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A State of the Art Update on Integrated CO_2 Capture and Electrochemical Conversion Systems

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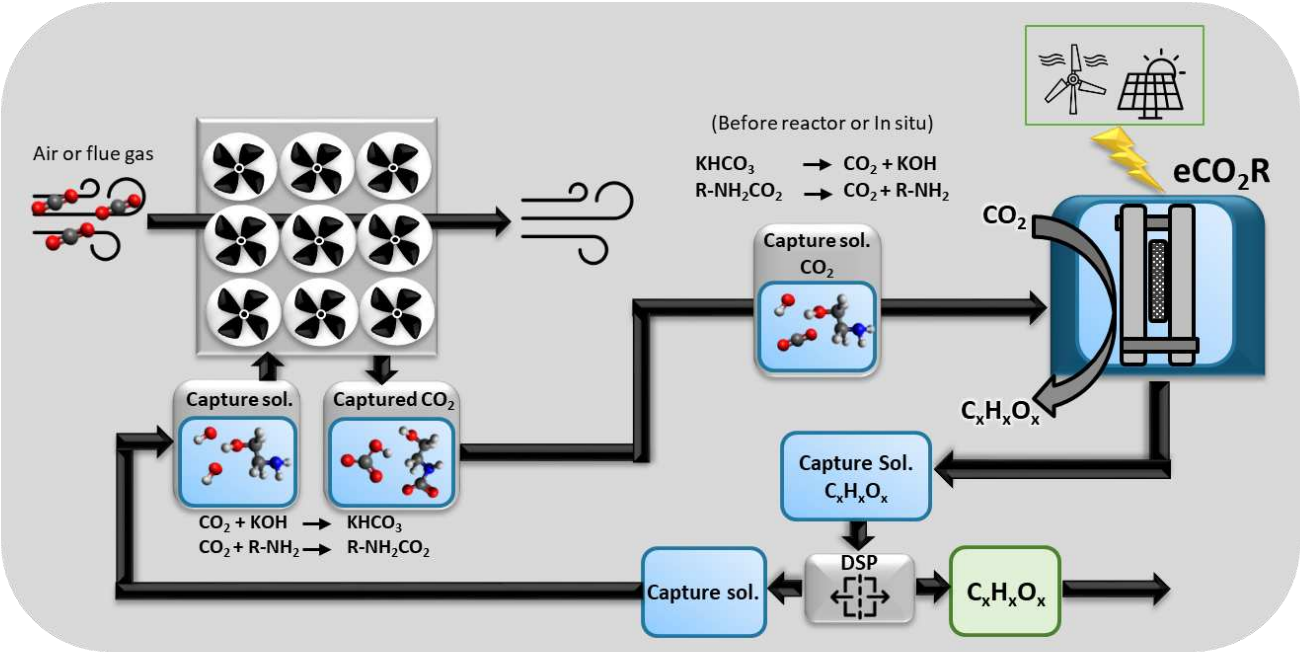

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Abstract

To valorize waste CO_2, capturing and utilizing it to produce chemical building blocks is currently receiving a lot of attention. In this respect, amine and alkali base solutions have shown to be efficient CO_2 capturing solutions and electrochemical CO_2 conversion is a promising technology to convert CO_2 and as such reduce greenhouse gas emissions. However, to date, CO_2 capture and utilization (CCU) technologies have been investigated almost exclusively as separate processes. This has the disadvantage that CO_2 has to be desorbed and compressed from the capture solution before sending it to the CO_2 electrolyzer, seriously increasing the capital and operational costs of the overall technology. To improve the valorization potential of the CCU technologies, integrating both technologies by directly utilizing the capture solution as an electrolyte for the electrochemical CO_2 reduction (eCO_2R) is a highly promising approach. This technology is however limited by low Faradaic efficiencies (FE) and partial current densities that can be achieved with these solutions. The main reason for this is the slow CO_2 release rate at the catalytic interphase. Nevertheless, in recent years, in light of tackling these challenges, several studies successfully managed to decrease the costs of the CO_2 capturing step and to electrochemically convert more efficiently the CO_2 capture solutions. Herein, we review the status of the integrated CO_2 capture and electrochemical conversion technology, discussing the recent developments and advances both in the field of CO_2 capture and eCO_2R.

Author Biographies

Oriol Gutiérrez-Sánchez obtained his B.S in chemistry from the University of Barcelona (Spain) in 2014, where he obtained the M.S. in materials chemistry in 2017, too. He is currently pursuing his Ph.D. at ELCAT (University of Antwerp, Belgium) under Prof. Tom Breugelmans guidance, in close collaboration with VITO (Belgium). His project focuses on integrating CO_2 capture and electrochemical conversion systems. His research interests include upscaling CO_2 electroreduction technologies and developing new electrocatalytic routes.

