

Integration of CO₂ Capture and Electrochemical Conversion

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Abstract

Integration of CO₂ capture and CO₂ conversion through electrochemical processes has emerged in recent years, offering a distinct advantage over the traditional independent methods by obviating the costly capture media recovery and compression steps. This review aims to provide a comprehensive overview of this promising research area. State-of-the-art studies of strategies involving independent processes, coupling in a single electrolytic cell, and integration into two electrolytic cells for CO₂ capture and conversion are discussed. Furthermore, the energy and production costs for three alternative methods are assessed and compared to highlight the benefits of integration systems. In addition, our personal perspectives on the challenges and opportunities in this emerging field, including high faradic efficiency and low cell voltage achieving, seawater exploration, and membrane-less configuration for high durability applications, are proposed.

CO₂ emissions are a global concern, as they are primarily responsible for global warming and climate change. Over the past 60 years, the world's annual industrial CO₂ emissions have increased by approximately 170%,¹ causing serious harm to the atmosphere and marine life. The CMIP6 model created by Swaminathan et al. predicts that atmospheric warming will exceed 2 °C by the end of the century,² and Tollefson found that the acidification speed of seawater induced by CO₂ has accelerated in recent decades.³ To address this issue, climate policies have been proposed with the aim of reducing the global averaged surface warming to a predetermined level and lowering the global warming threshold in a controllable manner.⁴ The Paris Climate Agreement, signed in 2015 at the 21st United Nations Climate Change Conference, highlighted two primary goals: (1) to limit the increase in global mean surface temperatures to below 2 °C relative to preindustrial levels and (2) to explore pathways that would limit warming to 1.5 °C at the same time.⁵ However, the current situation remains concerning.

The serious situation with relentlessly increased atmospheric CO₂ content has motivated the significant development of less carbon-intensive technologies. Over the past several decades, a wide range of strategies have been developed to manipulate the CO₂ level in the atmosphere, such as replacing fossil fuels using renewables,⁶ enhancing chemical production/energy efficiencies,^{7,8} and implementing carbon capture and conversion technologies.⁹ Among these methods, carbon capture and conversion technologies have undergone sustainable development and have become more attractive for carbon abatement and utilization.

The CO₂ capture and conversion process typically involves a CO₂ capture process and a CO₂ conversion process. Capturing CO₂ is one of the most direct ways to reduce CO₂ content, which can capture CO₂ at stationary point sources, such as flue gas from fossil fuel power plants, industrial manufacturing plants, and refineries, as well as CO₂ gas released from mobile sources, such as automobiles, ships, aircraft, etc. The CO₂ capture history could date back to the 1930s, when a patent was filed for CO₂ capture and stripping using a 30% monoethanolamine solution (Fig. 1a, L1)¹⁰. After decades of

development, a number of technologies based on amine-based CO₂ capture technologies (absorption of CO₂ in amine-based solutions) have been implemented at the industrial level.¹¹ However, some intrinsic shortcomings were exhibited, such as the corrosiveness of the amine solution and the high energy consumption in regenerating the capture medium. A report evaluating the use of amine-based solutions to reduce CO₂ emissions in pulverized coal-fired power plants (PC) was published by the Electric Power Research Institute (EPRI) and the International Energy Agency (IEA) (Fig. 1a, L4).¹² The report stated that implementing this solution would result in a 2.6-fold increase in the cost of coal-fired power generation, which may be difficult for governments and companies to support due to the associated high costs. Chemisorption of CO₂ using hydroxide solutions is another important technology for CO₂ capture, which has been studied and developed for over 60 years. Flue gas desulfurization using lime or limestone slurry scrubbing was first employed in industry in 1936, as indicated by historical records (Fig. 1a, L2)¹³. This method proved to be an effective way to capture CO₂ through the reversible reaction between lime and limestone (equation 1), which can capture and release CO₂ at different temperatures, such as 650 and 900°C, respectively. Despite undergoing sustainable investigations and optimizations, including temperature regulation and process refinement,^{14,15} and the use of hydroxide solutions as a capture medium instead of lime slurry,^{16,17} the calcination processes still require significant energy input. Therefore, the development of new alternative methods for CO₂ capture is necessary.



Recently, the electrochemical processes have emerged as a promising method for capturing CO₂.¹⁸ This process is able to alter the nucleophilicity of target species and control the reaction rates by controlling the potential, which avoids many challenges and inefficiencies associated with thermal systems, such as external high-temperature and high pressures/vacuum input or unexpected sorbent material degradation. The use of electrochemistry for CO₂ capture could be traced back to the late 1960s,¹⁹ when molten carbonates were employed as an electrolyte for CO₂ control in a manned

spacecraft. Currently, electrochemical CO₂ capture methods have been widely applied to all CO₂ streams with diverse concentrations (e.g., air, ocean, and flue gases). Moreover, high-purity CO₂ gas could be generated during the electrochemical process, which could be further integrated with the CO₂ conversion process to realize chemical upgrading.²⁰⁻²²

Following the CO₂ capture process, the collected high-purity CO₂ gas can be compressed and transported for direct usage (non-conversion of CO₂, such as enhanced oil recovery, food & beverage, heat transfer fluids, etc.) or indirect usage (conversion of CO₂ into chemicals, fuels, and building materials). The indirect method involves using pure CO₂ as a feedstock to produce valuable substances such as CO and formate, which has been extensively studied and achieved high efficiency. However, it is important to note that the entire process from dilute CO₂ to final products (dilute CO₂ → capture → high-purity CO₂ → compression → transportation → conversion → products) involves many steps and has low economic value.

Integrating electrochemical CO₂ capture and conversion, also called reactive capture and conversion (RCC) technology (dilute CO₂ → capture + conversion → products), represents a greener and more economical approach compared with the independent process, avoiding the high costs associated with the regeneration of the capture medium and subsequent CO₂ compression.²³⁻²⁵ Depending on how the captured CO₂ is subsequently converted, current research can be divided into four main categories: thermo-catalytic conversion,^{26,27} photochemical conversion,^{28,29} electrochemical conversion,^{30,31} and biological conversion.^{32,33} Among these, the thermo-catalytic conversion of the captured CO₂ is the most reported process, accounting for approximately 78.4% of these studies based on the data of the *Web of Science* by the end of 2022 (Fig. 1b). However, this process requires additional heat input (40-150 °C) to drive the reaction,³⁴⁻³⁶ high-pressure H₂ of over 5 bar as feedstock,^{36,37} and Ru-based catalysts to improve reaction kinetics,^{38,39} which significantly increases the production cost. In comparison, the electrochemical conversion of the captured CO₂ to valuable

chemicals/fuels driven by renewable electricity is one of the most promising processes, departing from the traditional industrial process using fossil fuels. This process relies on the electrons that act as strong redox reagents directly to drive the reduction reaction at the electrode/electrolyte interface. Several advantages, such as (1) operation at room temperature and ambient pressure; (2) sustainability with clean energy as input and decreasing clean electricity prices; and (3) environmental friendliness,^{6,40} have made this process receive strong momentum in recent years. The electrochemical conversion of captured CO₂ process accounted for 16.4% (42 articles) of the studies (Fig. 1b), and the number of articles has increased quickly in the most recent years (Fig. 1c).

In this review, we provide a comprehensive summary of the most recent progress in the coupling of electrochemical CO₂ capture and conversion, aiming to give an overview of this important field. Independent electrochemical CO₂ capture and electrochemical conversion processes are first introduced, emphasizing the advantages and capture/conversion procedures of electrochemical processes. After discussing the most recent advances in integrating CO₂ capture and electrochemical conversion, the energy and production cost comparison will be presented. Then our personal insight into the challenges and opportunities faced by coupling electrochemical CO₂ capture and conversion is provided. Our ultimate goal is to promote the development of this green and economically viable technology, which might help mitigate the global warming issue.

