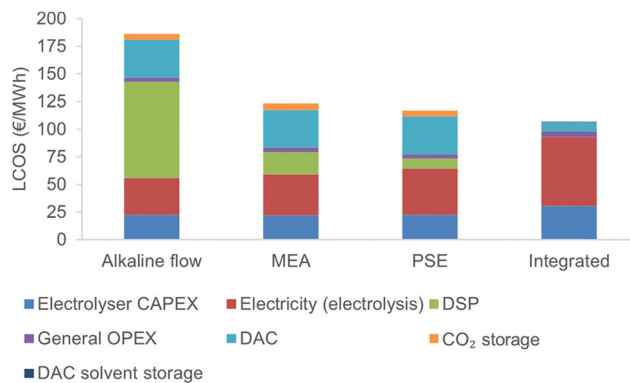


Fig. 17 Comparison of the LCOS of different routes of capture and electrochemical conversion of  $\text{CO}_2$  from air. The terms "alkaline flow," "MEA," and "PSE" (porous solid electrolyte) refer to the independent route using these respective cell configurations. The "General OPEX" category accounts for operational and maintenance costs. Reproduced with permission from ref. 188.

and  $\text{C}_2\text{H}_4$ . This conclusion is further supported by Debergh *et al.*,<sup>188</sup> who examined the economics of electrochemical syngas production *via* DAC. The authors compared the levelized cost of syngas (LCOS) for different  $\text{CO}_2$  capture and electrochemical conversion routes from air. They found that the integrated route offers the lowest LCOS due to reduced downstream separation (DSP) and  $\text{CO}_2$  capture costs from the air (*i.e.*, DAC), even though it incurs higher electrolysis costs (Fig. 17). Furthermore, their analysis revealed that CO is the most promising target for the integrated route among the various products.

Highly reduced products such as  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$  have important applications as chemical feedstocks. To improve the economic viability of producing these valuable compounds *via* the integrated route, it is essential to reduce the overall energy consumption. A significant portion of the energy used in these processes is attributed to the direct electrolysis of captured  $\text{CO}_2$  solutions. Currently, the electrocatalytic materials employed in these processes suffer from high overpotentials and low selectivity for  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$ , which drives up energy costs for electrolysis. Addressing this challenge requires developing novel electrocatalysts optimized for directly upgrading captured  $\text{CO}_2$  solutions to lower energy consumption and enhance the economic competitiveness of  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$  production. Methanol and ethanol, both valuable as fuels and chemical intermediates, can be produced through the electrochemical conversion of gas-fed  $\text{CO}_2$ . However, there are currently only a few reports of direct electrochemical conversion of captured  $\text{CO}_2$  into these products with low selectivity (*e.g.*,  $\text{FE}_{\text{ethanol}} < 20\%$ ).<sup>102</sup> Therefore, developing efficient and selective catalysts for the integrated process in these cases is essential for accurately evaluating their energy requirements and economic viability.

It should be noted that the integrated route for  $\text{CO}_2$  capture and conversion demonstrates a similarly high  $\text{CO}_2$  utilization efficiency as thermochemical  $\text{CO}_2$  conversion by hydrogenation, typically ranging between 70% and 90%.<sup>189–191</sup> The  $\text{CO}_2$





hydrogenation reactions are generally conducted at temperatures between 300 and 700 °C, enabling the production of valuable products such as CO, HCOOH, CH<sub>3</sub>OH, and CH<sub>4</sub>. While both CO<sub>2</sub> valorization methods achieve comparable CO<sub>2</sub> conversion efficiencies, thermochemical processes tend to produce higher CO<sub>2</sub> emissions due to their energy-intensive conditions, unless powered by carbon-neutral heat sources.

#### 5.4. Stability evaluation

The energy costs mentioned above are based on electrolysis data obtained from short-term experiments, typically lasting several hours to tens of hours. For industrial-scale applications, it is crucial to comprehensively study the long-term stability of integrated CO<sub>2</sub> capture and electrochemical conversion systems operating at high current densities. Unfortunately, only relatively few studies have addressed this issue.

