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## Materials and system design for direct electrochemical CO<sub>2</sub> conversion in capture media

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The electrochemical CO<sub>2</sub> reduction reaction (eCO<sub>2</sub>RR) has been regarded as a promising means to store renewable electricity in the form of value-added chemicals or fuels. However, most of the present eCO<sub>2</sub>RR studies focus on the conversion of pure CO<sub>2</sub>. The CO<sub>2</sub> valorisation chain – from CO<sub>2</sub> capture to the eCO<sub>2</sub>RR – requires significant energy and capital inputs in each of the capture, purification, conversion, and product separation steps. The integration of upstream CO<sub>2</sub> capture and downstream electrochemical conversion by direct electrolysis of capture media, such as amine and carbonate salts, offers a potential solution to energy- and cost-efficient utilisation of CO<sub>2</sub>. In this perspective, we first summarise the present advances in the direct eCO<sub>2</sub>RR from CO<sub>2</sub>-capture media. We then focus on potential development directions of materials and systems that boost the process to a phase of high selectivity towards valuable products (e.g., syngas, ethylene, and ethanol). We conclude by highlighting the major challenges and emerging opportunities in the area of integrated electrochemical CO<sub>2</sub> utilisation systems.

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### Introduction

The renewable energy-driven electrochemical CO<sub>2</sub> reduction reaction (eCO<sub>2</sub>RR) towards value-added feedstocks and fuels is a promising solution to develop carbon-neutral energy supply and distribution systems. The considerable recent growth of this field is not only driven by the continuously falling price of

renewable electricity, but also the fact that the eCO<sub>2</sub>RR processes are on the path towards commercially relevant levels.<sup>1</sup> However, most of the present eCO<sub>2</sub>RR studies are based on pure CO<sub>2</sub> as a feedstock while little attention has been paid to the entire CO<sub>2</sub> valorisation process.

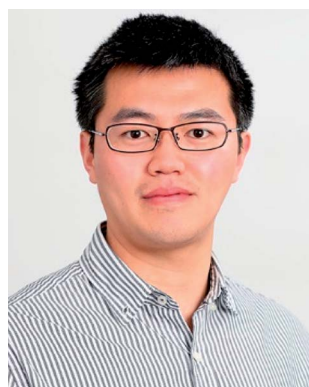
In the context of CO<sub>2</sub> utilisation that is aimed at carbon emission reduction, CO<sub>2</sub> has to be firstly captured using carbon-capture technologies from various CO<sub>2</sub> sources, such as point sources (e.g., flue gas from a coal-fired power plant), air and oceanwater.<sup>2–4</sup> Commercially relevant amine-based carbon-capture processes require heat to drive the regeneration of CO<sub>2</sub> from the capture media, which is the most costly step in the whole process chain: a typical amine scrubbing process costs around US\$50 to \$150 per tonne of CO<sub>2</sub> captured, with over 60% of the cost associated with the regeneration and compression steps.<sup>5–7</sup> Meanwhile, the heat for such capture solution regeneration usually comes from fossil fuels, inevitably bringing extra carbon emissions, which is against the scheme of a carbon neutral future.

Process intensification that integrates CO<sub>2</sub> capture and utilisation has shown potential to reduce the costs associated with separated carbon capture, storage and utilisation.<sup>8</sup> Value-added chemical production, such as production of organic carbonates, has been demonstrated in integrated CO<sub>2</sub> capture from power stations, combustion or flue gas, followed directly by chemical CO<sub>2</sub> conversion.<sup>9–11</sup> Electricity-driven electrochemical CO<sub>2</sub> conversion enables the employment of electrical energy – potentially from renewable sources – instead of thermal energy to regenerate and subsequently convert CO<sub>2</sub> from capture media. This also allows the captured CO<sub>2</sub> to be converted *in situ*

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to value-added products (e.g., syngas). This reaction pathway offers a promising solution to simplify the entire CO<sub>2</sub> valorisation chain and reduce the overall energy requirements and costs of the CO<sub>2</sub> utilisation process.<sup>12</sup>

To date, CO<sub>2</sub> capture and electrochemical conversion are mostly studied independently with only a few attempts at integrated CO<sub>2</sub> capture and conversion. This perspective summarises recent key studies regarding the integration of CO<sub>2</sub> capture and eCO<sub>2</sub>RR, and, on this basis, proposes a series of potential design principles and strategies for future development of such integrated CO<sub>2</sub> utilisation techniques. The perspective further discusses several techno-economic concepts that could serve as guidelines for future scale-up and concludes with major challenges and opportunities in this emerging field of research.

## Materials and systems for CO<sub>2</sub>-capture-medium reduction

### CO<sub>2</sub> capture

The use of CO<sub>2</sub> capture solvents as electrolytes, as high as several molar in concentration, circumvents the mass transfer limit of CO<sub>2</sub> that would otherwise be encountered in aqueous electrolytes where the CO<sub>2</sub> solubility is typically around 30 mM.<sup>12</sup> There are various choices of CO<sub>2</sub> capture media, from

polymer membranes to organic and inorganic liquid adsorbents,<sup>13</sup> and the mostly widely used ones are amine-based and alkaline absorption solvents, the focus of this perspective.