Barbara Bohlen obtained her B.S in chemistry from the Federal University of São Carlos (Brazil) in 2018 and her M.S. in renewable resources from the Technical University of Munich (Germany) in 2021. She is currently pursuing her Ph.D. in electrochemistry at the University of Antwerp (Belgium) under Prof. Tom Breugelmans guidance, focused on the CO_2 reduction from amine-based capture solutions. Her research interests include the development of catalysts for electrochemical processes, especially CO_2 reduction.

Dr. Nick Daems studied Bioscience Engineering at KU Leuven (Belgium) where he graduated as M.S. in catalysis in 2012. Later he obtained his Ph.D under the guidance of Prof. Pescarmona and Prof. Vankelecom at the Centre of Surface Chemistry and Catalysis (KU Leuven, Belgium) in 2016 and stayed as a postdoc until 2018. Then he joined Prof. Tom Breugelmans' research group ELCAT (University of Antwerp). Currently he is the technological manager of ELCAT.

Dr. Metin Bulut is business development manager at VITO (Belgium) and responsible for the outline of the CO_2 Capture and Utilization (CCU) research programs, by coordinating several projects and guiding Ph.D students. He combines market analysis and economic evaluation with technical insights in CO_2 conversion technologies. He is also involved as an expert in the Founding Consortium for a "European Association for CO_2 Utilization". Dr. Bulut gives lectures at University of Antwerp and Hasselt University on techno-economic analysis and CCU, too.

Dr. Deepak Pant is senior scientist at VITO (Belgium) working on electrosynthesis and resource recovery, specifically, the design and optimization of (bio)electrochemical systems for CO_2 conversion and microbial electrosynthesis. He has a Ph.D in environmental biotechnology and has 175 peer-reviewed publications ((H-index 68), 6 edited books, 6 patents and 38 book chapters to his credit. He is the Editor of Bioresource Technology Reports and Editorial board member of BioSource Technology, ACS Sustainable Chemistry & Engineering, iScience and several other journals.

Prof. Tom Breugelmans started his career as a research assistant in 2004 at the Artesis Hogeschool Antwerp (Belgium) and in 2010 he obtained his Ph.D in engineering sciences at the Free University of Brussels (VUB, Belgium). He is currently a professor at the University of Antwerp. He is head of the ELCAT research group and is active in the field of electrochemical engineering. Since 2020, he has taken up the mandate of Dean of the Faculty of Applied Engineering Sciences of the University of Antwerp.

Keywords

Carbon Capture & Utilization, Electrochemical CO_2 Reduction, Direct Air Capture, Carbamate Reduction, Bicarbonate Reduction

1 Introduction

Carbon Capture and Utilization (CCU) technologies have been postulated as one of the most promising strategies to relieve the increase in the concentration of CO_2 present in the atmosphere and introduce sustainable carbon cycles by using CO_2 directly from the air or flue gasses as a substrate in the chemical industry.[1–6] In this way, the CO_2, which is mostly released from energy production or industrial processes, can be converted back to fuels (like syngas or alcohols)[7,8] or chemical synthesis precursors (such as formic acid, carbon monoxide or oxalic acid).[9–12] However, capturing, storing and releasing the CO_2 to the chemical reactor is expensive and logistically cumbersome[13,14]. Therefore, integrating the capture and the conversion steps is crucial to decrease the costs and make the process efficient, and thus industrially attractive.[15]

One of the preferred CO_2 conversion technologies to be integrated to the capture step is the electrochemical conversion of CO_2 (eCO_2R). By using an electrocatalyst and renewable energy such as wind and solar, CO_2 can be selectively and efficiently converted towards a variety of end products depending on the applied potential and the catalyst, in a process commonly referred to as Power to X.[16] However, the main drawback of integrating CO_2 capture and eCO_2R is the inefficient route of delivering pure CO_2 to the electrochemical reactor after being captured. To achieve high Faradaic Efficiency (FE), CO_2 needs to be delivered in high concentration and purity, which requires a compression and regeneration step after being captured from the air or flue gases (decreasing to a great extent the efficiency of the process). Strategies to overcome this drawback involve using capturing agents such as alkaline hydroxides or amines to capture the CO_2, producing carbonates and carbamates. Then, the obtained solution is used directly as an electrolyte and as a CO_2 source in the electrochemical reactor. However, reducing directly (and efficiently) carbonates and carbamates was almost non-existing in literature until the last few years, which we discuss in the following chapters. Owing to the recent advances in directly reducing the captured CO_2 solution, the interest and feasibility of the integrated CO_2 capture and (electro)conversion technology increased and year after year new and more studies, publications and projects are appearing that target the optimization of the technology to achieve an efficient industrial CCU process.