Table 3 summarizes studies investigating the stability of electrochemical conversion of captured CO<sub>2</sub> for at least 5 hours at current densities of  $\geq 50$  mA cm<sup>-2</sup>. In an early report, Li *et al.* demonstrated the stable operation of an integrated system for 145 h using a Ag catalyst (Fig. 18a and b).<sup>72</sup> Here, a KOH solution was used to capture CO<sub>2</sub>, resulting in the formation of carbonate, which was then reduced to syngas while regenerating the KOH solution for another round of CO<sub>2</sub> capture *via* electrolysis. Throughout the operation, the current density remained stable at  $\sim 180$  mA cm<sup>-2</sup>, and the H<sub>2</sub>/CO ratio consistently ranged between 2 and 3. However, slight fluctuations in the syngas ratio and a decrease in FE<sub>CO</sub> were observed, attributed to metal contamination and deposition over time.

Later, Zhang *et al.* conducted electrolysis of a 3 M KHCO<sub>3</sub> solution over 80 h at an applied current density of 65 mA cm<sup>-2</sup> using a free-standing porous silver electrode.<sup>79</sup> Throughout the experiment, FE<sub>CO</sub> decreased by only 3% and the cell voltage increased by just 100 mV, demonstrating the good stability of the system. However, this stability was achieved by manually refreshing the 3 M KHCO<sub>3</sub> electrolyte every 500 s. When the free-standing electrode was replaced with silver-carbon composite electrodes, a much larger decrease in FE<sub>CO</sub> (16%) was observed over the 80 h electrolysis. Both Li *et al.* and Lees *et al.* also demonstrated that refreshing the captured CO<sub>2</sub> electrolyte was essential to maintaining good stability in their electrolysis systems.<sup>75,76</sup> Without refreshing the electrolyte, a gradual decrease in FE<sub>CO</sub> was observed due to the consumption of (bi)carbonate, resulting in an increase in pH over electrolysis time (Table 3).

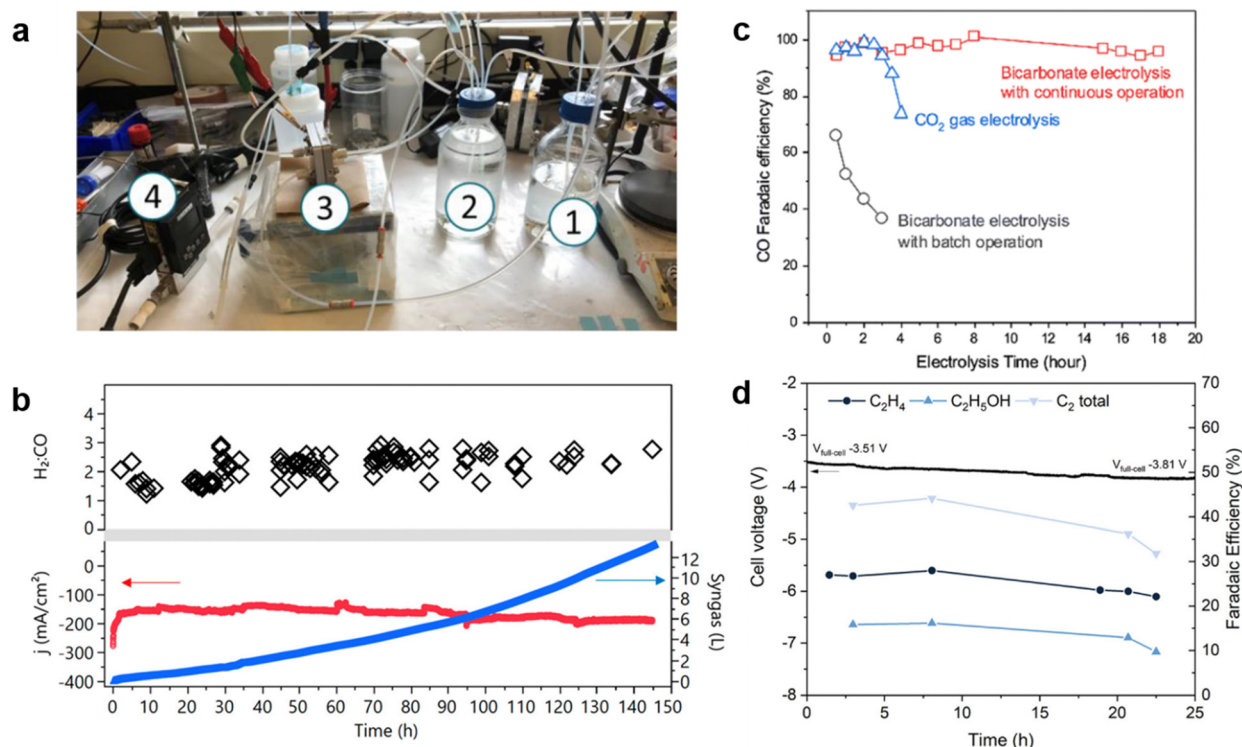
Recently, Song *et al.* investigated the electrolysis of a 3 M KHCO<sub>3</sub> solution with continuous CO<sub>2</sub> purging for 29 h using a Ni SAC. They found that the system remained very stable for continuous CO production with FE<sub>CO</sub> of  $> 90\%$  during the first 18 h due to the regeneration of bicarbonates by the CO<sub>2</sub> purging (Fig. 18c).<sup>90</sup> Under such conditions, electrolyte refreshing had no impact on the electrolysis performance, and therefore, it was not required. In contrast, the electrolysis of gas-fed CO<sub>2</sub> and 3 M KHCO<sub>3</sub> without CO<sub>2</sub> purging showed a rapid decline in FE<sub>CO</sub> under the same conditions. In addition, a slight decrease of FE<sub>CO</sub> to  $< 90\%$  was observed after 20 h of