Amine-based CO<sub>2</sub> capture is the most mature and commonly used capture means for industrial CO<sub>2</sub> sources.<sup>6</sup> It usually consists of two steps (Fig. 1): the amine first reacts chemically with CO<sub>2</sub> to form carbamate *via* reaction (1); in the subsequent stage, the carbamate is regenerated by heating at approximately 100–120 °C.<sup>14</sup>



For a typical chemical absorption based direct air capture process, CO<sub>2</sub> in the atmosphere is captured by a hydroxide solution to form carbonate and/or bicarbonate *via* reactions (2) and (3), and then regenerated from CaCO<sub>3</sub> through the high-temperature calcination step (>900 °C).<sup>4,15</sup> This pathway requires carbonate salt palletisation, calcination, and compression to produce pressurised CO<sub>2</sub> (Fig. 1).

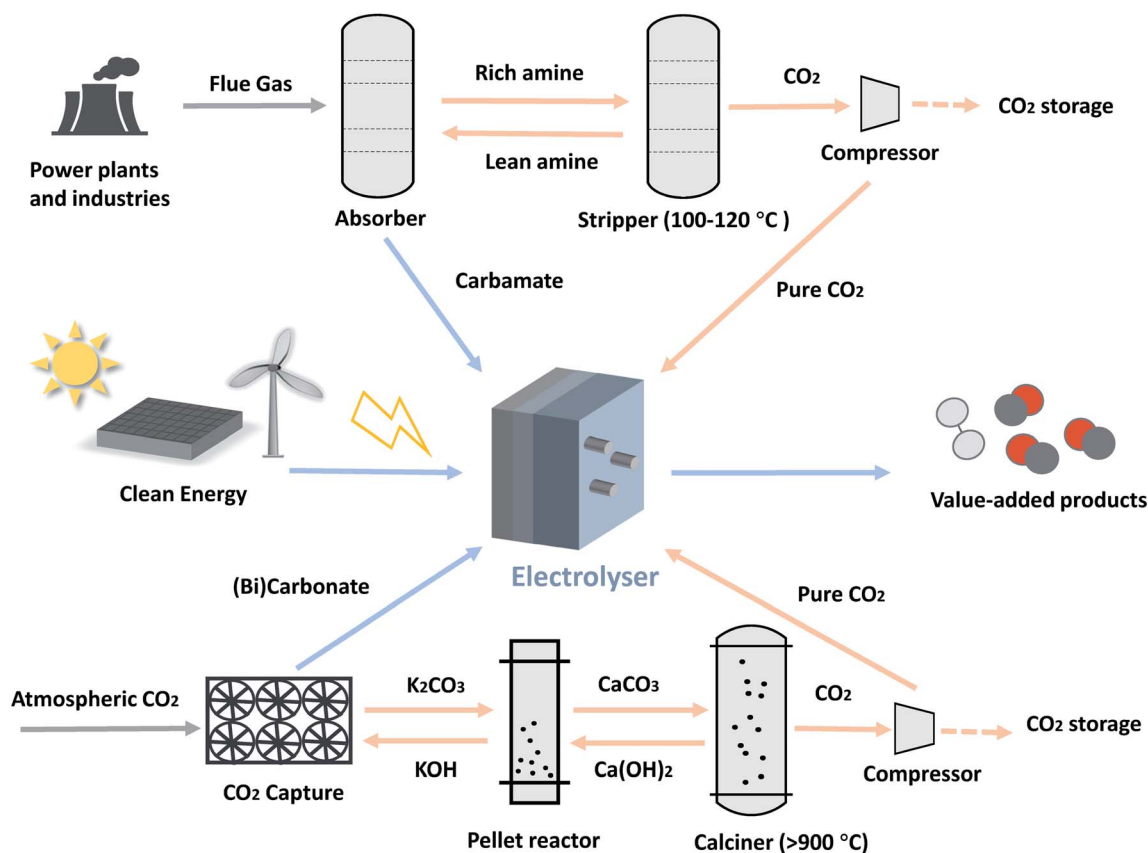
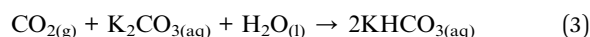
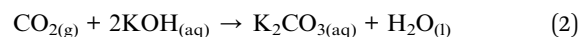


Fig. 1 Simplified process flow diagrams for direct capture media electrolysis and gaseous conventional CO<sub>2</sub> electrolysis pathway. The blue line indicates the integration utilisation pathway; the orange line indicates the traditional CO<sub>2</sub> utilisation pathway.

### Amine based CO<sub>2</sub> conversion

In 2017, Chen *et al.* reported electrochemical CO<sub>2</sub> conversion using a range of electrodeposited metallic electrodes (*e.g.*, Pb, Cu, In; Fig. 2a–c) in a CO<sub>2</sub> saturated 30% (w/w) monoethanolamine (MEA) aqueous solution.<sup>16</sup> Compared with the smooth counterpart, the porous electrode showed improved CO<sub>2</sub>RR selectivity, which the authors attributed to an increase of local pH and thus suppression of the competing hydrogen evolution reaction (HER) caused by the consumption of protons inside the pores. The authors further found a drastic improvement of CO<sub>2</sub>RR selectivity when a surfactant, cetyltrimethylammonium bromide (CTAB), was added into the reaction medium (Fig. 2d), and ascribed this enhancement to the adsorption of CTAB to inhibit the HER.

In this work, the authors argued – based on the control experiments where using MEA aqueous solution without free molecular CO<sub>2</sub> resulted in H<sub>2</sub> as the dominant product – that the CO and formate came from dissolved CO<sub>2</sub> in MEA solution instead of carbamate.