In this compact review, we cover the most recent advances towards the integration of CO_2 capture and eCO_2R technologies, specifically by reviewing the most important studies in CO_2 capture and very recent literature in eCO_2R using CO_2 captured solutions (2018-2021). The elaboration of this review is motivated by the fact that crucial strategies to integrate CO_2 capture and eCO_2R (such as an efficient procedure to directly reduce carbamate or (bi)carbonate solutions which were, until recently, almost unreported and experimentally unfeasible) have been published in the last couple of years, thus unlocking one of the limitations the technology had: using the CO_2 that is chemically bound to the capturing solution. A broader compilation of these new studies is needed to understand the current status on integrating CO_2 capture and eCO_2R as much ground has been covered in this field since, to the best of our knowledge, only a (mini-)review touching this topic was published.[17] Compared with the majority of other available review articles in the field of eCO_2R, where they mainly target more fundamental aspects (such as catalyst configuration or reaction mechanism), we look more from an industrial point of view, exploring the aspects that can contribute to upscaling the technology and in optimizing the energy efficiency of the overall CCU process. We focus on CO_2 capture technologies (giving special attention to the source of CO_2, the capturing agent and what kind of solution is delivered afterwards) and on eCO_2R systems where the source of CO_2 is a (real or mimicked) CO_2 captured solution (looking at the reactor design, used membranes and catholyte composition). Finally, we provide a glimpse of what these new emerging technologies represent for the integration of both systems.

2. CO_2 source: Capture and delivery technologies

2.1 CO_2 Capture

2.1.1 CO_2 from the air: Direct air capture (DAC)

Direct air capture (DAC) is a type of negative emission technology, able to retrieve CO_2 directly from the atmosphere, where CO_2 is present in low concentrations (i.e. 400-420 ppm).[18] This makes the technology challenging since a high volume of air is needed to obtain usable amounts of CO_2. The main technology proposed for DAC uses concentrated alkaline solutions, such as KOH, to react with CO_2, generating carbonate. To recover CO_2 in the form of a high purity concentrated gas, carbonate is typically precipitated with calcium hydroxide and the calcium carbonate is calcined at elevated temperatures to generate calcium oxide and CO_2.[19] An alternative to concentrated alkaline bases is the use of a solid sorbent (such as zeolites, supported amines or porous carbon),[20] which requires less energy for the desorption of CO_2 but is impossible to use as a feed for CO_2 electrolysis. The DAC process, however, has two major disadvantages. On the one hand, it is highly energy-intensive (huge amounts of air need to be processed to capture significant amounts of CO_2, which needs to be subsequently released and compressed, further adding to the energy cost) and, on the other hand, it typically also results in water evaporation, especially when the air is dry.[21] Sanz-Pérez *et al.* published a thorough review on the direct capture of CO_2 from the air and presented new materials that could be used in this technology such as alkali carbonates, amine-supported materials or metal-organic frameworks (MOFs).[22]

Although it is a costly technology (typically ranging from 100 to 1000 US\$ t^{-1}),[23] according to the International Energy Agency (IEA), there are currently 19 DAC (pilot) plants operating in Europe, the United States and Canada, capturing more than 9000 tCO_2 $year^{-1}$ (Table 1).[24] However, most of these plants are still on small scale and the CO_2 captured cannot be delivered in significant quantities, limiting its applicability. Nevertheless, Carbon Engineering in partnership with Occidental Petroleum is developing a large-scale DAC plant able to capture 1 $MtCO_2$ $year^{-1}$ and it is planned to be operational in 2023. Furthermore, Climeworks, in partnership with Carbfix has recently launched Orca, a plant that can capture up to 4000 tCO_2 $year^{-1}$, almost half the amount of the total CO_2 captured by the 19 DAC plants worldwide currently operating.

Table 1: Some of the current operational DAC (pilot) plants in Europe, the United States and Canada.

Company (Country)	Location	CO_2 removed t $year^{-1}$	Technology	Reference
Climeworks (Switzerland)	Zurich	900	Solid sorbent	[25]
Climeworks (Switzerland) + Carbfix (Iceland)	Iceland	4000	Solid sorbent	[26]
Carbon Engineering (Canada)	British Columbia, Canada	1 t per day	Liquid sorbent (KOH)	[27]
Global Thermostat (USA)	Huntsville, Alabama	Project: up to 40 Kt	Liquid (amine-based)	[28]

Carbon Engineering (Canada)	USA	Planned for 2024: Up to 1 million (1 Mt)	Liquid sorbent	[29]
Prometheus Fuels (USA)	USA	Planned for 2022: 4450 t per year	Combines DAC with eCO_2R	[30]

2.1.2 CO_2 from flue gas

Considering flue gas as the source of CO_2, the most utilized applied capture technology is from post-combustion gases, mainly because of the ease of installing this end-stage technology in the existing plants.[31]

Various processes for the post-combustion capture have been used to this date, for example, membranes, solid adsorbents or solvent-based absorption.[32] Among the different absorption solvents, amine scrubbing is the most dominant technology used for post-combustion CO_2 capture, due to its maturity: the process was already patented in the 1930s and first evaluated at scale in 1991.[33] Different amines can be used as absorbent molecules and the choice of amine depends on factors such as the capacity of absorbing CO_2, absorption rate and heat of absorption.[34] Monoethanolamine (MEA) is a primary amine and the most used in the industrial amine scrubbing process at concentrations up to 30 wt%, due to its low cost, availability and the combination of important CO_2 absorption factors, such as ideal viscosity and high CO_2 absorption capacity.[35,36] The drawbacks of this process are the high energy consumption for the regeneration of the amine, possible thermal degradation, large freshwater consumption and the generation of toxic waste and corrosive fumes during the process.[37,38]