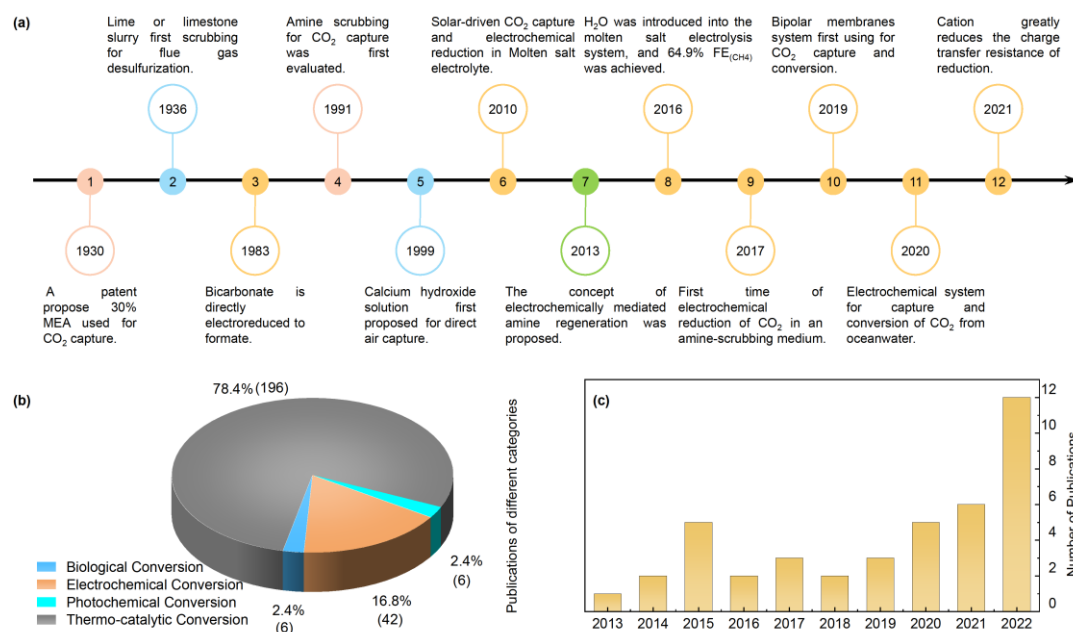


Figure 1. (a) The progress of coupling CO₂ capture and electrocatalytic CO₂ conversion. Timeline showing landmarks (L = 1-12) leading up to the research on amine-based solution capture (rose red), calcium oxide and calcium hydroxide solution capture (blue), electrochemical CO₂ capture (green), and coupling of carbon dioxide capture and electrocatalysis (orange). (b) Percentage and number of 4 different types of publications including thermo-catalytic conversion, photochemical conversion, electrochemical conversion, and biological conversion based on the data of Web of Science. (c) The number of publications on coupling CO₂ capture and electrochemical conversion according to the Web of Science. (As of December 31, 2022. The keywords used to search articles, including “CO₂ capture”, “CO₂ conversion”, “coupling,” and “integration” for the title, then read the abstract to divide the type of the article).

1. Independent CO₂ capture and electrochemical conversion

1.1 Conventional chemical CO₂ capture methods and their disadvantages

Conventional CO₂ capture and conversion processes in industry are independent and separated into different steps, typically including capture, stripping, compression, and subsequent reduction steps (Fig. 2). To give readers a better understanding of the capture process, two representative CO₂ capture technologies based on amine or hydroxide solutions are briefly introduced here.

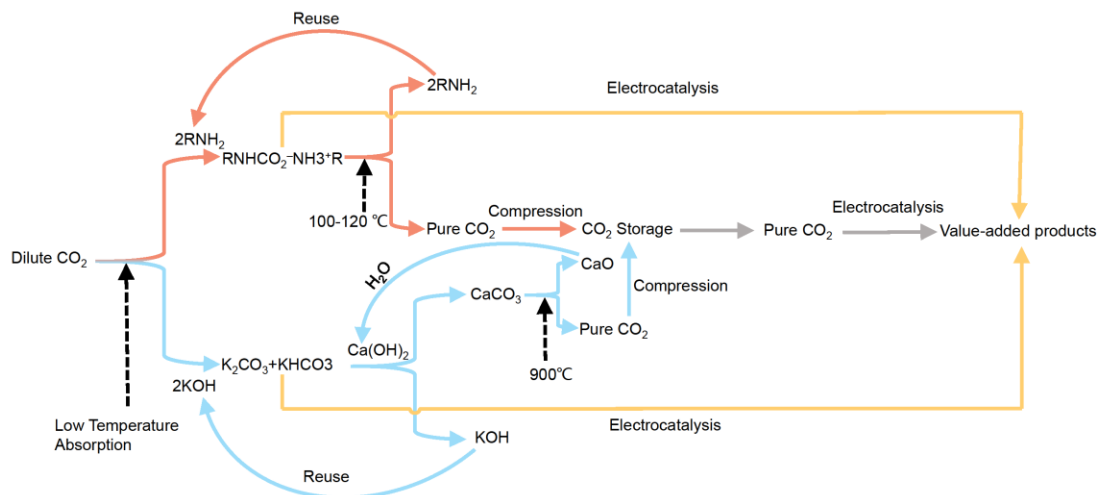
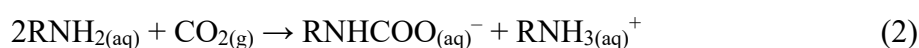


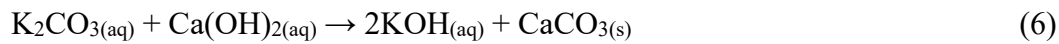
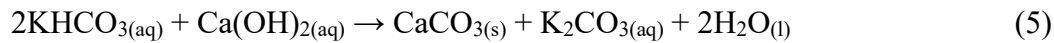
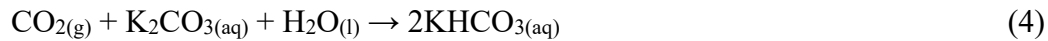
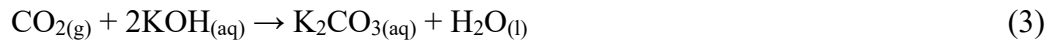
Figure 2. The process of independent/integrated CO₂ capture and electrochemical CO₂ conversion. The rose-red and blue lines represent the conventional CO₂ capture pathways. The gray line is the conventional electrochemical pathway to convert CO₂ into valuable products with the feeding of the released pure CO₂. The orange line is the coupled electrochemical pathway fed directly with the captured CO₂.

One process is based on equation 2, in which dilute CO₂ gas is absorbed by the aqueous amine under ambient conditions to form the carbamate. After reaching the CO₂-rich condition, as shown in the rose-red pathway in Fig. 2, the resulting CO₂-rich amine is then transported to a stripper and regenerated to reusable amine at 100-120 °C while releasing high-purity CO₂. The released CO₂ could be compressed and stored for subsequent electrochemical reduction.



Another traditional process for CO₂ capture relies on the chemical reaction between CO₂ and hydroxide solutions. Benefiting from the high absorption rate with CO₂, the calcium hydroxide solution was proposed as early as 1999 for the direct capture of CO₂ from air (Fig. 1a, L5)⁴¹. However, the low solubility of calcium hydroxide in water (33 mmol/L at room temperature) severely limits the capture capability.⁴² To address this problem, sodium hydroxide (1 mol/L) and potassium hydroxide (1.5 mol/L) solutions, which have high solubility in water, were developed as alternatives to absorb CO₂.^{16,17} The adsorption pathway using the potassium hydroxide solution as an adsorbent is shown by the blue line in Fig. 2. In the adsorption chamber, the dilute CO₂ gas first

reacts with potassium hydroxide to form potassium carbonate (equation 3) and/or potassium bicarbonate (equation 4), after which the potassium carbonate and potassium bicarbonate solutions are transferred to the precipitation chamber, where they react with the calcium hydroxide solution to form a calcium carbonate precipitate and reusable potassium hydroxide (equation 5 and 6). The calcium carbonate precipitate is separated and dried and then subjected to the calcination process (the reverse reaction of equation 1) to produce pure CO₂ and CaO. The CO₂ is then compressed and stored for subsequent electrochemical conversion, while the CaO is recovered and used to prepare calcium hydroxide.



Although both methods have been widely used over the past decades, there remain some intractable problems—the capture media regeneration and CO₂ compression processes require significantly extra energy and cost. For example, in a typical amine-scrubbing process, €90-120 is needed to obtain one ton of high-purity CO₂ in 2010,⁴³ and about half of the cost is related to the energy-intensive process considering the power cost, capital costs, and operating and maintenance costs.^{44,45} In addition, the regeneration processes are fueled by combustion of fossil fuels, leading to additional CO₂ emissions that are less environmentally friendly. Furthermore, the amine suffers from both thermal and oxidative degradation, limiting the amine concentration and capture capacity.^{46,47} Additionally, for CO₂ capture using hydroxide solutions, the as-formed carbonate formed can precipitate in the reboiler and pipeline, leading to extra costs.⁴⁸

1.2 Electrochemical CO₂ capture methods

Compared with the conventional CO₂ capture process using amine and hydroxide

solutions, the electrochemical capture process powered by clean electricity could potentially overcome major barriers to the current carbon capture technologies—regeneration energy penalties, high costs, and complex procedures. The electrochemical potential gradient between the cathode and anode is the main driving force that can be precisely controlled to drive the chemical reaction in an isothermal manner for CO₂ capture without loss of active absorbents. The basic principle of the process is that the electrochemical potential controls the generation of nucleophilicity H⁺ and OH⁻ to mediate the capture and release of CO₂. In addition, the released high-purity CO₂ can be directly used in the subsequent electrochemical reduction to produce highly valuable chemicals/fuels through another electrolytic cell (we will discuss it in the 2.2 section). This section presents three different electrochemical CO₂ capture technologies, including electrochemical-driving pH swings, electrochemical active organic redox-active compounds, and electrochemically mediated amine regeneration.