Very recently, Goetheer *et al.* studied an integration platform of CO<sub>2</sub> capture media electrolysis system using a mixture of 2-amino-2-methyl-1-propanol (AMP) and propylene carbonate (PC) solution as the electrolyte.<sup>17</sup> The direct electrolysis of captured CO<sub>2</sub> in this mixed medium produced various products, such as formate, glycolate, oxalate, and CO, with a formate faradaic efficiency (FE) up to 50%. Increasing the temperature from 20 to 75 °C steered selectivity to CO with an FE up to 45%. The authors believed that carbamate/bicarbonate species were not themselves directly reduced; instead, with increasing temperature, it was the desorbed CO<sub>2</sub> from the carbamate species that underwent electrochemical reduction.

Kratz *et al.* evaluated several commercially available amine compounds including MEA, ethylenediamine (EDA), and decylamine (DCA) on glassy carbon and Cu electrodes, and found that EDA, owing to its dual capturing sites, showed the best efficiency compared with the others. The authors discovered that the carbamate electrolysis towards CO was significantly improved when using Cu as the catalyst material, with a FE of 58% in EDA. In comparison, the CO FE was 2.3% on glassy carbon. Cu also significantly improved the current density up to 18.4 mA cm<sup>-2</sup> (*vs.* 0.63 mA cm<sup>-2</sup> on glassy carbon) at –0.76 V *vs.* the reversible hydrogen electrode (RHE).<sup>18</sup>

One challenge for direct carbamate reduction is that the electrostatic repulsion between the negatively charged carbamate and negative potential imposed on the cathode makes it difficult for the carbamate to approach the electrode for the reduction to take place. To address this, Sargent and co-workers tailored the electrochemical double layer so that the chemisorbed CO<sub>2</sub> in the form of carbamate can be directly reduced. With the aid of an alkali cation and accelerated mass transport by further system design (temperature and concentration), they demonstrated a direct carbamate conversion to CO with an FE of 72% at 50 mA cm<sup>-2</sup>.<sup>19</sup>

### (Bi)carbonate-based CO<sub>2</sub> conversion

The direct utilisation of bicarbonate (HCO<sub>3</sub><sup>-</sup>) or carbonate (CO<sub>3</sub><sup>2-</sup>) as a source of carbon is compelling as they are the major carbon species in commonly used neutral and weak basic solutions with a saturated concentration (*e.g.*, 3.3 M for KHCO<sub>3</sub>) an order of magnitude higher than that of dissolved CO<sub>2</sub>, offering a much higher achievable reduction current. Ocean-water, which accounts for absorption of ~40% of anthropogenic

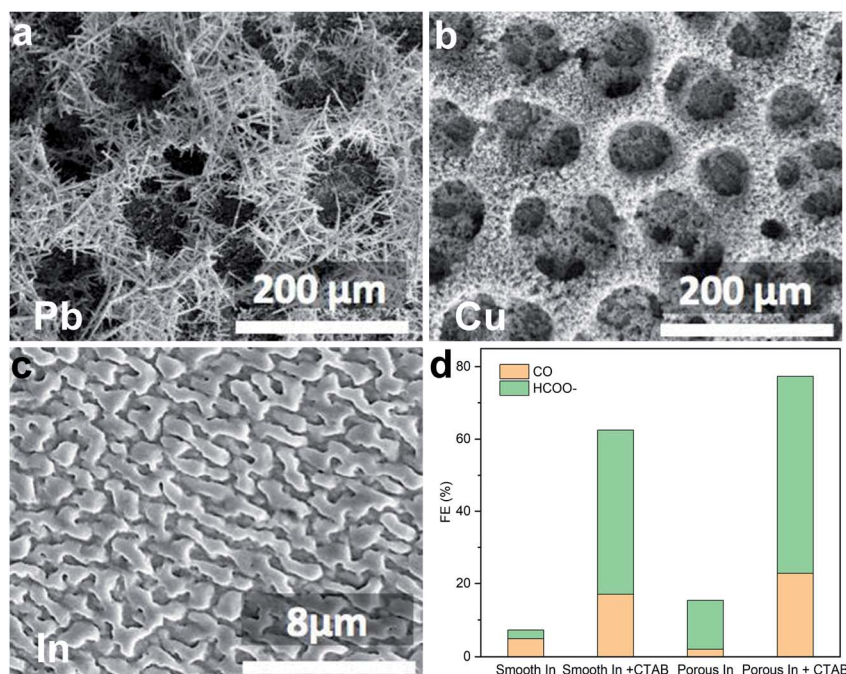


Fig. 2 (a–c) Scanning electron microscopy (SEM) images of the porous structure Pb, Cu, and In electrodes. (d) Faradaic efficiency of CO and formate on In electrodes. Reprinted from ref. 16 with permission. Copyright 2017 Wiley-VCH.

CO<sub>2</sub> since the industrial revolution, can potentially be the tank of such carbon sources as the current oceanwater CO<sub>2</sub> capture relies on the CO<sub>2</sub>/bicarbonate equilibrium.<sup>20–23</sup>

Direct bicarbonate electroreduction dates back to 1983 when Hori reported an H-cell architecture with a Hg electrode that produced formate from the reduction of a 1.0 M NaHCO<sub>3</sub> solution without a CO<sub>2</sub> feed but at a small partial current density (<1 mA cm<sup>-2</sup>).<sup>24</sup> In 2015, Kanan and co-workers reported that a Pd catalyst in an H-cell was able to reduce 2.8 M KHCO<sub>3</sub> into formate at a current density of 3.2 mA cm<sup>-2</sup>.<sup>25</sup> These early studies showed the feasibility of direct electrochemical reduction of bicarbonate, but they are limited by low current density and product selectivity (only formate reported).