Amine scrubbing is usually associated with the regeneration of the solvent and desorption of CO_2, which is then compressed and stored in geological sites. However, the safety and the consequences of pumping CO_2 into the soil are not fully understood until today, thus requiring other solutions (like the combined technology under investigation here).[31,39] Besides, the regeneration of the amine is an energy-consuming process, since it requires the heating of the capture solution to cleave the C-N bond.[40] According to the literature, the energy consumption of the CO_2 desorption from MEA-H_2O solutions is up to 3.8 GJ t^{-1} CO_2 and 70% of the total operating costs of the process are due to this desorption and regeneration step.[41,42]

Several studies have been carried out to decrease the energy consumption associated with the amine scrubbing process, in an attempt to decrease and/or completely avoid the necessity of heating for regeneration. In this respect, ionic liquid solutions have been studied as an alternative to the aqueous 30 wt% amine solution as they require almost 40% less energy.[42] Another alternative is the use of phase change adsorbent where Li *et al.* studied the combination of five different amines and three alcohols to investigate their behavior after CO_2 absorption. Blends constituted by the mixture of amine/alcohol/water have the characteristic of forming distinct phases after CO_2 absorption and, with that, only the CO_2-rich phase needs to be heated, decreasing the amount of energy required.[41] A final alternative is promoting the electrochemically mediated amine regeneration, where heating is no longer required. The latter is discussed in more detail later in section 3.1.[43,44]

2.2 Catalytic CO_2 capture: improving capture rates

In this case, the capturing solution has the role to react with the CO_2 and form a stable product, such as carbamate or carbonate, to be treated and delivered afterwards. However, due to the low concentration of CO_2 present in the gas mixtures used as CO_2 carriers (especially in air), the energy required for the capturing process is high.[22] Decreasing the time needed to capture a certain quantity of CO_2 is directly translated as decreasing the costs of the technology since the amount of kWh used per ton of CO_2 captured will decrease. For this reason, several studies have focused on how to increase the kinetic rate of the reaction between the CO_2 and the capturing agent, specifically with KOH but possibly to be extrapolated to amines.[45]

Most of the studies that focused on increasing the rate constant of the reaction between CO_2 and OH^- to form bicarbonate are inspired by the enzymatic reaction found in nature which is catalyzed by the enzyme carbonic anhydrase (CA).[46,47] The co-factor of carbonic anhydrase is a metal complex formed by Zn^{2+} and three histidine terminals from the enzyme. This structure can easily bind water molecules and decrease to a great extent its pK_a (from 14 to 6.9), promoting its deprotonation and the formation of a fixed activated OH^- structure which then binds CO_2 to form bicarbonate (Figure 1).[48] The rate constant of the CO_2 hydration in CA is at least 10^6 M^{-1} s^{-1}, thus there is interest in integrating these systems in current CO_2 capture technologies as this could significantly enhance the capture rate.[49,50] One of the strategies is to integrate the biomimetic system in components such as membranes or porous materials. This increases the reusability of the enzyme as well as the mechanical resistance of the capturing material. Wen *et al.* synthetized a reusable membrane for converting CO_2 to bicarbonate based on a bimetal (Zn^{2+} and Cu^{2+})-protein hybrid hydrogel.[51] This material presented a recovery activity of 70% compared to analogous control experiments where the activity was 35% (Zn-based support) and 10% (Cu-based support). On the other hand, Jin *et al.* developed a re-usable, stable, MOF with structural similarities to the Zn-coordination complex in CA to improve CO_2 absorption kinetics and proposed a model to convert CO_2.[52] They evaluated the material by investigating the hydrolysis of *para*-nitrophenyl acetate, usually used to evaluate the performance of the CA enzyme, probing the biomimetic properties of the material. Other research exploited the engineering challenges of the technology, such as finding durable support for the immobilization of the CA onto surfaces. Kim *et al.* explored the stability of the CA immobilized onto the renewable support material diatom bio-silica.[53] This biomaterial showed high reusability and no enzyme leakage even at elevated temperature conditions. Molina-Fernandez *et al.* recently reviewed further strategies to immobilize CA in surfaces for industrial implementation.[54] Another approach exploited is to use the CA or the biomimetic material directly suspended in the capturing solution. Sivanesan *et al.* evaluated a series of Zn-coordinated metal complexes in a tertiary amine medium by calculating the rate constant of the CO_2 hydration in each case scenario for its implementation in CO_2 capture from industrial gas waste.[55] In a similar strategy, Hanunsch *et al.* studied the performance of a metal-free pyrrolizidine catalyst for DAC and CO_2 conversion applications.[56]