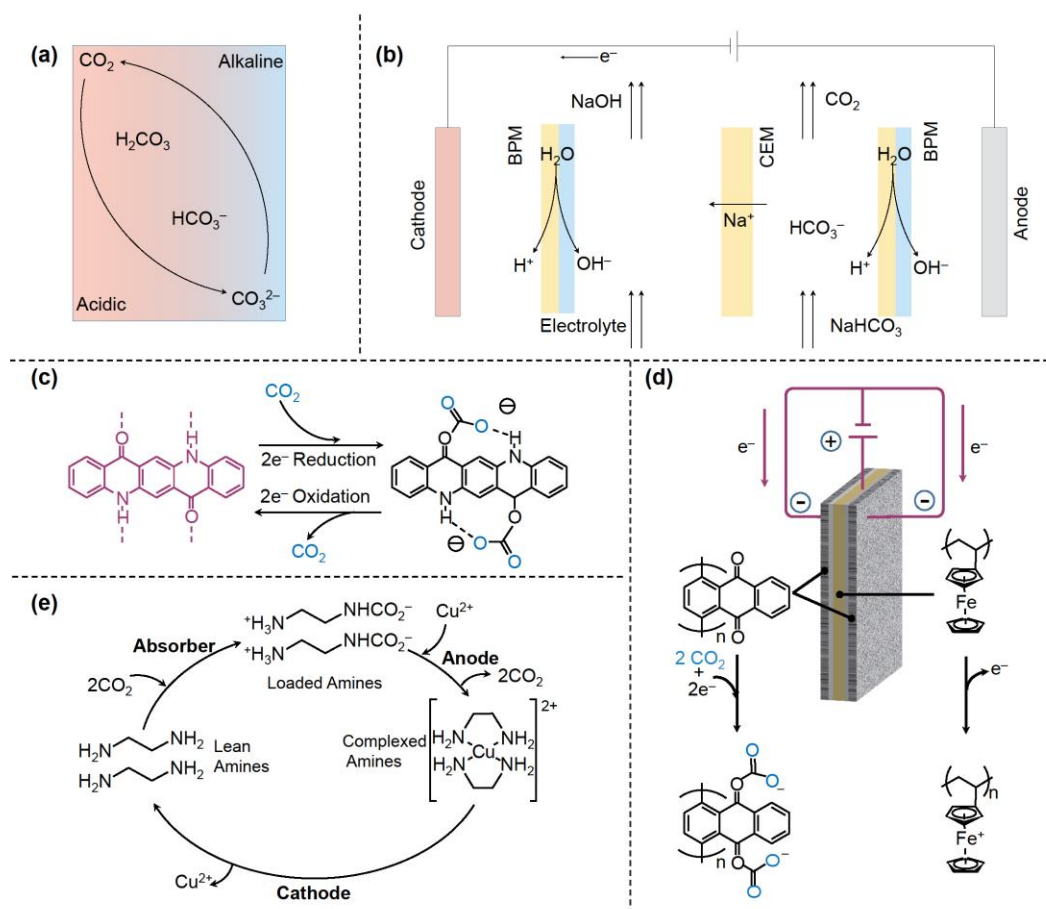


Figure 3. (a) Schematic of the pH-swing concept. (b) Schematic illustration of a typical bipolar membrane system for CO₂ capture and release. (c) Proposed mechanism for electrochemical capture and release of CO₂ using the quinacridone (QNC) pigment.

Reproduced with permission: Copyright 2014, Wiley.⁴⁹ (d) Schematic of a single electro-swing adsorption electrochemical cell with porous electrodes and electrolyte separators. Reproduced with permission: Copyright 2019, Royal Society of Chemistry.⁵⁰ (e) EMAR CO₂ separation cycle for EDA and copper. Reproduced with permission: Copyright 2013, Royal Society of Chemistry.⁵¹

1.2.1 CO₂ capture based on pH swing

In section 1.1, we discussed the CO₂ capture process using alkaline solutions, where CO₂ release is accomplished by the calcination of calcium carbonate. In this section, another promising alternative approach, i.e., the pH swing process, will be introduced. As shown in Fig. 3a, once captured in an aqueous hydroxide or carbonate solution, CO₂ could simply be released by acidifying the (bi)carbonate solution.^{52,53} Electrochemical approaches can efficiently change the local pH of the cathodic and anodic compartments,^{54,55} creating a high local pH environment for capturing CO₂ and a low pH environment to release CO₂, avoiding pH drifts in operation that reduce CO₂ capacity.⁵² Currently, there are five main types of electrolysis methods based on the electrochemically mediated pH swing process, including (membrane) electrolysis, bipolar membrane electrodialysis, proton-coupled electron transfer mediated CO₂ capture/release agents, capacitive deionization methods, and hybrid processes.⁵⁶ Recently, the advances of these methods and their performance comparisons in terms of energy consumption and capture efficiency have been demonstrated by D. A. Vermaas and P. Strasser.^{18,56} Here, we only emphasize the CO₂ capture/release by means of bipolar membrane electrodialysis as an example, while the detailed pH swing process will not be elaborated. Fig. 3b shows a typical bipolar membrane system for CO₂ capture and release. The electrodialysis system consists of repeated units of a bipolar membrane (BPM) and cation exchange membrane (CEM) electrodes at both ends, dividing the system into feed and alkaline regeneration compartments. The feed compartment is supplied with an alkali metal bicarbonate solution between the BPM and the CEM on one side of the anode, while the alkaline regeneration compartment is on the other side. Under an applied voltage, protons from the BPM are generated and supplied to the feed chamber, producing gaseous CO₂. Meanwhile, the alkaline metal

ions move through the CEM to the alkaline regeneration chamber to combine with hydroxyl ions generated from another bipolar membrane, achieving alkaline metal hydroxide solution regeneration.

1.2.2 Electrochemical CO₂ capture based on organic redox-active compounds

Using organic compounds to capture CO₂, such as benzalaniline⁵⁷ and α,β -unsaturated ketones,⁵⁸ have been identified over the last 50 years. Recently, CO₂ capture and release through the electrochemical reduction and oxidation of organic reduction mediators have received great attention, such as quinone derivatives,⁵⁹ bipyridine,⁶⁰ and disulfide.⁶¹ They are similar to amine-based capture media. The organic compounds are electrochemically reduced to generate or release potent nucleophilic reagents, which are capable of attacking electron-philic carbon atoms in CO₂, generating adducts (similar to carbamate). The difference between these two processes is that electrochemical oxidation rather than heating is used in the subsequent release of CO₂ and regenerates the capture agent. In 1989, Mizen et al. investigated the electrochemically induced reversible chemical reaction of 9,10-phenanthrenequinone (PAQ) with CO₂, which allows for the capture and release of CO₂ through a two-step single electron transfer process.⁶² Subsequently, in 2014, a breakthrough was made using quinacridone (QNC) films (100 nm thick) deposited on indium tin oxide (ITO)-coated slides that were electrochemically reduced in an acetonitrile electrolyte solution for CO₂ capture.⁴⁹ As shown in Fig. 3c, the CO₂ gas reacts with the reduced QNC pigment, forming the QNC-carbonate anion. This reduce-and-capture approach was found to achieve CO₂ uptake values of 4.61 mmol g⁻¹, which is comparable to aqueous amine-based capture processes (8 mmol g⁻¹).⁴⁹ However, a major drawback of this approach is that the electrodes tend to degrade after 15 repeated cycles, highlighting the urgent need for improving electrode stability during the electrochemical process. Very recently, Voskian et al. demonstrated an electrochemical cell that uses a poly-(anthraquinone-carbon nanotube) composite negative electrode for CO₂ capture and release. The electrode has a sandwich structure, with the outer electrode coated with a

poly-1,4-anthraquinone composite that captures CO₂ by carboxylation of the quinone at a reduction potential and releases CO₂ when the polarity is reversed. The inner electrode containing polyethylene ferrocene serves as an electron source and receiver for quinone reduction and oxidation, respectively (Fig. 3d). The electrode not only concentrates CO₂ from 0.6% (6000 ppm) to 10%, but also exhibits excellent durability, with only 30% capacity loss after 7000 cycles.⁵⁰ In addition, Buttry et al. investigated the electrochemical capture and release of CO₂ using 4,4'-bipyridine and benzylthiolate,^{63,64} which share the same basic principles as the method described above. Both methods have provided a solid foundation for the subsequent reduction process.