In 2019, Berlinguette and colleagues introduced a flow cell system that converted a model carbon-capture solution (3 M KHCO<sub>3</sub>) into CO. Using a bipolar membrane (BPM) as the ion-exchange membrane, a high H<sup>+</sup> flux is transported from the anode side to the cathode side, where HCO<sub>3</sub><sup>-</sup> reacts with these protons to generate local high-concentration CO<sub>2</sub> at the catalyst/electrolyte interface. The product observed other than formate was CO, with FEs of 81% at 25 mA cm<sup>-2</sup> and 37% at 100 mA cm<sup>-2</sup>.<sup>12</sup> This product selectivity is reasonable as Ag, which favours production of CO in the eCO<sub>2</sub>RR, was used as the electrode material and the species that was reduced on the electrode was essentially CO<sub>2</sub> instead of bicarbonate anions.

The same group further used a free-standing porous Ag electrode to improve the selectivity and stability of the conversion.<sup>26</sup> The FE of CO reached 78% at 100 mA cm<sup>-2</sup>, and the performance loss after 80 hours of operation was less than 3%. These performances obtained in bicarbonate electrolysis were comparable to the CO<sub>2</sub>-fed CO<sub>2</sub>RR in gas-diffusion-based flow cells. It was believed that the performance improvement came from innovations in electrode materials. First, the addition of Ag nanowires significantly increased the electrochemical surface area (ECSA) of the Ag electrode and increased the abundance of exposed corner and edge active sites that promote chemisorption of both reactants and key intermediates. Additionally, the high length-to-diameter ratio, afforded by nanowire decoration, provided excess pores and channels for the transport of CO<sub>2</sub> and electrolyte that resulted in a faster reaction rate. In the same year, they reported that a similar flow cell system with a bismuth-coated carbon (Bi/C) cathode produced formate with a FE of 64% at a current density of 100 mA cm<sup>-2</sup>, which was also comparable with CO<sub>2</sub>-fed electrolyzers.<sup>15</sup>

To reduce device voltage and thereby energy input, the hydrogen oxidation reaction was used to replace the oxygen evolution reaction (OER) at the anode.<sup>27</sup> As a result, the electrolysis of bicarbonate to CO reached a commercially relevant current density of 500 mA cm<sup>-2</sup> at a full-cell voltage of 2.2 V. In comparison, the full-cell voltage of a similar cell configuration that operates the OER and bicarbonate reduction was 4.4 V to maintain a current density of 100 mA cm<sup>-2</sup>.

It is worth noting that, in a typical alkaline CO<sub>2</sub> absorption system, CO<sub>2</sub> is converted to carbonate. A further reaction step is required to convert it to bicarbonate, requiring additional energy.<sup>28</sup> Thus, it is more valuable for direct carbonate electroreduction. On this front, the Sargent group reported a similar BPM

strategy to locally generate CO<sub>2</sub> from carbonate for the production of syngas.<sup>29</sup> Syngas (3 : 1 H<sub>2</sub> : CO ratio) was generated at a current density of 150 mA cm<sup>-2</sup> with an energy efficiency of 35%, achieving 100% carbon utilisation across the system. The carbonate-to-syngas system operated stably for 145 h.

## Future directions and considerations

### Catalytic materials design

One of the greatest challenges in carbamate electrolysis is to break the C–N bond in carbamate to achieve a high local CO<sub>2</sub> concentration or to facilitate the direct carbamate electrolysis. Ongoing experiences in catalyst design and mechanistic studies aimed at lowering the regeneration energy based on the current thermal regeneration mode can be borrowed into the carbamate electrolysis. For example, solid acid catalysts (*e.g.*, ZrO<sub>2</sub> and Ag<sub>2</sub>O/Ag<sub>2</sub>CO<sub>3</sub>) have been intensively investigated, which potentially reduce the CO<sub>2</sub>-amine regeneration energy requirement, as the acidic site facilitates weakening of the C–N bond. The metal atom (Lewis acid) and protons (Brønsted acid) can attach to the carbamate to grab its lone pair of electrons, subsequently changing the configuration of N atoms from sp<sup>2</sup> to sp<sup>3</sup> and weakening the C–N bond by stretching. As the C–N bond in carbamate is weakened, it could be broken with less energy and CO<sub>2</sub> can be released more easily.<sup>30,31</sup>

Presently, direct capture media electrolysis products are limited to C<sub>1</sub> products (*i.e.*, CO and formate; Table 1). Progress on the transformation of CO<sub>2</sub> into multicarbon (C<sub>2+</sub>) products has been sought after. However, the challenges are obvious: the formation of C<sub>2+</sub> products from the eCO<sub>2</sub>RR relies on the formation of the C–C bond.<sup>32</sup> Cu provides excellent C–C coupling ability and produces C<sub>2+</sub> chemicals in gas-fed eCO<sub>2</sub>RR systems.<sup>33</sup> However, there is currently no report with appreciable selectivity towards C<sub>2+</sub> products from direct electrolysis of carbamate or (bi)carbonate. On the other side, even in the gas-fed eCO<sub>2</sub>RR, the long-term stability of Cu electrodes faces considerable challenges. This presents a conundrum in the presence of corrosive amines in carbamate electrolysis. The strategies to suppress the corrosion of electrocatalysts could be potential solutions to achieve activity and stability of the Cu electrode.<sup>34,35</sup>