Using materials that mimic the enzymatic reaction of CA is an interesting approach to decrease the costs of capturing CO_2. However, there still exist some drawbacks and challenges to consider before applying this technology in an upscaled system. For instance, for materials involving the immobilization of the enzyme, the stability of the enzyme is an issue. Flue gas streams use to be at elevated temperatures in the range of 150-1200 °C. At this temperature range, CA degrades.[57] On the other hand, using an enzymatic suspension in the capturing solution could be suboptimal if we consider that the solution will be later used as the electrolyte in the electrochemical cell. A separation and recovery step should be needed, increasing the costs of the technology. The most optimal route seems to be synthesizing thermoresistant materials (such as carbon-based or MOFs) that bio-mimic the enzymatic reaction of the CA without the necessity of integrating the enzyme, acting as heterogeneous catalysts. These materials would be easily removed from the solution without the necessity of adding extra steps to the capturing process.

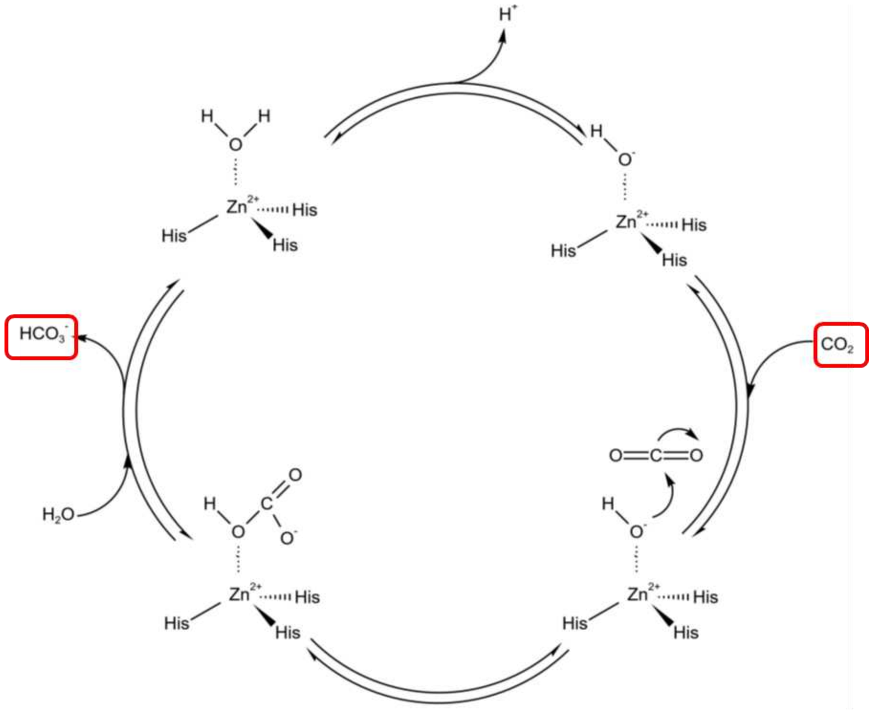

Figure 1: Mechanism of the hydration of CO_2 in the metal cofactor of the enzyme carbonic anhydrase (adapted from Freeman *et al.*, 2012)

3. Post-capture Electrochemical CO_2 conversion

3.1 CO_2 conversion from carbamate

The use of CO_2 directly from the amine (in form of carbamate) capture solution presents an added advantage, apart from avoiding the thermal solvent regeneration process, that is evading the sequestration of CO_2 into geological sites and the generation of chemicals of industrial interest, such as fuels and syngas.[35,41,58] Chen *et al.* published the first report on the direct electrochemical reduction of CO_2 from amine capture solutions. Different metal catalysts were tested for the generation of products such as carbon monoxide and formate and two techniques were applied to improve the performance towards CO_2 reduction: increase of the catalyst surface area and the addition of a surfactant; a FE for formate of up to 60.8% was reached with a porous Pb electrode in the presence of the surfactant.[35] Lee *et al.* presented more recently a study on the effect of the addition of cations on the direct electrochemical CO_2 reduction of the amine scrubbing medium. Cations were added to the MEA solution to modify the electrochemical double layer and improve the reduction reaction. A FE of 72% for CO was achieved by using an Ag catalyst, at a current density of 50 mA cm^{-2} by using 2 M KCl as salt.[58] Adding alkali salts to promote CO_2 conversion from amines was also explored in the same year by Khurram *et al.*.[59] In their study, they investigate the role of individual electrolyte salt constituents across multiple cations and anions in DMSO electrolytes to clearly understand the role of these salts in the performance of the reaction. They concluded that although the anion appears to have a minor effect, the cation is found to strongly modulate the thermochemistry of the amine–CO_2 adducts through electrostatic interactions. Pérez-Gallent *et al.* evaluated the performance of an amine-based capture solvent as electrolyte for CO_2 conversion achieving up to 50% FE for formate and up to 45% for CO with carbon conversion of 30%. They promoted the reaction rate by a factor of 10 by increasing the temperature up to 75 °C.[60]