Table 3 Stability assessment of electrochemical conversion of captured CO<sub>2</sub> (since 2019)<sup>a</sup>

| Captured CO <sub>2</sub>                           | $ j $ (mA cm <sup>-2</sup> ) | Cell voltage (V) | Product FE                            | Duration of electrolysis (h) | Reason for performance decrease                                               | Ref. |
|----------------------------------------------------|------------------------------|------------------|---------------------------------------|------------------------------|-------------------------------------------------------------------------------|------|
| Captured CO <sub>2</sub> in 2 M KOH                | $\sim 180$                   | 3.8              | CO: 33–25%                            | 145                          | Contamination by metal deposition                                             | 72   |
| 3 M KHCO <sub>3</sub>                              | 100                          | $\sim 3.5$       | CO: 37–27% <sup>b</sup>               | 5                            | Consumption of KHCO <sub>3</sub> and pH increase                              | 75   |
| 3 M KHCO <sub>3</sub>                              | 100                          | 3.5–3.7          | CO: 42–32% <sup>b</sup>               | 8                            | Consumption of KHCO <sub>3</sub> and pH increase                              | 76   |
| 3 M KHCO <sub>3</sub>                              | 65                           | 3.4–3.5          | CO: 88–85% <sup>b</sup>               | 80                           | Consumption of KHCO <sub>3</sub> and pH increase                              | 79   |
| Captured CO <sub>2</sub> in 2 M KOH                | 100                          | 3.3              | CO: 40–36%                            | 23                           | N.A.                                                                          | 73   |
| 1 M K <sub>2</sub> CO <sub>3</sub>                 | 200                          | $\sim 3.7$       | CO: 42–35%                            | 25                           | N.A.                                                                          | 74   |
| 3 M KHCO <sub>3</sub> with CO <sub>2</sub> purging | 200                          | $\sim 3.2$       | CO: 95–86%                            | 29                           | Partial detachment of Ni SAC                                                  | 90   |
| Captured CO <sub>2</sub> in 2 M KOH                | 200                          | 3.5–3.8          | C <sub>2</sub> products: 42–32%       | 22.5                         | Degradation of the CEM interposer pore structure                              | 103  |
| Captured CO <sub>2</sub> in 2 M KOH                | 100                          | 3.4–3.5          | C <sub>2</sub> products: 22–18%       | 50                           | Reduction of exposed Cu(OH) <sub>2</sub> nanowire catalyst                    | 105  |
| 5 M K <sub>2</sub> CO <sub>3</sub>                 | 100                          | $\sim 3.7$       | C <sub>2</sub> H <sub>4</sub> : 10–9% | 23                           | Consumption of K <sub>2</sub> CO <sub>3</sub> , degradation of Cu–Ag catalyst | 104  |

<sup>a</sup> Data selected with  $|j| \geq 50$  mA cm<sup>-2</sup> and electrolysis time of  $\geq 5$  h. <sup>b</sup> Electrolyte refreshed at regular intervals.