1.2.3 CO₂ capture based on electrochemically mediated amine regeneration

Another method that can couple with electrochemical CO₂ reduction is electrochemically mediated amine regeneration (EMAR), a concept that was proposed by Stern et al. in 2013 (Fig. 1a, L7)⁵¹. As shown in Fig. 3e, the EMAR cycle relies on the redox agent (Cu²⁺), which replaces CO₂ in the amine-CO₂ adducts to form chelated complexes with the amines. First, CO₂ is absorbed by the amine in an absorption column, which is similar to conventional approaches. Then, the CO₂-rich amine stream from the absorber is delivered into the anode compartment of an electrochemical cell, where Cu²⁺ is produced electrochemically from a copper plate anode ($\text{Cu}^0 \rightarrow \text{Cu}^{2+} + 2\text{e}^-$) to induce the dissociation of amine-CO₂ to liberate CO₂. The Cu²⁺-rich stream is regenerated by electrochemical plating of copper on the cathode from the copper-amine complex. Compared to conventional thermal processes that desorb only approximately 50% of the CO₂ bound to the loading amine, the EMAR system is able to remove approximately 80% ~ 90% of the absorbed CO₂, considerably increasing the adsorption efficiency.⁵⁶ In recent years, with the continued development of research on EMAR, some critical issues related to the process have been addressed, such as the precipitation of copper particles from the anode,⁶⁵ and engineering estimates of the key characteristics of the technology, including energetics and sizing.⁶⁶ Currently, this technology has shown potential for large-scale applications. However, to our

knowledge, reports on the combination of this technology with CO₂ electrochemical reduction remain rare, which may be an optional future route to address current energy consumption as well as environmental issues.

1.3 Electrochemical CO₂ conversion

After obtaining high-purity CO₂ through capturing process, utilization of the CO₂ as feedstock to produce fuels and commodity chemicals is naturally becoming an attractive way to store energy and mitigate emissions. The traditional CO₂ conversion technology involves synthesizing CO and a range of short-chain hydrocarbons, such as methanol and formate, in an industrial grade. However, this process faces cost-effectiveness issues due to the reactive inertness of CO₂ molecules, which necessitates high temperature, high pressure, high-value feedstock, and appropriate catalysts for the reactions.³⁶ For example, CO production requires a high temperature exceeding 800 °C to achieve an 80% conversion rate,⁶⁷ and methanol production requires high pressures of 20-80 bar H₂ gas to achieve high selectivity.⁶⁸ In comparison, the electrochemical conversion of CO₂ using renewable energy offers a more attractive strategy that can achieve high selectivity for the target product at room temperature and atmospheric pressure, without other high-value feedstock. Additionally, the electrochemical system is directly controlled by regulating the applied electrode potential and can be readily scaled up to meet the application's needs.⁶⁹ In a typical CO₂ electrolyzer, an anode and a cathode are separated by an ion-conducting membrane. This membrane enables the conduction of charged ions while preventing the crossover of redox-active species (as illustrated in Fig. 4a). Powered by electricity, water is oxidized to oxygen at the anode, while CO₂ is reduced at the cathode to different products (CO, H₂C₂O₄, C₂O₄²⁻, HCOOH, HCOO⁻, HCHO, C, CH₃OH, CH₄, C₂H₅OH, C₂H₆, C₃H₇OH) with the coexistence of a competing hydrogen evolution reaction (HER). As of 2023, more than 3000 articles related to CO₂ electrochemical conversion have been published based on the Web of Science, and many review articles have been published to summarize the recent progress of catalytic CO₂ reduction processes, covering catalyst development,

catalytic reaction mechanisms, and electrolyte effects.⁷⁰⁻⁷⁴ To avoid overlap, the contents relating to the electrochemical CO₂ reduction reaction (CO₂RR) are not stressed here.

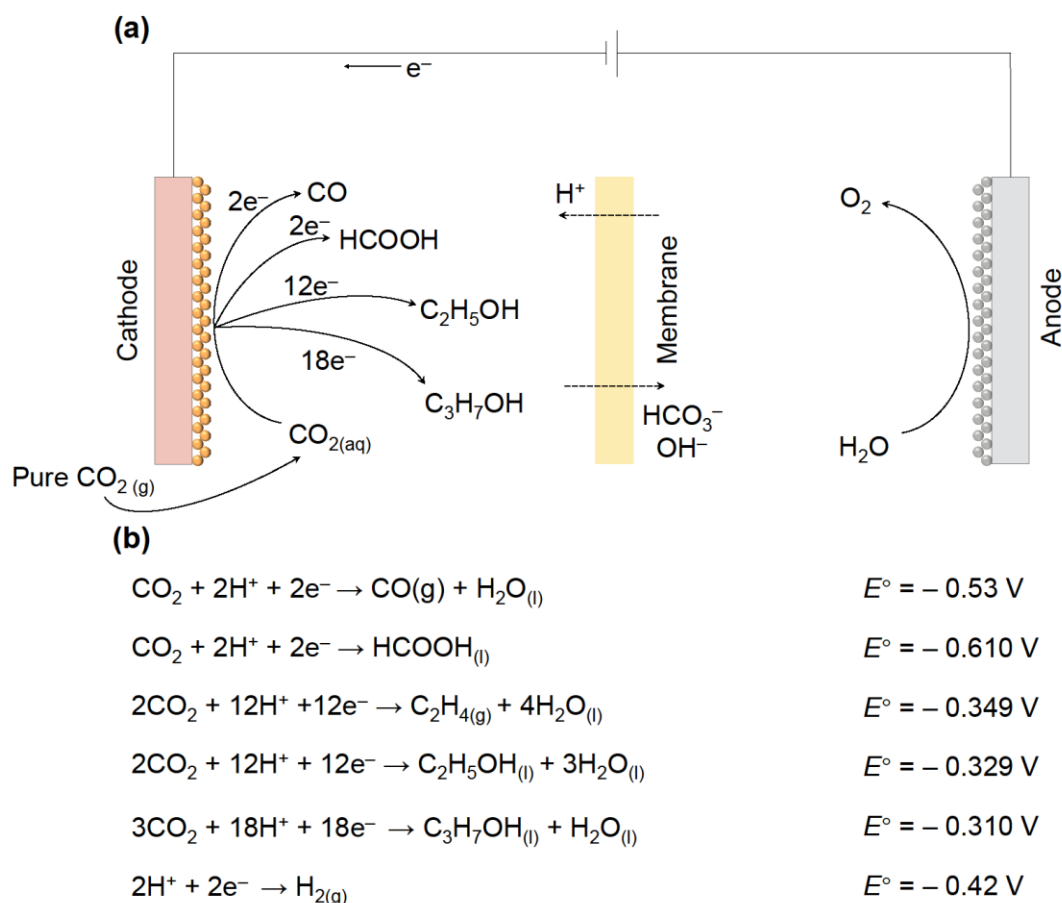


Figure 4. (a) Schematic illustration of an electrolyzer for the electrochemical reduction of CO₂. (b) Standard equilibrium potentials (SHE, pH = 7) for electrochemical CO₂ reduction toward various C₁ and C₂₊ products and cathodic hydrogen evolution reaction in a half-cell reaction.

2. Integrating CO₂ capture and electrochemical conversion

In contrast to the interdependent CO₂ capture and conversion process depicted by the orange line in Fig. 2, the integration of CO₂ capture and conversion technology enables the conversion of CO₂ (in the form of carbonate, bicarbonate, etc.) into value-added products, bypassing complex procedures such as medium regeneration, CO₂ compression, and storage.⁷⁵ Since the 1970s, researchers have realized that CO₂ could be used as a feedstock to synthesize energy storage medium such as methanol or formic

acid via the electrochemical reduction in a neutral solution.^{76,77} However, the low solubility of CO₂ in water has limited further development possibilities. In 1983, a new strategy was proposed, whereby the electrochemical reduction of bicarbonate to formate via Hg electrodes was achieved (Fig. 1a, L3)⁷⁸, providing an important basis for subsequent coupled CO₂ capture and electrochemical reduction. In the following sections, we will classify the recent studies of coupled CO₂ capture and electrochemical reduction based on system design and capture medium, with critical development points interspersed to enhance the reader's understanding of the integration process.

2.1 Single electrolytic cell systems

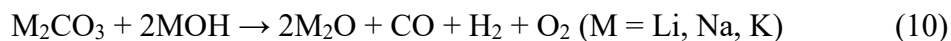
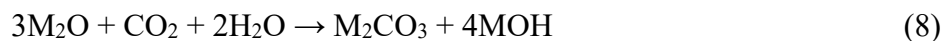
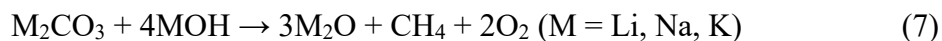
The process of independent CO₂ capture and electrochemical conversion typically involves multiple procedures, such as CO₂ capture, compression, and storage, which can lead to low CO₂ conversion efficiency. To improve carbon utilization and save production energy, researchers have focused on integrating CO₂ capture and conversion in a single electrochemical cell. This section discusses the design principles and recent advances in coupled CO₂ capture and electrochemical reduction using single electrolytic cells. Since the configurations and reaction mechanisms of the cells differ depending on the electrolyte, a detailed discussion of these studies based on the different electrolytes is presented.