It is clear that based on the studies published in recent years and discussed in this paper, reducing CO_2 that has been previously captured by an amine holds promise but there is still room for improvement as compared to the typical gaseous CO_2 electrolyzers in terms of FE and current density. However, thanks to the advancement in understanding how to dissociate the CO_2 from the amine in the electrochemical reactor, the next studies can focus on optimizing engineering aspects of the reactor to achieve higher overall energy efficiency,

3.2 CO_2 conversion from bicarbonate

CO_2 is captured in the form of bicarbonate when strong bases like KOH are used as capturing solutions. Bicarbonate can be easily stored and delivered to the electrochemical reactor.

However, its feasibility as a substrate for the direct electrochemical bicarbonate reduction reaction has been discussed within the community for a long time since extremely low FE towards carbon products has been observed when bicarbonate electrolytes that have not been previously purged or saturated with CO_2 are used, with H_2 being the main product.[61]

The role of bicarbonate in the eCO_2R has been continuously studied and debated. On the one hand, some reports are claiming that bicarbonate is reduced in pure (or saturated with CO_2) bicarbonate electrolytes acting as a substrate of the electrochemical reduction reaction.[62–64] Later on, bicarbonate was identified as a carbon donor, releasing CO_2 from the equilibrium near the active sites, and CO_2 being the actual substrate of the reaction. Dunwell *et al.* proposed that bicarbonate, at concentrations below 0.5 M, acts as a carbon donor feeding CO_2 to the surface of the electrode during the eCO_2R.[65] Later, Ooka *et al.* identified that when the concentration of bicarbonate is higher (>1 M), bicarbonate acts as a proton donor instead of a carbon donor, promoting to a great extent the Hydrogen Evolution Reaction (HER), in accordance with the experimental observations done up to date.[66] This effect was recently confirmed by Gutierrez-Sanchez *et al.*, where the proton donor ability of bicarbonate was inhibited by covering the surface of the electrode with a hydrophobic layer, thus allowing only CO_2 to trespass and increasing the selectivity to carbon products by 60%.[61,67] They conclude that since the desorbed CO_2 from bicarbonate is most likely the main electrochemical active species, to achieve high selectivity it is important to promote its release and avoid bicarbonate to act as a proton donor.

Based on these recent findings, the research on developing an electrochemical bicarbonate reduction reactor has drifted towards promoting the carbon donor ability of bicarbonate, to increase the in-situ concentration of CO_2 at the surface of the electrode and thus increase the FE and partial current density towards carbon products. The main strategy followed nowadays to perform the electrochemical bicarbonate reduction reaction is to build the set up in a zero-gap flow electrolyzer, using a bipolar membrane (BPM) as a separator. In a zero-gap configuration, the protons formed in the BPM from the water dissociation heavily influence the catholyte next to the electrode surface and the performance of the reaction.[68] The protons formed from the BPM react with the bicarbonate to form water and dissolved CO_2, which will then be the substrate of the electrochemical reaction (Figure 2). Li *et al.* used a zero-gap flow electrolyzer and a BPM to develop an electrochemical reactor that reduces bicarbonate from a 3 M bicarbonate electrolyte to CO with a FE of 81% at 25 mA cm^{-2} and 37% at 100 mA cm^{-2}.[69] Lees *et al.* further explored the electrochemical reduction of bicarbonate to CO by performing an optimization study of the working electrode.[70] They concluded that commonly used components that improve the performance of gas-diffusion electrodes (GDE) used as catalyst support additives for CO_2 reduction flow cells, such as PTFI and microporous layers, are not beneficial for the performance of the electrochemical bicarbonate reduction. Since CO_2 is diffused from bicarbonate, gas-diffusion layers are no longer needed and they could limit the performance of the electrode. Later on, they also reduced bicarbonate to formate in a similar set up achieving a FE of 60% at 100 mA cm^{-2} but using Bi as an electrocatalyst.[71]

Thanks to the understanding of how the electrochemical reduction of bicarbonate works achieved in recent years (2019-2021), electrolyzers that involve bicarbonate as the single carbon donor species can now compete in terms of FE and partial current density with state-of-the-art gaseous CO_2 electrolyzers. However, the technology remains a step below in terms of optimization. To make it feasible, either additives in the electrolyzer (usually undesired in terms of downstream processing) or the necessity to use a BPM (high cell voltage at current densities > 300 mA cm^{-2}) is currently needed. Despite these drawbacks, being able to convert directly a bicarbonate CO_2 captured solution adds a higher value to the valorization of the whole CCU process. Overstepping costly CO_2 treatment steps previous to the delivery to the electrochemical cell might compensate for the higher energy requirements for the conversion step. Thus, further optimization of the reactor and the components directly influencing the reaction (such as the BPM and the electrocatalyst) is needed to increase the overall energy efficiency and finally achieve a positive capture-conversion energy balance.