**Fig. 18** Stability evaluation of the integrated CO<sub>2</sub> capture and electrochemical conversion. (a) Experimental setup, where CO<sub>2</sub> is captured into 2 M KOH (1) to generate carbonate, which is then pumped into a new bottle (2) and reduced in a direct carbonate cell (3). The gas products are measured by a mass flow meter (4) to determine the total volume. (b) Syngas production performance during electrolysis at a constant potential of 3.8 V using a Ag catalyst with the same experimental setup. Reproduced with permission from ref. 72. (c) Stability comparison of electrolysis between gas-fed CO<sub>2</sub> and 3 M KHCO<sub>3</sub> with/without CO<sub>2</sub> purging at a constant current density of 200 mA cm<sup>-2</sup> using a Ni SAC. Reproduced with permission from ref. 90. (d) Long-term operation for CO<sub>2</sub> capture and electrolysis in a 2 M KOH solution, performed with a Cu/CoPc-CNTs electrocatalyst and a 135 mm MEC interposer. Reproduced with permission from ref. 103.

electrolysis, which was attributed to the partial detachment of the catalysts.

Similar stability was observed in the electrochemical conversion of (bi)carbonate solution to C<sub>2</sub> products, such as C<sub>2</sub>H<sub>4</sub>. Ma *et al.* observed a decrease in FE for C<sub>2</sub> products and increased cell voltage during the first 10 h of electrolysis of captured CO<sub>2</sub> in a 2 M KOH solution using a Ag-Cu(OH)<sub>2</sub> nanowire catalyst.<sup>105</sup> The authors attributed this initial performance deterioration to the reduction of the exposed Cu(OH)<sub>2</sub> nanowires. After this phase, the system remained stable for 40 h of operation. Song *et al.* evaluated the stability of converting 5 M K<sub>2</sub>CO<sub>3</sub> solution to C<sub>2</sub>H<sub>4</sub> using a Cu-Ag catalyst at an applied current density of 100 mA cm<sup>-2</sup>.<sup>104</sup> The FE for C<sub>2</sub>H<sub>4</sub> was stable for the first 9 h but decreased after 18 h, attributed to various factors, including the consumption of K<sub>2</sub>CO<sub>3</sub> and degradation of the Cu-Ag catalyst.

Lee *et al.* constructed a prototype system capable of operating CO<sub>2</sub> capture and electrochemical conversion to continuously produce C<sub>2</sub> products, similar to a previously reported system by the group (Fig. 18a).<sup>103</sup> The authors employed a Cu/CoPc-CNT catalyst (CoPc denotes cobalt phthalocyanine) and used a porous hydrophilic mixed cellulose ester (MCE) as the interposer to establish a well-defined spacing between the catalyst layer and the ion exchange membrane. They demonstrated continuous

operation of the setup for 20 h at a current density of 200 mA cm<sup>-2</sup>. However, they observed a decline in performance after 8 h of operation (Fig. 18d), which was attributed to the degradation of the pore structure in the MCE membrane. This resulted in an increase in cell voltage and HER.

These results highlight the importance of optimizing the catalyst, electrolyte, interposer materials, and electrode configuration to enhance the stability of electrolysis of the captured CO<sub>2</sub> solution under relevant conditions. Note that during continuous operation, the electrolyte is refreshed through the reaction of CO<sub>2</sub> with the continuously basified electrolyte. One potential solution to address stability issues is the incorporation of additives or specifically engineered functionalities to prevent degradation of the catalyst and interposer. Until now, most stability studies have concentrated on the (bi)carbonate system, with limited research on the carbamate system. Furthermore, continuous CO<sub>2</sub> capture and electrochemical conversion over extended periods (≥ 1000 h) has not yet been demonstrated experimentally for either system, a crucial milestone for ensuring long-term durability in CO<sub>2</sub> capture and conversion.

### 5.5. Scalability consideration

Scalability is another important metric for integrated CO<sub>2</sub> capture and electrochemical conversion that has not yet been