Recently, supported organometallics, metal–organic frameworks (MOFs), and single-atom catalysts are starting to show promising rates in the eCO<sub>2</sub>RR.<sup>36</sup> Also, high FE towards C<sub>2+</sub> products at high current density (>200 mA cm<sup>-2</sup>) was reported in neutral electrolytes through molecular tuning on heterogeneous electrocatalysts.<sup>37</sup> These novel catalyst design means may be a promising solution to achieve C<sub>2+</sub> product formation in the capture medium reduction systems.

Mechanisms underpinning the capture medium electrolysis are still unclear, and the lack of such mechanistic guidelines retards the development of effective catalyst materials. An in-depth understanding of the dynamic environment (catalytically active site, diffusion and adsorption of reactants, identity of intermediates, and desorption of products) at the catalyst surface by *in situ* studies are desirable. *In situ/operando*

Table 1 Summary of progress of direct eCO<sub>2</sub>RR from CO<sub>2</sub> capture media

Materials	Reaction media	Applied potential	Products	FE (%)	$j$ (mA cm <sup>-2</sup> )	Ref.
Porous In	30% (w/w) MEA aqueous solution containing 0.1% (w/w) of CTAB	−0.8 V vs. RHE	CO	22.8	n.a.	16
Porous Bi			HCOO <sup>−</sup>	54.5		
Porous Pb			HCOO <sup>−</sup>	36		
Porous Ag			HCOO <sup>−</sup>	60.8		
Pb coil			CO	38.2		
	2 M 2-amino-2-methyl-1-propanol and 0.7 M tetraethylammonium chloride in propylene carbonate solution	−2.5 V vs. Ag/AgCl	HCOO <sup>−</sup>	50	25	17
Au foil			CO	45		
Glassy carbon	Pure EDA	−0.76 V vs. RHE	CO	2.3	0.63	18
Cu	Pure EDA	−0.76 V vs. RHE	CO	58	18.4	
Ag nanoparticle	30 wt% MEA and 2 M KCl	~−0.75 V vs. RHE	CO	72	50	19
Hg	1 M NaHCO <sub>3</sub>	n.a.	HCOO <sup>−</sup>	n.a.	<1 <sup>b</sup>	24
Pd	2.8 M KHCO <sub>3</sub>	−0.35 V vs. RHE	HCOO <sup>−</sup>	88	3.45 <sup>b</sup>	25
Ag	3 M KHCO <sub>3</sub>	−3.5 V <sup>a</sup>	CO	37	100	12
Porous Ag	3 M KHCO <sub>3</sub>	−3.5 ± 0.1 V <sup>a</sup>	CO	78	100	26
Bi on carbon	3 M KHCO <sub>3</sub>	−4 V <sup>a</sup>	HCOO <sup>−</sup>	64	100	15
Ag foam	3 M KHCO <sub>3</sub>	−2.2 V <sup>a</sup>	CO	15	500	27
Ag	1 M K <sub>2</sub> CO <sub>3</sub>	−3 V <sup>a</sup>	CO	28	100	29

<sup>a</sup> Full-cell potential. <sup>b</sup> Partial current density.

spectroscopies (e.g., *operando* X-ray absorption spectroscopy and *operando* Raman spectroscopy) coupled with computational modelling may provide powerful toolkits. Such efforts of fundamental mechanistic studies would guide the design of novel catalysts and optimise reaction conditions.

### Electrode structure design

The direct capture medium electrolysis system is different from the gas-fed electrolyser. In the gas-fed system, the formation of a three-phase interface (CO<sub>2</sub>/catalyst/electrolyte) at the gas-diffusion electrode (GDE) is critical to achieve high reactivity

and stability. However, in the capture medium electrolysis, CO<sub>2</sub> comes from the liquid phase rather than the gas phase and thus a gas-diffusion layer (GDL) that facilitates CO<sub>2</sub> transport is not a necessity. Therefore, optimisation for gas-fed flow cell systems may not be transferrable to the design of electrode structures for capture medium electrolysis.

Berlinguette and colleagues found that the hydrophobic GDL components (Fig. 3) decreased *in situ* CO<sub>2</sub> generation from bicarbonate and thus reduced the formation of CO.<sup>38</sup> This observation suggests that GDL used in liquid-fed electrolyser is expected to efficiently transport the liquid-phase streams, which is opposite to the hydrophobic requirement in gas-fed



Fig. 3 Cross-sectional SEM micrograph and schematic diagram of a GDE. Reprinted from ref. 38 with permission. Copyright 2020 American Chemical Society.

CO<sub>2</sub> electrolyzers to prevent excessive accumulation of liquid (so called 'flooding'). New strategies in tailoring electrocatalyst distribution, hydrophobicity, and ion transport characteristics of the GDEs are desired to achieve a long stability and efficient conversion for the direct capture medium electrolysis.