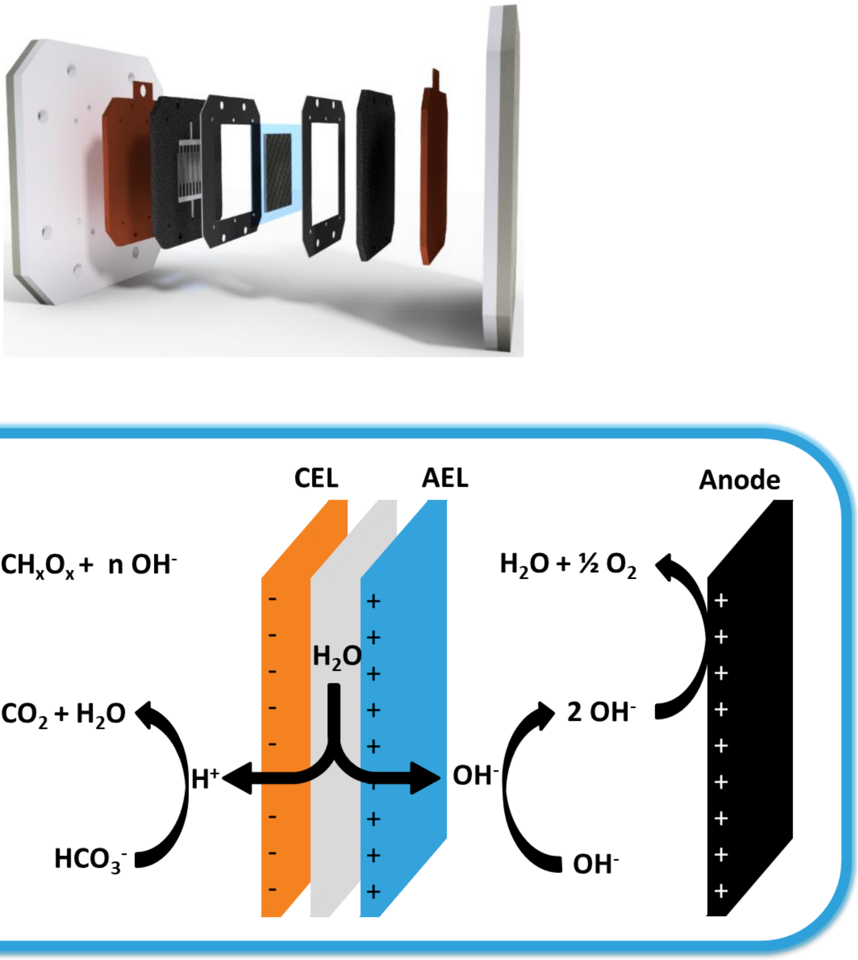

Figure 2: Zero-gap flow cell reactor configuration (obtained from De Mot *et al*., 2021) and the schematic representation of the mechanism of bicarbonate electrochemical reduction in reactors involving a BPM.

4. Emerging technologies: CO_2 Capture and Conversion from Ionic Liquids and Covalent Organic Frameworks

Besides the well-established processes based on amine and alkaline media, different sorbents have been investigated as agents for CO_2 capture.[72] Among these, two types are prominent, whose directed design leads to a wide range of application directed materials: ionic liquids (IL), a type of liquid sorbent, previously mentioned as an alternative for the amine scrubbing solution, and covalent organic frameworks (COFs), a solid sorbent.[73] Changing the combination of cations and anions of ILs or the organic precursors of the COFs, their characteristics can be tuned, for example for an increased selectivity towards CO_2, which is important for the capture from sources with a low concentration of CO_2 or a mixture of gases.[74,75] Both technologies are in the conceptual phase of industrial readiness, nonetheless, they are promising techniques with efficient capture potential.

In addition to the advantageous use as capture agents, ILs are interesting electrolytes for the CO_2R because these are not aqueous solutions, so the competing HER is suppressed and the efficiency of the CO_2R increased. Besides, the CO_2 molecule captured by the IL has a bent structure, which leads to smaller overpotentials required for the reduction reaction.[73] Lu *et al.* present a type of IL as capture solution and electrolyte for the photoelectrochemical conversion of CO_2 to formate with a FE of 94.1%. [76] COFs present a high affinity towards CO_2, which poses an advantage of their use as capture agents and is one characteristic that encouraged the investigation of these materials as catalysts for the CO_2R. This is a solid sorbent, thus the combination with the electrochemical process will be different than for the liquid absorbents, its capability of being used as a catalyst for the CO_2R may lead to the development of one-step capture and conversion processes. Ozdemir *et al.* present a series of different studies that utilized COF as catalysts for the CO_2R.[74] Liu *et al.* present an amine COF as a catalyst on a silver electrode for the CO_2R to CO, with notably enhanced performance and chemical stability.[77]

Studies presenting the use of these capture agents in the eCO_2R demonstrate the feasibility of the combination of capture and conversion.[78] Increasing investments and research in this topic will lead to the development of the technologies, decreasing the associated cost and increasing the competitiveness to the state of the art processes.