Table 4 Summary of the three typical approaches for electrochemically reactive CO<sub>2</sub> capture

| Systems                       | RNH <sub>2</sub> (aq.)                                                             | OH <sup>−</sup> /CO <sub>3</sub> <sup>2−</sup> (aq.)                                                   | Molten oxide                                                                                                          |
|-------------------------------|------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------|
| Captured CO <sub>2</sub>      | RNHCOO <sup>−</sup> (aq.)                                                          | CO <sub>3</sub> <sup>2−</sup> /HCO <sub>3</sub> <sup>−</sup> (aq.)                                     | Molten carbonate                                                                                                      |
| Direct or indirect conversion | Both possible                                                                      | Both possible                                                                                          | Direct                                                                                                                |
| Main products                 | CO, HCOO <sup>−</sup>                                                              | CO, HCOO <sup>−</sup> , CH <sub>4</sub> , C <sub>2</sub> H <sub>4</sub>                                | C, CO, CH <sub>4</sub>                                                                                                |
| Key benefits                  | Room-temperature operation; fast CO <sub>2</sub> absorption kinetics               | Room-temperature operation; improved stability and durability; larger  j  and FE for product formation | More compatible with flue gas systems; larger  j  and FE for product formation                                        |
| Key challenges                | Prone to thermal and oxidative degradation; lower  j  and FE for product formation | Inefficiency of CO <sub>3</sub> <sup>2−</sup> (aq.) in capturing CO <sub>2</sub> from the air          | Operation at high temperature; batch production; interruptions due to buildup of solid carbon products on the cathode |

thoroughly explored in the literature. The production rate, which reflects the scalability of a specific target product, is determined by the current density and FE achieved during electrolysis, as well as the geometric area of the electrode. Therefore, increasing these parameters is expected to enhance the production of target products. It should be noted, however, that there is a trade-off between current density and electrode area when aiming for a specific production rate. The current density determines the size of the electrolyzer. At lower current densities, the conversion of captured CO<sub>2</sub> is more energy efficient and incurs lower operating costs due to reduced energy losses from internal resistance, but this results in larger electrolyzers, increasing capital costs. In addition, it should be noted that scaling up production can be achieved either by increasing the size of the electrolyzer or by stacking multiple electrolyzers. An optimal current density balances operating and capital costs, estimated to be 200–400 mA cm<sup>−2</sup> for the electrochemical conversion of gas-fed CO<sub>2</sub>.<sup>192,193</sup> Such current densities are achievable for the electrolysis of captured CO<sub>2</sub> in many systems (Table 1).

To determine the electrolyzer size required to produce CO at a scale of 1 ton day<sup>−1</sup>, we may use the optimal performance metrics reported by Song *et al.* (Table 3).<sup>90</sup> This calculation shows that operating electrolysis at a current density of 200 mA cm<sup>−2</sup> with FE<sub>CO</sub> = 90% can achieve a CO production rate of 22.6 kg m<sup>−2</sup> day<sup>−1</sup>. Accordingly, an electrolyzer with a total electrode area of 44.2 m<sup>2</sup> or an electrolyzer stack reaching this total area would be needed to reach the target production of CO. Doubling the current density is expected to reduce the electrolyzer size by half. Based on this calculation, scaling up the production of other products, such as C<sub>2</sub>H<sub>4</sub>, would require significantly larger electrolyzers due to the lower FE currently achieved for this product (<40%, Table 1).

## 6. Conclusions and perspective

### 6.1. Summary

The electrochemical conversion of captured CO<sub>2</sub> has garnered increasing attention in recent years due to its advantage of bypassing the traditional CO<sub>2</sub> release, purification, compression, transport, and storage steps. In this review, we outlined the four key factors that influence the success and applicability of this emerging technology. Table 4 summarizes the

three typical approaches for electrochemically reactive CO<sub>2</sub> capture.

(1) The choice of capture medium plays a crucial role in determining the thermodynamics and kinetics of the CO<sub>2</sub> absorption process and its subsequent electrochemical conversion. Each capture medium reviewed exhibits unique chemical properties that can be exploited to minimize the energy penalties associated with both capture and electrochemical conversion. Aqueous amines are the most widely studied medium for post-combustion CO<sub>2</sub> capture, although they are particularly vulnerable to thermal and oxidative degradation. Due to the strength of the C–N bond, the electrochemical reduction of the carbamate typically results in low current density values (<50 mA cm<sup>−2</sup>). Capturing CO<sub>2</sub> as a (bi)carbonate solution using aqueous carbonate and hydroxide solutions has emerged as a more economical and thermally stable alternative to amine scrubbing. The reduction of (bi)carbonate has shown higher reaction rates than carbamate reduction. However, several acid–base equilibria between CO<sub>2</sub> and (bi)carbonate complicate mechanistic investigations to identify the electrochemically active species at the electrode surface. Molten alkali carbonates are particularly beneficial for capturing CO<sub>2</sub> from flue gas, as this medium is compatible with the high temperature of such streams. Electrochemical conversion of captured CO<sub>2</sub> in molten carbonates typically occurs at temperatures ranging from 500–950 °C, with the added advantage of generating solid carbon in many cases, thereby eliminating the need for costly separation and purification processes.