2.1.1 Electrochemical CO₂ capture and conversion using molten salt electrolyte

Molten salt is one of the first classes of electrolytes to be used for CO₂ capture coupled with electrochemical CO₂ reduction. It offers higher solubility and electrical conductivity compared to water, and is less expensive than ionic liquids.⁷⁹ This process, also known as CO₂ capture and electrochemical transformation (MSCC-ET), is typically performed in high-temperature molten salts, where CO₂ gas is captured and electrochemically transformed into fuels such as CO and useful carbonaceous materials, with oxygen as the anode product. There are typically three types of available electrolytes for MSCC-ET, i.e., alkali metal carbonates, chloride-(Li⁺/Ca²⁺) oxide, and

alkali metal carbonate-chloride (Tab. 1). The working principle is simply shown in Fig. 5a. During electrolysis, CO₂ is first captured by O²⁻ to produce CO₃²⁻, which is then reduced to CO and C at the cathode. Early studies do not combine the CO₂ capture process with the molten salt electrolysis and require high energy input from fossil fuels to heat the salt.⁸⁰⁻⁸² It was not until 2010 a new system was invented by Licht et al. (Fig. 1a, L6)⁸³, where solar energy was used to drive the capture and electrochemical reduction of CO₂ (Fig. 5b) to carbon powder and CO. From this system, CO₂ can be captured by 750-950 °C molten Li₂CO₃ electrolyte and show solar energy efficiency over 50%. After that, an increased coulombic efficiency of over 70% was achieved by Yin et al.,⁴⁰ who used the electrolytic cell system consisting of a eutectic mixture of Li-Na-K carbonates, a Ni cathode, and an inert SnO₂ anode to capture CO₂ at 500 °C, then electrochemically reduced to amorphous carbon with high BET surface areas of more than 400 m² g⁻¹. However, these systems' required concentration of CO₂ source remains high, which bears little resemblance to air and flue gases. In 2013, a breakthrough was achieved by using a ZrO₂ solid electrolyte as the anode and CaCl₂-CaO molten salt as the electrolyte.⁸⁴ It was found that the averaged current for carbon production was not depend on the CO₂ concentration or the CO₂ flow rate, but rather was determined by the electrical conductivity of the anode, which can be controlled by tuning the temperature of the ZrO₂ solid electrolyte (conductivity increases with temperature). At 900 °C, this system realized efficient capture and electrochemical conversion of low concentrations of CO₂ gas (9.7%) with a faradaic efficiency (FE) of 78.5% toward solid carbon products.⁸⁴ Inspired by this work, a borage range of molten salt electrolytes, such as alkali metal carbonate-fluoride melt, alkali metal carbonates-alkali metal hydroxide, and alkali metal carbonate-sulfate, have been widely developed as electrolytes in MSCC-ET.⁸⁵⁻⁸⁷ For example, in 2016, Wu et al.⁸⁸ developed a new green system for synthesizing methane (CH₄) in an alkali carbonate/LiOH electrolyte. By optimizing the electrolysis conditions, including the temperature, proportion of the carbonate/LiOH electrolyte, operating current and electrocatalytic cathode (600 °C, 0.3:1, 12.5 mA cm⁻², and Fe cathode), this system showed a high FE of 97.4% with rich products comprising 64.9% methane, 34.8% H₂, and 0.3% C₂₊ hydrocarbons (Fig. 1a,

L8). More strikingly, H₂O and CO₂ were employed as sources, which are closer to the composition of flue gas. During the electrolysis process, CH₄ is produced from alkali metal carbonate/hydroxide electrolysis (Equation 7), and the reaction of the alkali oxide by introduced CO₂ and H₂O simultaneously renews the electrolyte (Equation 8) and leads to the simple electrolysis of CO₂ and H₂O to CH₄ and O₂ (Equation 9). In addition, it was found that when the temperature of molten salt was lowered, the CO yield increased continuously with a CO yield of 17.1% at 500 °C. This is very interesting because it means that CO/H₂ syngas generation at a lower temperature is possible by using a molten salt electrolysis system. It should be noted that syngas production has previously been obtained by methane reforming,⁸⁹ coal gasification,⁹⁰ and natural gas conversion,⁹¹ most of which, however, require temperatures above 800 °C and easily deactivated catalysts. Just one year later, the same team used the same system by rational design of molten salt mixture (Li_{0.85}Na_{0.61}K_{0.54}CO₃/0.08LiOH), achieving a maximum FE of ~94.5% at 450 °C with 8.15 mA cm⁻² and leads to CO, H₂ and C_xH_y percentages of 31.1%, 55.6%, and 13.3%, respectively.⁹² During the electrolysis process, M₂CO₃ (M = Li, Na, K) decomposes into the intermediate alkali oxide, M₂O (M = Li, Na, K), along with the generation of CO, while the hydroxide (i.e., MOH) decomposes into M₂O with the generation of H₂ (Equation 10). M₂CO₃ and MOH can both be regenerated by reacting M₂O with the further supplied CO₂ and H₂O, respectively (Equation 11). However, research in the past several years seems to focus more on improving the carbon production efficiency by adjusting the molten salt composition, while a deep understanding of the mechanism for the influence of molten salt composition on the gas behavior at the electrode/electrolyte interface is lacking.^{85,93,94}



In short summary, molten salts have attracted considerable attention for their potential in CO₂ capture and conversion due to their high thermal stability, fast ion migration and diffusion, and excellent CO₂ solubilization ability. While the process can be powered by renewable energy sources such as solar energy and wind power, the high energy demand necessitates additional facilities to maintain a stable working temperature irrespective of light intensity and wind conditions, which may increase the process's capital cost. In addition, the current study does not introduce N₂ and H₂O simultaneously, which account for 70-75% and 5-7% of the flue gas composition, respectively. Under high-temperature conditions over 500 °C, reactions involving N₂, such as N₂ + H₂ = NH₃, are likely to occur during the electrochemical process,⁹⁵ which may decrease the generation efficiency of the carbon-containing product and increase the difficulty of subsequent gas separation.

Table 1. Progress summary of the direct electrochemical CO₂ reduction from CO₂ capture media using molten salt as electrolyte.

Cathode/Anode	Capture media	Products	FE (%)	j (mA cm ⁻²)	Temperature (°C)	Ref .
Ti/Graphite	Li ₂ CO ₃	CO	~100	100	900	96
Ni/Pt	Li ₂ CO ₃	C	-	100-500	750-950	83
Ni/SnO ₂	Na ₂ CO ₃ -K ₂ CO ₃ - Li ₂ CO ₃	C	70-90	100-2100	450-650	40
W /TiO ₂ -RuO ₂	CaCl ₂ -CaO	C	-	1100	850	79
Stainless Steel/ZrO ₂	CaCl ₂ -CaO	C	78.5	500	900	84
Mild Steel/Stainless Steels	Li ₂ CO ₃ -K ₂ CO ₃	C	65-100	1000-6000	540-700	97
W/Pt	Li ₂ CO ₃ -LiCl	C	-	300-400	700	98
Stainless Steel/C	CaCl ₂ -CaO	CO	37	100-200	900	99
Fe/Ni	Li ₂ CO ₃ -Na ₂ CO ₃ - K ₂ CO ₃ -LiOH	CH ₄ /H ₂	64.9	12.5	600	88
Fe/Ni	Li ₂ CO ₃ -Na ₂ CO ₃ - K ₂ CO ₃ -MOH (M=Li, Na, and K)	Syngas (CO/H ₂)	84.7 (31.1/5 5.6)	8.15	450	92
Fe/Ni	Li ₂ CO ₃ -Na ₂ CO ₃ -	CH ₄ /H ₂	63.34	15	575	93

	K ₂ CO ₃ -LiOH					
Mo/Pt	LiF-Li ₂ CO ₃	C	-	50-70	700	87
Ni/SnO ₂	Li ₂ CO ₃ -K ₂ CO ₃ - Na ₂ CO ₃ -Li ₂ SO ₄	Sulfur- doped carbon	65-73	22-280	475	86
Ti/Stainless Steel	Li ₂ CO ₃ -Na ₂ CO ₃ - K ₂ CO ₃ -(LiOH- NaOH/KOH- NaOH)-(KCl- LiCl)	CH ₄ /C ₆ H ₁₄ / CO	(94.6) 2/58/32 .4/2.2	-	500	85
Fe/Ni	Li ₂ CO ₃ -ZrO ₂	C	75.9	10	750	94