### Considerations in the reaction environment

There is a large family of CO<sub>2</sub>-capture media, especially the amine-based ones.<sup>39</sup> Amine design or using a mixed amine system as the electrolyte could be another solution to accelerate breaking the C–N bond. Several factors should be taken into account along this research path. An increase in the number and bulkiness of the substituent in amines tends to lower regeneration energy as the C–N bond becomes weaker, but this comes at the expense of lower absorption rate.<sup>40</sup> Meanwhile, different from aqueous electrolytes, amines normally have a high viscosity. Using amines with high concentration or high viscosity as electrolytes for direct electrolysis may lead to a decrease in reaction rate and efficiency due to mass transfer limitations.<sup>41</sup>

Trace impurities, such as SO<sub>x</sub> and NO<sub>x</sub>, are common in point source emissions.<sup>42</sup> The influence of these impurities should be considered carefully. Jiao *et al.* studied the impact of SO<sub>2</sub> and various NO<sub>x</sub> (including NO, NO<sub>2</sub>, and N<sub>2</sub>O) on CO<sub>2</sub> electrolysis with various catalysts in gas-fed flow cells.<sup>43,44</sup> Their results indicated that the presence of SO<sub>2</sub> and NO<sub>x</sub> reduces the efficiency of CO<sub>2</sub> electrolysis due to the preferential reduction of these impurities. In the case of Ag and Sn, the effect of the SO<sub>2</sub> impurity is reversible. In contrast, a selectivity shift to formate was observed on the Cu catalyst with the suppression of C<sub>2+</sub> products, indicating that Cu is highly sensitive to SO<sub>2</sub> impurities. The impact of NO<sub>x</sub> impurities is reversible. It is expected that the challenges of these impurities, especially SO<sub>x</sub>, are present in the direct electrolysis of carbon capture media and thus a pre-electrolysis purification is possibly a necessity. The CO<sub>2</sub> obtained from direct air capture technology may be more suitable as the CO<sub>2</sub> sources are cleaner than fossil sources.<sup>43,44</sup>

As discussed in the preceding section, it is challenging for the negatively charged carbamate and (bi)carbonate to approach the cathode due to electrostatic repulsion. Tuning ion species in the electrical double layer<sup>19</sup> or using alternative amines hold promise to overcome this fundamental challenge.

### Considerations in techno-economics

A techno-economic assessment is useful to establish performance targets and offers guidance for future technology development. Compared with the existing, separated process of CO<sub>2</sub> capture and electrochemical conversion means, direct electrolysis has considerable advantages. Besides bypassing the costly capture media regeneration and gas compression steps, another significant advantage of the direct electrolysis in improving economic viability is that it reduces capital and maintenance costs of the overall CO<sub>2</sub> capture and utilisation process. Taking the typical amine absorption process as an example, the current process (Fig. 1) requires a two-section process including an amine absorption and a stripping tower

while the direct electrolysis does not require the stripping process. This has potential to reduce the capital and equipment maintenance costs associated with the stripping process. Jens *et al.* reported an assessment of cost-saving by integrating CO<sub>2</sub> capture with utilisation and concluded that, with a feed upstream containing >30 mol% CO<sub>2</sub>, 46% savings in energy demand can be achieved compared to a process without integration.<sup>45</sup> Gao *et al.* found that, although the higher operating voltages of the integrated electrolysis system cause higher energy and operating expenses than those for the gas-fed alternative, it reduces significantly the capital costs since several units, such as the stripper, are no longer required.<sup>46</sup>

The eCO<sub>2</sub>RR generates a number of possible products; aiming at the most economically viable products would bring advantage to improve the market competitiveness. A techno-economic assessment showed that, under the current gas-fed eCO<sub>2</sub>RR conditions, CO and formic acid are the most economically viable products with the net present values (NPVs) of US\$13.5 million and US\$39.4 million, respectively.<sup>47</sup> Both products have been reported by the current direct capture medium process. Among the products, syngas (a mixture of CO and H<sub>2</sub>), as a valuable intermediate used for manufacture of chemicals and fuels with a considerable global market size, should be highlighted as one of the most feasible targets for the direct capture medium electrolysis.<sup>48</sup> One advantage of the direct capture medium electrolysis over the gas-fed eCO<sub>2</sub>RR process is that the single-pass conversion efficiency could be much higher (if not 100% due to the small amount of unreacted CO<sub>2</sub> locally generated) as the gaseous product would not be otherwise diluted by the large amount of unreacted CO<sub>2</sub>.

A complete energy and economic analysis are favoured to look at the entire CO<sub>2</sub> capture and valorisation chain. This may start from different sources of CO<sub>2</sub>, each step in the valorisation process, and the end product applications, market size, and energy supply systems involved.

## Conclusion and outlook

The attempts of direct electrolysis of carbon capture media have made some considerable progress. Industrial-level current densities ( $\geq 100$  mA cm<sup>-2</sup>) have been achieved through advances in materials and system design (Table 1). Besides, the direct (bi)carbonate electrolysis offers a promising way to solve the 'carbonate formation' issue which troubles the low-temperature gaseous CO<sub>2</sub> electrolysis in neutral and alkaline electrolytes.<sup>49</sup>

Despite these recent advances, the direct electrolysis of both carbamate and (bi)carbonate is limited by low CO<sub>2</sub> availability at the interface of electrode/electrolyte. Further advances towards one-step reduction require strategies to ease the cleavage of the C–N bond and to increase the accessibility of negatively charged carbon-containing species. Physical chemistry characterisation of bond formation and cleavage and the adsorption and desorption on the electrode surface may shed light on mechanisms underpinning new materials design strategies. Additionally, the corrosive nature of amines to metals, the most widely used electrode materials for

electrocatalysis, presents a potential challenge in maintaining electrolyser lifetime and catalyst stability. The evaluation of the impact of such corrosion on the durability and robustness of systems should be taken into consideration.