(2) Various carbonaceous products can be produced through the electrochemical conversion of captured CO<sub>2</sub>. The product types are determined mainly by the choice of catalysts, although the capture medium can also have an impact. For the electrochemical conversion of aqueous carbamate and (bi)carbonate solutions, CO is typically generated using Ag nanoparticles or SACs, formate is produced over Bi and Sn, while CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> are formed using Cu-based catalysts. This pattern mirrors that observed in the electrochemical conversion of gas-fed CO<sub>2</sub>. In molten carbonate systems, the product outcome is more temperature dependent, with CO formed at ~900 °C and carbon materials at lower temperatures (~500 °C). Notably, the conversion of captured CO<sub>2</sub> can follow either an indirect pathway, where CO<sub>2</sub> is generated *in situ* and converted, or a direct pathway, where the captured CO<sub>2</sub> is directly converted at the electrode.





(3) Several other factors also significantly impact the electrochemical conversion of captured CO<sub>2</sub>. Key elements such as the electrolyzer design, electrode materials, electrolyte composition, ion exchange membranes, and operating conditions (*e.g.*, temperature, pressure, and flow plate design) can all affect conversion efficiency. These factors influence the availability of *in situ* generated CO<sub>2</sub> by shifting the dissociation equilibrium between carbonate, bicarbonate, or carbamate, and free CO<sub>2</sub>, as well as impacting proton production and transport. Thus, optimizing these operational parameters is essential for improving the overall conversion efficiency.

(4) Based on these understandings, integrating CO<sub>2</sub> capture with subsequent conversion for practical applications becomes feasible. The outcomes of this integration will vary depending on the source of CO<sub>2</sub> (*i.e.*, air or flue gas), as each source contains different levels of CO<sub>2</sub>, O<sub>2</sub>, and gas impurities. These factors impact, *e.g.*, the availability of the CO<sub>2</sub> reactant, the charge transfer processes (*e.g.*, CO<sub>2</sub> *vs.* oxygen reduction), and catalyst poisoning. For effective integration, the rates of capturing CO<sub>2</sub> and its subsequent conversion should be aligned. A comparison of energy costs between the conventional independent route (Fig. 1, Route 1) and the integrated route (Fig. 1, Route 3) shows that the integrated route consumes less energy and, as a result, achieves higher overall efficiency for the entire process, spanning from CO<sub>2</sub> capture from dilute sources to the production of the final products.

## 6.2. Challenges and potential solutions

Although previous studies have highlighted the significant potential for the electrochemical conversion of captured CO<sub>2</sub>, several key challenges impede the rapid advancement of this emerging field and its large-scale implementation.

(1) The mechanism behind the conversion of captured CO<sub>2</sub> remains a topic of debate. It is not always clear whether the CO<sub>2</sub>-bound capture agent itself or the CO<sub>2</sub> released from it is the actual species converted at the electrode. Most reports show that (bi)carbonate and carbamate are converted *via* the *in situ* generation of CO<sub>2</sub> at the electrode interface, although some reports indicate that they can also be directly converted. Due to the equilibrium between (bi)carbonate/carbamate and CO<sub>2</sub> during electrochemical conversion, determining the exact reaction pathway using only *ex-situ* techniques can be difficult. Kinetic studies are crucial for this clarification, and *in situ/operando* techniques, such as infrared reflection-absorption spectroscopy and Raman spectroscopy, are valuable for identifying the adsorbed reactive species (bicarbonate/carbamate *vs.* CO<sub>2</sub>) at the catalytic sites during the conversion process.<sup>194,195</sup> For example, Lu *et al.* recently reported an electrolysis optical coherence tomography platform to visualize the chemical reactions occurring in a CO<sub>2</sub> electrolyzer, including reactants, intermediates, and products.<sup>77</sup> This platform, or a similar one, may serve as an effective tool for monitoring the dynamic movement of the various species during the electrolysis of captured CO<sub>2</sub>, providing valuable insight into the mechanism. Furthermore, theoretical simulations based on DFT calculations can be employed to determine the adsorption energy of

reactive species and intermediates, as well as the free energy change of each elementary step in the conversion process.<sup>196,197</sup>