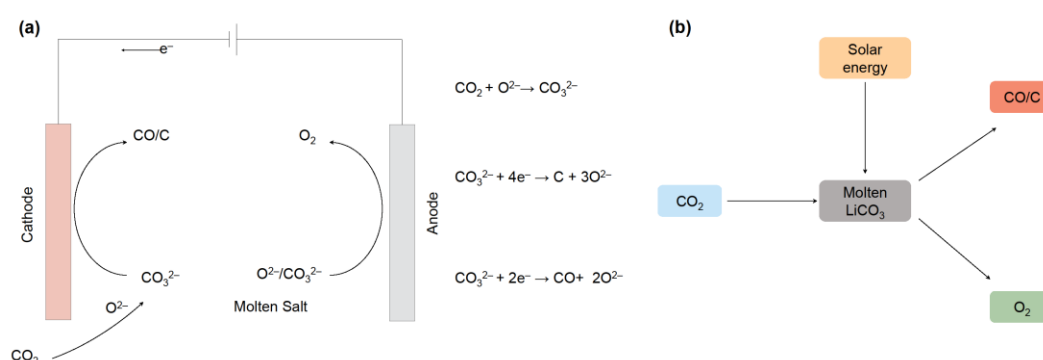


Figure 5. (a) Schematic illustration of the molten salt CO₂ capture and electrochemical transformation process. (b) Schematic illustration of the solar-driven capture and electrochemical reduction of CO₂ to CO₂/C. Reproduced with permission: Copyright 2010, American Chemical Society.⁸³

2.1.2 Electrochemical CO₂ capture and conversion using an amine solution as the electrolyte

Amine solutions are another attractive electrolyte for electrochemical CO₂ capture and conversion, which has emerged in the past few years. Most current studies employ CO₂-saturated amine-based solutions as the electrolyte to ensure sufficient ionic species in the solution to provide high conductivity for electrochemical reduction. In a typical process, flue gas or CO₂ gas is flowed into the amine solution, forming an amine-CO₂ adduct, which is then electrochemically reduced to valuable chemicals. Additionally, unlike in molten salt electrolytes where only oxygen is a byproduct, in aqueous amine solutions, the hydrogen evolution reaction (HER) serves as a competitive cathodic reaction during CO₂ reduction.^{100,101} Therefore, CO₂ reduction in CO₂-saturated amine

solutions requires consideration of catalyst design, capture medium, and additives to obtain the highest selectivity toward target value-added products. Most studies are carried out within an H-type cell, where the cathode and anode are separated by an anionic membrane. As shown in Fig. 6a, during the electrocatalytic process, the amine capture intermediates are thought to be reduced to CO and HCOO⁻ at the cathode. In 2017, Chen et al. (Fig. 1a, L9)¹⁰² first reported the electrocatalytic reduction of CO₂ in 30% (w/w) monoethanolamine (MOEA) aqueous solutions using a variety of porous metal electrodes (In, Sn, Bi, Pb, Pd, Ag, Cu, and Zn) with cetyltrimethylammonium bromide (CTAB) as a cationic surfactant to inhibit the HER pathway. At a potential of -0.8 V vs. reversible hydrogen electrode (RHE), the indium electrode exhibited the highest FE_(C1) with a total value of 77.3%, with FE_(CO) and FE_(HCOO⁻) of 22.8% and 54.5%, respectively (Fig. 6b). The Pb and Ag electrodes demonstrated the highest conversion rates for different single products, achieving an FE_(HCOO⁻) of 60.8% at Pb electrodes and an FE_(CO) of 38.2% at Ag electrodes, respectively. However, the strong binding of MOEA to CO₂^{75,103} suggest that the free CO₂ molecule (0.03 M) in the amine-based solution may also be active for direct reduction, and therefore the observed performance may not come from the reduction of MOEA-CO₂ adduct. So in subsequent reports, N₂ or Ar was purged into the CO₂-saturated amino solution for at least 10 minutes to remove the dissolved CO₂ and exclude the influence of the dissolved CO₂.^{104,105} Recently, Lee et al. (Fig. 1a, L12)¹⁰⁴ found that the inactive reaction of amine-CO₂ reduction was due to the long ethanol ammonium ion blocking electron transport from the cathode electrode to RNHCOO⁻. This problem was effectively solved by adding cations (Li⁺, Na⁺, K⁺, Rb⁺ and Cs⁺) to regulate the electron transport rate (Fig. 6d). Under optimized conditions, a 72% FE_(CO) was obtained at an applied current density of 50 mA cm⁻². Kim et al.¹⁰⁵ employed another strategy to use the weak cation sensitivity catalyst (Ni catalyst embedded on N-doped carbon (Ni-N/C)) to decrease the hampers effect of the bulky cations, which can maintain the FE_(CO) above ~50% with a different type of amine electrolytes. In addition, the number of CO₂ capture sites of the amine molecule also affects the catalytic activity, and a variety of commercially available amine-based capture solvents, including monoethanolamine

(MOEA), ethylenediamine (EDA), and decylamine (DCA), were tested by Abdinejad et al.¹⁰⁶ As shown in Fig. 6c, by using copper as electrodes and EDA as a solvent, the system delivers the highest $FE_{(CO)}$ of 58% at -0.76 V vs. RHE, which is almost three times the efficiency exhibited by the other two electrolytes. It was suggested that EDA has two viable capture sites ($-NH_2$), making it more efficient in the CO_2 capturing process compared to MOEA and DCA with only one capture site. Besides, the form of the captured CO_2 also affects the FE, Langie et al.¹⁰³ show that their system can achieve a $FE_{(CO)}$ over 35% a current density of -50 $mA\ cm^{-2}$ with trimethylamine (TREA) as the capture media, much better than with MOEA and diethanolamine (DAA) (below 15%). The high performance is due to the bicarbonate formation of the TREA reacting with CO_2 , which is more favorable for direct conversion of CO_2 compared with carbamates formed by the other two amine electrolytes.

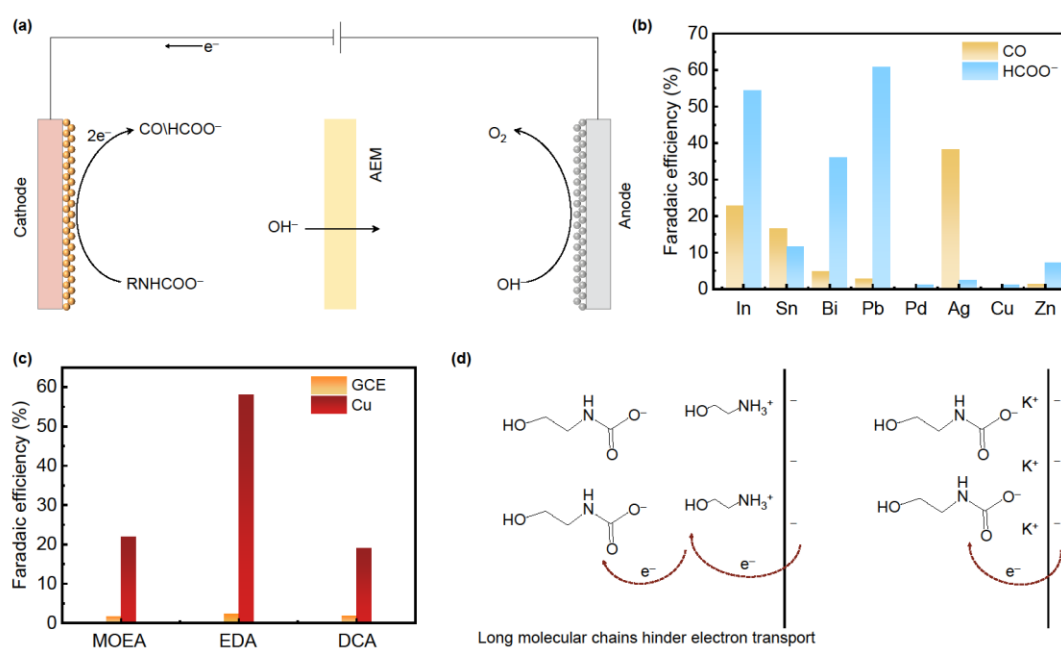


Figure 6. (a) Typical cell configuration for amine-based solution capture and electrochemical reduction of CO_2 . (b) FE for the generation of CO and $HCOO^-$ determined for eight porous metal electrodes at -0.8 V versus RHE in CO_2 -saturated 30% (w/w) MOEA aqueous solution. Reproduced with permission: Copyright 2017, Wiley.¹⁰² (c) FE for CO generation by using Cu electrodes and glassy carbon electrodes in three different amine-based solutions. Reproduced with permission: Copyright 2020, American Chemical Society.¹⁰⁶ (d) Proposed interfacial structure near the electrode surface of MOEA- CO_2 electrolyte and MOEA- CO_2 with alkali salt electrolyte. Reproduced with permission: Copyright 2020, Springer Nature.¹⁰⁴