To summarise, previous studies have proven the feasibility of direct electrolysis and show considerable economic benefits relative to a separated CO<sub>2</sub> valorisation system. Further advances in targeted strategies for catalyst materials, electrolyser and system designs, and mechanistic understanding, are warranted.

## Conflicts of interest

There are no conflicts to declare.

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## References

- 1 F. P. García de Arquer, C.-T. Dinh, A. Ozden, J. Wicks, C. McCallum, A. R. Kirmani, D.-H. Nam, C. Gabardo, A. Seifitokaldani, X. Wang, Y. C. Li, F. Li, J. Edwards, L. J. Richter, S. J. Thorpe, D. Sinton and E. H. Sargent, *Science*, 2020, **367**, 661–666.
- 2 B. D. Patterson, F. Mo, A. Borgschulte, M. Hillestad, F. Joos, T. Kristiansen, S. Sunde and J. A. Van Bokhoven, *Proc. Natl. Acad. Sci. U. S. A.*, 2019, **116**, 12212–12219.
- 3 M. Bui, C. S. Adjiman, A. Bardow, E. J. Anthony, A. Boston, S. Brown, P. S. Fennell, S. Fuss, A. Galindo and L. A. Hackett, *Energy Environ. Sci.*, 2018, **11**, 1062–1176.
- 4 E. S. Sanz-Pérez, C. R. Murdock, S. A. Didas and C. W. Jones, *Chem. Rev.*, 2016, **116**, 11840–11876.
- 5 M. Ramdin, T. W. de Loos and T. J. Vlugt, *Ind. Eng. Chem. Res.*, 2012, **51**, 8149–8177.
- 6 G. T. Rochelle, *Science*, 2009, **325**, 1652–1654.
- 7 K. Li, W. Leigh, P. Feron, H. Yu and M. Tade, *Appl. Energy*, 2016, **165**, 648–659.
- 8 W. A. Smith, T. Burdyny, D. A. Vermaas and H. Geerlings, *Joule*, 2019, **3**, 1822–1834.
- 9 A. Barthel, Y. Saih, M. Gimenez, J. D. Pelletier, F. E. Kühn, V. D'Elia and J.-M. Basset, *Green Chem.*, 2016, **18**, 3116–3123.
- 10 I. S. Metcalfe, M. North, R. Pasquale and A. Thursfield, *Energy Environ. Sci.*, 2010, **3**, 212–215.
- 11 A. Chapman, C. Keyworth, M. Kember, A. Lennox and C. Williams, *ACS Catal.*, 2015, **5**, 1581–1588.
- 12 T. Li, E. W. Lees, M. Goldman, D. A. Salvatore, D. M. Weekes and C. P. Berlinguette, *Joule*, 2019, **3**, 1487–1497.
- 13 B. Li, Y. Duan, D. Luebke and B. Morreale, *Appl. Energy*, 2013, **102**, 1439–1447.
- 14 C. Sun and P. K. Dutta, *Ind. Eng. Chem. Res.*, 2016, **55**, 6276–6283.
- 15 T. Li, E. W. Lees, Z. Zhang and C. P. Berlinguette, *ACS Energy Lett.*, 2020, **5**, 2624–2630.
- 16 L. Chen, F. Li, Y. Zhang, C. L. Bentley, M. Horne, A. M. Bond and J. Zhang, *ChemSusChem*, 2017, **10**, 4109–4118.
- 17 E. Pérez-Gallent, C. Vankani, C. Sánchez-Martínez, A. Anastasopol and E. Goetheer, *Ind. Eng. Chem. Res.*, 2021, **60**, 4269–4278.
- 18 M. Abdinejad, Z. Mirza, X.-A. Zhang and H.-B. Kraatz, *ACS Sustainable Chem. Eng.*, 2020, **8**, 1715–1720.
- 19 G. Lee, Y. C. Li, J.-Y. Kim, T. Peng, D.-H. Nam, A. Sedighian Rasouli, F. Li, M. Luo, A. H. Ip, Y.-C. Joo and E. H. Sargent, *Nat. Energy*, 2021, **6**, 46–53.
- 20 C.-F. de Lannoy, M. D. Eisaman, A. Jose, S. D. Karnitz, R. W. DeVaul, K. Hannun and J. L. Rivest, *Int. J. Greenhouse Gas Control*, 2018, **70**, 243–253.
- 21 M. D. Eisaman, J. L. Rivest, S. D. Karnitz, C.-F. de Lannoy, A. Jose, R. W. DeVaul and K. Hannun, *Int. J. Greenhouse Gas Control*, 2018, **70**, 254–261.
- 22 T. DeVries, *Global Biogeochem. Cycles*, 2014, **28**, 631–647.
- 23 I. A. Digdaya, I. Sullivan, M. Lin, L. Han, W.-H. Cheng, H. A. Atwater and C. Xiang, *Nat. Commun.*, 2020, **11**, 4412.
- 24 Y. Hori and S. Suzuki, *J. Electrochem. Soc.*, 1983, **130**, 2387.
- 25 X. Min and M. W. Kanan, *J. Am. Chem. Soc.*, 2015, **137**, 4701–4708.
- 26 Z. Zhang, E. W. Lees, F. Habibzadeh, D. A. Salvatore, S. Ren, G. Simpson, D. G. Wheeler, A. Liu and C. P. Berlinguette, *ChemRxiv*, 2021, DOI: 10.26434/chemrxiv.12891071.v3.
- 27 Z. Zhang, E. Lees, S. Ren, A. Huang and C. Berlinguette, *ChemRxiv*, 2021, DOI: 10.26434/chemrxiv.13665074.v1.
- 28 A. J. Welch, E. Dunn, J. S. DuChene and H. A. Atwater, *ACS Energy Lett.*, 2020, **5**, 940–945.
- 29 Y. C. Li, G. Lee, T. Yuan, Y. Wang, D.-H. Nam, Z. Wang, F. P. García de Arquer, Y. Lum, C.-T. Dinh, O. Voznyy and E. H. Sargent, *ACS Energy Lett.*, 2019, **4**, 1427–1431.
- 30 U. H. Bhatti, S. Nam, S. Park and I. H. Baek, *ACS Sustainable Chem. Eng.*, 2018, **6**, 12079–12087.
- 31 U. H. Bhatti, D. Sivanesan, S. Nam, S. Y. Park and I. H. Baek, *ACS Sustainable Chem. Eng.*, 2019, **7**, 10234–10240.
- 32 R. Kortlever, J. Shen, K. J. P. Schouten, F. Calle-Vallejo and M. T. Koper, *J. Phys. Chem. Lett.*, 2015, **6**, 4073–4082.
- 33 S. Nitopi, E. Bertheussen, S. B. Scott, X. Liu, A. K. Engstfeld, S. Horch, B. Seger, I. E. Stephens, K. Chan and C. Hahn, *Chem. Rev.*, 2019, **119**, 7610–7672.
- 34 X. Li, S. Fu, W. Zhang, S. Ke, W. Song and J. Fang, *Sci. Adv.*, 2020, eabd1580.
- 35 J. Peng, B. Chen, Z. Wang, J. Guo, B. Wu, S. Hao, Q. Zhang, L. Gu, Q. Zhou and Z. Liu, *Nature*, 2020, **586**, 390–394.
- 36 R. I. Masel, Z. Liu, H. Yang, J. J. Kaczur, D. Carrillo, S. Ren, D. Salvatore and C. P. Berlinguette, *Nat. Nanotechnol.*, 2021, **16**, 118–128.
- 37 F. Li, A. Thevenon, A. Rosas-Hernández, Z. Wang, Y. Li, C. M. Gabardo, A. Ozden, C. T. Dinh, J. Li, Y. Wang, J. P. Edwards, Y. Xu, C. McCallum, L. Tao, Z.-Q. Liang, M. Luo, X. Wang, H. Li, C. P. O'Brien, C.-S. Tan, D.-H. Nam, R. Quintero-Bermudez, T.-T. Zhuang, Y. C. Li, Z. Han, R. D. Britt, D. Sinton, T. Agapie, J. C. Peters and E. H. Sargent, *Nature*, 2020, **577**, 509–513.