(2) In general, the conversion efficiency for captured CO<sub>2</sub> is low. Over the past decades of intensive research, the electrochemical conversion of gas-fed CO<sub>2</sub> can now be achieved at a large current density ( $>1\text{ A cm}^{-2}$ ) and with high FE ( $>95\%$ ) for producing CO and formate.<sup>198,199</sup> In comparison, the current density (usually  $<200\text{ mA cm}^{-2}$ , although  $400\text{ mA cm}^{-2}$  can be achieved under certain conditions) and the product FE (usually  $<80\%$ , with 90% achievable under certain conditions) are much lower for the electrochemical conversion of captured CO<sub>2</sub> (Table 1), making the technology less efficient. The main reason for this is the low CO<sub>2</sub> concentration at the electrode/electrolyte interface, caused by the slow dissociation of carbonate/bicarbonate/carbamate to generate *in situ* CO<sub>2</sub> in the indirect conversion or the electrostatic repulsion between the negatively charged electrode and the carbonate/bicarbonate/carbamate ions in the direct conversion. Different strategies should be adopted to overcome these obstacles. For instance, modifying the electrode configuration, ion exchange membrane, and even the anolyte can enhance proton production and transport, thereby increasing the generation of *in situ* CO<sub>2</sub> and improving the conversion process. Drawing inspiration from electrochemical nitrate conversion, where negatively charged species are also involved, functionalizing the electrode surface with positively charged groups can reduce electrostatic repulsion and concentrate carbonate/bicarbonate/carbamate ions, promoting their direct conversion.<sup>200,201</sup> Additionally, designing new catalysts specifically tailored for captured CO<sub>2</sub> conversion is crucial to enhance efficiency.

(3) Inefficient integration of CO<sub>2</sub> capture and conversion can hinder practical applications. To date, most studies have focused on improving the electrochemical conversion efficiency of captured CO<sub>2</sub> (*i.e.*, carbonate, bicarbonate, or carbamate). A few examples demonstrate that integrating the two processes is feasible at the proof-of-concept stage. However, these reports rarely address the recyclability of the resulting electrolyte for CO<sub>2</sub> capture, nor do they explore the impact of different CO<sub>2</sub> sources or the long-term stability of the capture-conversion cycles. Currently, the electrolysis of captured CO<sub>2</sub> has been conducted for no longer than 150 h, with performance degradation arising mainly due to electrolyte basification and catalyst deactivation. Electrolyte basification can be mitigated by continuous and efficient CO<sub>2</sub> capture, along with a judicious selection of the capture medium, tailored to the specific operating conditions.

While air has a low concentration of CO<sub>2</sub>, flue gas has a much higher CO<sub>2</sub> concentration but also includes gas impurities such as NO<sub>x</sub> and SO<sub>x</sub>. In an air capture scenario, a medium with selective and fast CO<sub>2</sub> uptake is necessary to concentrate the low levels of CO<sub>2</sub> for subsequent conversion. Molten oxides would be a suitable option in this case. For flue gas, aqueous amine and carbonate solutions can be effective for CO<sub>2</sub> capture, but careful attention must be given to selecting catalysts resistant to gas impurities. The decision to extract CO<sub>2</sub> from flue gas or ambient air depends on various factors,



including location, emission sources, available resources, and technological readiness. Additionally, new catalysts that demonstrate long-term stability for extended electrolysis periods are needed, or additives and specialized functionalities should be introduced to the electrode or electrolyte to prevent catalyst deactivation. Ideally, the electrochemical conversion process should regenerate the capture medium with minimal loss or degradation. Ultimately, the full integration of the capture and conversion processes must operate stably for hundreds or even thousands of hours without a significant decline in efficiency for both CO<sub>2</sub> capture and conversion.

One promising approach is integrating the capture and conversion sites at a molecular level. This approach closely mimics the working mechanism of enzymes, creating a precise microenvironment for molecular recognition and specific catalysis.<sup>202</sup> These studies highlight the strategy of tailoring microenvironments at a molecular level to enhance the performance of CO<sub>2</sub> capture and conversion.