2.1.3 Electrochemical CO₂ capture and conversion based on an alkaline solution electrolyte

The electrolysis of CO₂-saturated aqueous HCO₃⁻ solution is one of the widely used methods for carbon capture and conversion. Some researchers have attempted to use HCO₃⁻ as the carbon source for electrochemical production of carbon-based products due to the high concentration of HCO₃⁻ (KHCO₃: ~ 3.3 M) compared with CO₂ (~ 0.03 M).^{78,107} However, this approach often delivers low current density at a high overpotential.¹⁰⁸ Most previous studies on HCO₃⁻ reduction have demonstrated lower current densities and FE when compared to CO₂-fed systems.^{78,108,109} To address this problem, the protonation of carbonate or bicarbonate at the cathode to release CO₂ by using bipolar membrane (BPM) assembly techniques is currently attracting considerable interest (Fig. 7). Unlike conventional anionic membrane electrolytic cell systems, the BPM-based electrolytic system could dissociate water into protons and hydroxide anions and avoid the oxidation of CO₃²⁻ and HCO₃⁻ at the anode, thus demonstrating high CO₂ utilization efficiency. Li et al.¹¹⁰ first demonstrated the coupling of CO₂ capture and electrochemical conversion by applying bipolar membranes with Ag as the cathode and Ni as the anode. The KOH-CO₂ adduct (K₂CO₃) is formed by purging CO₂ with KOH electrolyte before electrochemical testing. N₂ is then employed to remove dissolved CO₂ to ensure that the carbon source is the CO₃²⁻. During electrolysis, the electrolyte circulates to the cathode via a peristaltic pump, allowing the whole system could achieve FE_(CO) over 30% at 150 mA cm⁻² and 100% carbon utilization (Fig. 1a, L10). After that, several different cathode catalysts be used in the same system to give rise to different products. For example, a Cu/Ag bilayer cathode delivered a 41.6% FE_(C₂+) at 100 mA cm⁻²,¹¹¹ while Ag/GDL and Ni SACs cathodes achieved 37% and 62% FE_(CO) at 100 mA cm⁻² and a Bi/C cathode achieved 62% FE_(HCOO⁻) at 100 mA cm⁻².^{108,112,113} To further increase the FE of the CO₂RR, some strategies to increase the catalyst's local CO₂ concentration and CO₂ solubility have been employed, like using the cationic surfactant,¹¹⁴ decreasing the catalyst layer thickness,¹¹⁵ and increasing the operating pressure.¹¹⁶ For instance, Zhang et al.¹¹⁶

found that several factors such as the operation temperature, pressure, electrolyte flow rate, and flow channel shape significantly influence product FE for electrochemically converting KHCO_3 to CO . By using a porous Ag cathode at 100 mA cm^{-2} , 78% and 95% of $\text{FE}_{(\text{CO})}$ were obtained with an inlet electrolyte temperature of $70 \text{ }^\circ\text{C}$ at 1 atm and $20 \text{ }^\circ\text{C}$ at 4 atm, respectively, while only 59% of $\text{FE}_{(\text{CO})}$ was achieved at 1 atm and $20 \text{ }^\circ\text{C}$. However, for a bipolar membrane, an applied voltage of $>0.83 \text{ V}$ is required to decompose water into OH^- and H^+ , and the oxygen evolution reaction (OER) at the anode accounts for 90% of the equilibrium cell potential, making it very difficult to design an electrolyzer with a high yield that can operate in an industrial environment ($<3 \text{ V}$).^{117,118} To address this issue, Berlinguette's group.¹¹⁹ proposed a new strategy using cation exchange membranes instead of bipolar membranes and conducting a hydrogen oxidation reaction (HOR) at the anode to generate protons, which are then transported through the CEM and migrate to the cathode surface for the CO_2RR , reaching a 15% $\text{FE}_{(\text{CO})}$ at a commercially relevant current density of 500 mA cm^{-2} with a low cell voltage of 2.3 V. Besides, a further improved performance of 44% $\text{FE}_{(\text{CO})}$ at the same current density in this work was achieved under 3.5 atm of pressure because of the increasing CO_2 solubility.

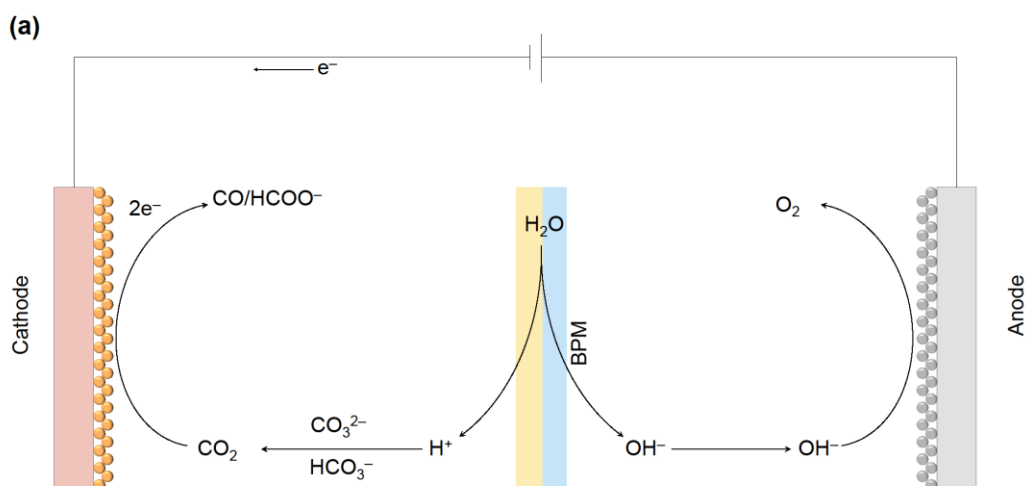


Figure 7. Schematic representation of the dominant chemical and electrochemical reactions occurring in a system containing a BPM: reaction of H^+ with CO_3^{2-} or HCO_3^- to form CO_2 at the membrane interface and the electrochemical reduction of CO_2 at the cathode to form CO and OH^- .

2.2. Additional possible design and energy cost analysis

Dual electrolytic cell systems. In the previous section, we discussed the capture and electrochemical reduction of CO₂ by using different electrolytes, including molten salt, amine-based solutions, and alkaline electrolyte solutions. The amine-based solutions are directly involved in electrochemical reduction as a reactant. In alkaline solutions, the CO₂ is released after the protonation of carbonate/bicarbonate at the cathode, and can be subsequently used for electrochemical reduction. However, this is a relatively new area and does not allow for perfect combination and utilization of the progress made in independent CO₂ capture and reduction over the past few decades. Therefore, dual electrolytic cell systems that integrate CO₂ capture and conversion may be more attractive in the future. A proposed schematic is shown in Fig. 8, where the first cell captures CO₂ waste from a dilute source at the cathode and releases pure CO₂ at the anode. The pure CO₂ is then imported into the second electrolytic cell for CO₂ reduction.⁷⁵ This approach allows for the regeneration of the capture medium through electrochemical reactions under mild conditions, avoiding the CO₂ compression process and significantly reducing energy consumption.

Applications of dual electrolytic cell systems-effective method for the capture and reduction of CO₂ in seawater. Current research is still focused on CO₂ reduction in saturated capture media, a process that can be achieved by passing point sources (e.g., air, flue gas) through the capture media. The world's oceans constitute the largest carbon sink, having absorbed approximately 40% of anthropogenic CO₂ since the beginning of the industrial era, which is a factor of 120 times larger than that in the atmosphere.¹²⁰ A pH swing is an efficient way to capture CO₂ in seawater, and the use of a dual electrolytic cell system seems to be an effective way to convert carbon sources in seawater into valuable chemicals. Digdaya's group (Fig. 1a, L11)¹²¹ reported a direct-coupled electrochemical system using a bipolar membrane/cation exchange membrane coupled with a reversible redox system to effectively release CO₂ from seawater and subsequently direct the CO₂ vapor into a conversion system for reduction. The capture

efficiency of the entire system is 71%, and the $FE_{(CO)}$ is up to 95%. The smart cell configuration design and superior performance demonstrate the great potential of the dual electrolytic cell system.

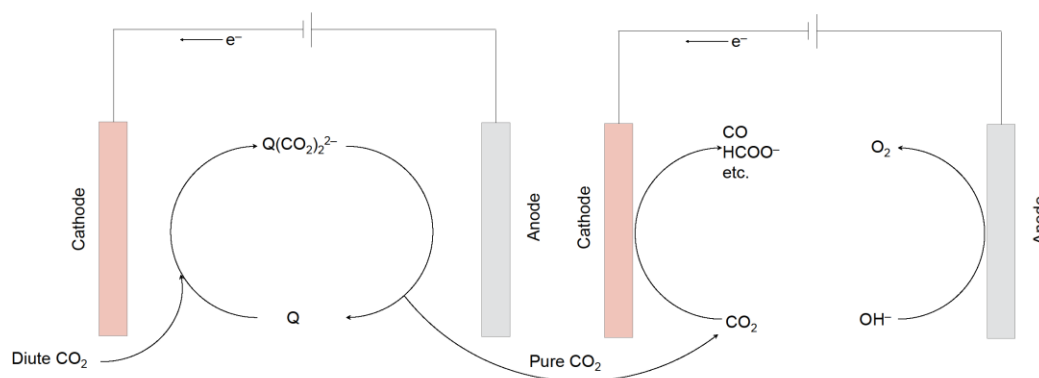


Figure 8. Schematic illustration of a dual electrolytic cell system for CO_2 capture and conversion.