- 38 E. W. Lees, M. Goldman, A. G. Fink, D. J. Dvorak, D. A. Salvatore, Z. Zhang, N. W. Loo and C. P. Berlinguette, *ACS Energy Lett.*, 2020, **5**, 2165–2173.
- 39 W. Gao, S. Liang, R. Wang, Q. Jiang, Y. Zhang, Q. Zheng, B. Xie, C. Y. Toe, X. Zhu and J. Wang, *Chem. Soc. Rev.*, 2020, **49**, 8584–8686.
- 40 F. A. Chowdhury, H. Okabe, H. Yamada, M. Onoda and Y. Fujioka, *Energy Procedia*, 2011, **4**, 201–208.
- 41 E. Pérez-Gallent, C. Vankani, C. Sánchez-Martínez, A. Anastasopol and E. Goetheer, *Ind. Eng. Chem. Res.*, 2020, **60**, 4269–4278.
- 42 J. Zhang, P. Xiao, G. Li and P. A. Webley, *Energy Procedia*, 2009, **1**, 1115–1122.
- 43 W. Luc, B. H. Ko, S. Kattel, S. Li, D. Su, J. G. Chen and F. Jiao, *J. Am. Chem. Soc.*, 2019, **141**, 9902–9909.
- 44 B. H. Ko, B. Hasa, H. Shin, E. Jeng, S. Overa, W. Chen and F. Jiao, *Nat. Commun.*, 2020, **11**, 5856.
- 45 C. M. Jens, L. Müller, K. Leonhard and A. Bardow, *ACS Sustainable Chem. Eng.*, 2019, **7**, 12270–12280.
- 46 N. Gao, C. Quiroz-Arita, L. A. Diaz and T. E. Lister, *J. CO<sub>2</sub> Util.*, 2021, **43**, 101365.
- 47 M. Jouny, W. Luc and F. Jiao, *Ind. Eng. Chem. Res.*, 2018, **57**, 2165–2177.
- 48 T. Haas, R. Krause, R. Weber, M. Demler and G. Schmid, *Nat. Catal.*, 2018, **1**, 32–39.
- 49 J. A. Rabinowitz and M. W. Kanan, *Nat. Commun.*, 2020, **11**, 5231.