(4) The scalability and economics of integrated systems have not yet been thoroughly explored. The few existing studies on such systems remain on the laboratory scale. In contrast, other large-scale CO<sub>2</sub> technologies have reached pre-commercial stages, including high-temperature electrochemical CO<sub>2</sub>-to-CO production,<sup>203</sup> thermal catalytic hydrogenation of CO<sub>2</sub> to methanol,<sup>204</sup> and biological CO<sub>2</sub> upgrading to methane.<sup>205</sup> These technologies can serve as valuable reference points for evaluating the scalability of integrated CO<sub>2</sub> capture and electrochemical conversion.

Any technology nearing scalability requires a comprehensive techno-economic analysis (TEA), which should extend beyond energy cost analysis. This means factoring in operational expenditures (OPEX) and capital expenditures (CAPEX) to fully understand the economic viability of the process.<sup>206</sup> This assessment should encompass the entire value chain, including CO<sub>2</sub> capture methods (post-combustion or DAC), electrolysis using various capture media, and downstream processes for product purification and recycling of unconverted CO<sub>2</sub>. While a detailed TEA is beyond the scope of this review, it would be highly beneficial for experts in the field to explore these aspects further. An important direction would be to conduct a comparative TEA of the integrated and independent routes over the entire life cycle of the CO<sub>2</sub> capture and conversion system.

To scale up the electrochemical conversion of captured CO<sub>2</sub> from a technological point of view, several parameters, such as current density, faradaic efficiency, and electrode area, must be optimized to increase product formation rates. However, once a target production rate is defined, a balance must be struck between current density and electrode area, as these factors heavily influence the economic feasibility of the electrolysis process. For instance, operating at lower current densities tends to be more energy efficient and reduces OPEX by minimizing energy losses from internal resistance. However, this approach requires larger electrolyzers, driving up CAPEX. Conversely, higher current densities might lower CAPEX but increase OPEX due to less efficient energy usage. In any case,

highly durable electrolyzer systems are essential to reduce overall costs, as frequent replacement of electrolyzer components incurs additional expenses and should, therefore, be minimized.

### 6.3. Future directions

In addition to addressing the challenges mentioned, there are numerous other opportunities to advance this emerging field. Two potential future directions are outlined below:

**6.3.1. Exploring new capture agents for reactive CO<sub>2</sub> capture.** So far, electrochemical conversion of captured CO<sub>2</sub> has primarily focused on carbamate, bicarbonate, and carbonate formed using conventional amine, carbonate, and molten oxide solutions as capture agents. Recently, various redox-active organic mediators, such as quinones and bipyridine-based types, have shown considerable promise for CO<sub>2</sub> capture through electrochemical swing.<sup>207</sup> In this process, the redox-active mediator is first electrochemically reduced, triggering the CO<sub>2</sub>-binding step. The resulting CO<sub>2</sub>-adduct can then be further reduced at the electrode, leading to the production of various compounds and regeneration of the organic carrier. Notably, these redox-active mediators, as well as conventional amines, can be tethered to the active electrode surface, offering a novel approach for CO<sub>2</sub> capture and conversion.<sup>208</sup> In this configuration, the captured CO<sub>2</sub> is located close to the electrode rather than in the electrolyte solution, reducing mass transport limitations and potentially increasing conversion efficiency. The use of ionic liquids also represents a promising pathway due to their strong affinity for CO<sub>2</sub> while still activating CO<sub>2</sub> conversion.<sup>209</sup>

**6.3.2. Reactive CO<sub>2</sub> capture from the ocean.** The ocean is a major carbon reservoir, with a CO<sub>2</sub> concentration ~50 times higher than in the air. As described in Section 5.1.3, a reported coupled system successfully captured and converted CO<sub>2</sub> from ocean water into valuable products such as CO and C<sub>2</sub>H<sub>4</sub>. Although not fully integrated, this highlights the immense potential of such an approach. The next step would be to fully integrate the ocean capture and conversion processes to reduce energy consumption by eliminating the CO<sub>2</sub> release step. However, several challenges must be addressed for successful implementation, such as optimizing electrochemical processes, developing corrosion-resistant catalysts, and addressing ecological impacts on marine life and ocean chemistry.

## Author contributions

All authors contributed to the manuscript's writing, reviewing, and revising. K. Daasbjerg coordinated and supervised the overall project.

## Data availability

All data supporting the findings in this review are available from the referenced sources listed in the manuscript. The data presented in the tables are derived from the corresponding



literature references. For the calculated values in Table 2, details of the calculation methodology are provided in the ESI.†

## Conflicts of interest

There are no conflicts to declare.

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