Conclusions and perspectives

Integrating CO_2 capture and electrochemical conversion remains a challenge due to the high energy requirements in capturing the CO_2 (specifically from the air) and the difficulty to valorize the CO_2 afterwards. However, thanks to the recent advances in converting CO_2 directly from the capturing solution (in form of carbamate and bicarbonate), the technology is now approaching feasibility in terms of total energy and carbon balance, since previously one of the most cost-intensive steps was the compression and purification of CO_2 from the capturing solution. Nevertheless, the energy efficiency of the electrochemical reaction is still too low for industrial applicability. CO_2 conversion from carbamates showed promising results, but the current density is still too low for upscaling (in the range of 50 mA cm^{-2}) and most of the systems still involve heating and thus an extra energy cost. On the other hand, CO_2 conversion from bicarbonate solutions showed satisfactory results in terms of current density (more than 300 mA cm^{-2} in some studies) and FE (more than 50%) but using a BPM (high ohmic drop) and a zero-gap configuration (limited applicability) is required. Further research in optimizing these reactors is needed to valorize the high energy requirements of capturing CO_2 from the air or flue gas. For instance, parameters such as the morphology of the catalyst material, the flow rate of the electrolyte or the configuration of the BPM might influence the performance of the reactor. Another interesting approach could be to use of real DAC or flue gas captured samples as electrolyte for the eCO_2R since now it is experimentally proven that the captured solution (although artificially prepared) can be converted.

The coupling of capture solution and CO_2 valorization, based on renewable energy can be a future sustainable approach to restrain the advance of CO_2 emissions and fossil fuel usage and tackle the consequences of anthropogenic actions in the environment. For that, many improvements can be made in the direct electrochemical CO_2 reduction from capture medium, especially focusing on enhanced performance, if investments are directed to this increasing field of research.

Conflicts of interest

There are no conflicts to declare.

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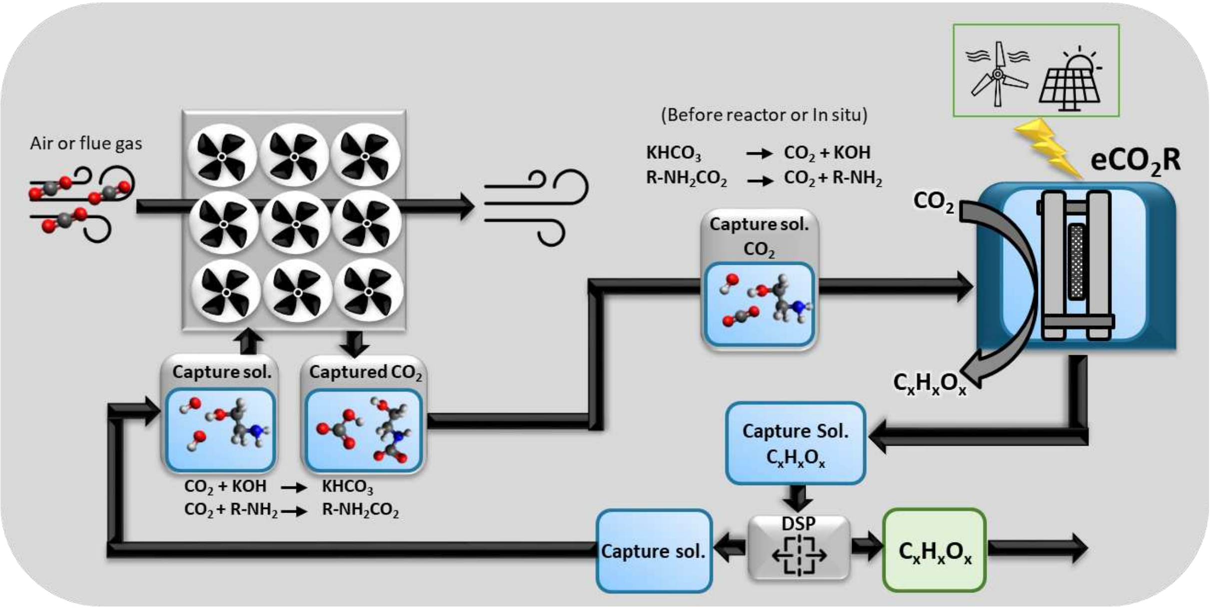

To improve the valorization potential of the Carbon Capture & Utilization technologies, integrating both the capture and the conversion strategies by directly utilizing the capture solution as an electrolyte for the electrochemical CO_2 reduction (eCO_2R) is a highly promising approach. We review the status of the integrated CO_2 capture and electrochemical conversion technology, discussing the recent developments and advances both in the field of CO_2 capture and eCO_2R.