Energy and production costs for independent systems, single electrolytic cell systems, and dual electrolytic cell systems. Techno-economic analysis (TEA) was conducted to further compare the energy and production costs for three different electrochemical CO_2 capture and reduction processes with the operation parameters shown in Tab. S1. The energy spent on every single step to produce 100-ton CO is presented in Fig. 9a. For an independent system, 55.56 GJ energy was needed to produce 1-ton CO, among which 53.7% of the total energy was used to regenerate the capture media and release the pure CO_2 , 5.0% of the energy was used for compression, and 41.3% of the energy used was for electrochemical conversion at 200 mA cm^{-2} with a 90% FE. For the single electrolytic cell system, taking Berlinguette's study as an example,¹¹⁶ a 95% FE was achieved at 100 mA cm^{-2} with about 3.6 V cell voltage. The energy cost was only focused on driving electroreduction, which accounted for about 49.3 % of the energy cost by using the independent system. The dual electrolytic cell system, which integrates CO_2 capture and conversion, is more complex than the independent systems focusing solely on capture or conversion. A recent study has shown that it requires about 120 KJ to separate 1 mol CO_2 from a 0.1 bar inlet and concentrate into a 1 bar using an electrochemical pH swing way at 100 mA cm^{-2} .¹²²

This energy consumption will be used to calculate the CO₂ capture part, while the parameters used for the electrochemical conversion part will be the same as those in the independent system. Based on this, it was found that about 48.3% of the total energy was used for the capture media regeneration in the dual electrolytic cell system, which is slightly lower compared to the energy consumption of the independent system. The estimated CO production costs for different systems are shown in Fig. 9b. The independent systems and the dual electrolytic cell system show a similar cost trend, with the capture energy cost and conversion energy cost being the two main parts of the total cost, specifically accounting for 12.6% and 48.6% respectively in an independent system, and 9.0% and 48.0% respectively in a dual electrolytic cell system. In comparison, over 70% of the cost was attributed to the electrochemical conversion because the high cell voltage of the single electrolytic cell system. In addition, the optimized condition shows the cost can even decrease to nearly \$224 ton⁻¹ CO with a low cell voltage of 2.1 V (Fig. 9c) of the single electrolytic cell system, and \$342 ton⁻¹ CO with a 60% conversion rate in the dual electrolytic cell system (Fig. 9d).

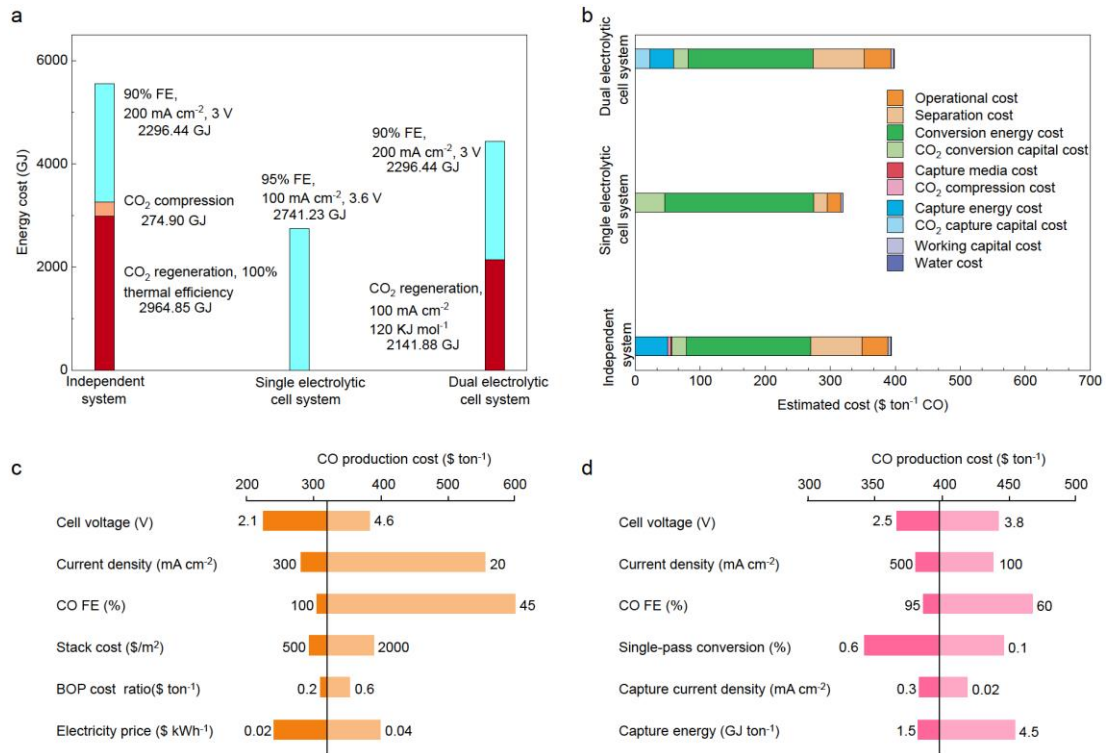


Figure 9. (a) Schematic illustration of the energy cost for different systems to produce 100000 kg CO. (b) The CO production cost of different systems estimated by using TEA. CO Production cost with different parameters by using (c) a single electrolytic

cell system and **(d)** a dual electrolytic cell system, the values shown in the figures indicate each optimistic and pessimistic parameter.

3. Challenges and solutions

While the coupling of CO₂ capture and electrochemical conversion has shown significant advantages in terms of energy savings and carbon footprint reduction, there are several challenges that need to be addressed to enable the industrial-scale adoption of this technology.

The low CO₂ concentration at the electrode/electrolyte interface is one of the crucial problems that need to be solved. In section 1.2, we discuss some representative electrochemical CO₂ capture technologies that could potentially be applied to double electrolytic cell systems. These technologies share some similarities with bipolar membrane systems, as they both release the captured CO₂ for postreduction. However, the concentration of CO₂ near the catalytic active site is typically low, severely limiting the kinetics of the electrochemical CO₂ reduction process, so that a commercial current density can hardly be achieved. In recent years, some strategies have been developed that could possibly solve this problem: (1) The use of alkaline metal ions to regulate the local CO₂ concentration at the catalyst surface has been recently investigated, in which the hydrolysis of alkali metal cations (K⁺, Rb⁺, and Cs⁺) can buffer a decrease in pH near the cathode, leading to an increase in the local concentration of dissolved CO₂.¹²³ (2) Structural engineering of catalysts. It has been reported that a sharp tip electrode can greatly enhance the performance of the CO₂RR.^{124,125} The sharp tips of electrodes induce a localized high electric field that concentrates alkali metal cations in the electrolyte, which in turn causes a high local concentration of CO₂ close to the active CO₂ reduction reaction surface. Consequently, the electrochemical reaction overpotential was reduced, and the conversion rate was improved. This mechanism is somewhat similar to (1), but a relatively high CO₂ concentration can be achieved at a lower concentration of relevant salts. (3) For dual electrolytic cell systems, the use of a

gas diffusion layer (GDL), a porous carbon film treated with hydrophobic polytetrafluoroethylene (PTFE), is effective to enhance gas transport to the electrochemical interface, which is expected to prolong the contact of the CO₂ molecules with the electrocatalyst, thus overcoming the mass transport limitations during the electrochemical reduction process.¹²⁶

Another problem is the low FE and high cell voltage of single-cell systems based on the amine- or alkaline-based solutions, significantly limiting the energy saved. Most of the work show FE of less than 75% for CO and HCOO⁻ production at current density over 50 mA cm⁻². In addition, a high voltage is needed to drive the cell, which costs more energy than the independent approach for electroreduction (Fig. 9). The low FE is mainly due to the competitive cathodic HER reaction. To enhance the FE of the electrochemical CO₂ reaction, several possible protocols can also be applied: (1) Inhibiting HER by modifying the electrodes or utilizing additives in the electrolyte. For example, polytetrafluoroethylene (PTFE) was developed to coat electrodes, or pyridinium-based additives were employed in electrolytes.^{127,128} Both of these methods can delocalize the proton concentration near the electrode and suppress H₂ production with little influence of CO₂ mass transport. (2) Preparation of a high selectivity catalyst. Some single-atom catalysts have demonstrated high selectivity of close to 100% for CO₂ reduction. For example, Lu et al.^{100,129} reported the large-scale preparation of ultrahigh-density single-atom catalysts (kilogram scale) with a variety of metal centers by combining impregnation and a two-step annealing process, which is attractive for industrial applications. (3) Increasing the concentration of carbon sources. For amine-based solutions, developing amines with multiple CO₂ capture sites is an effective and promising strategy. It is thus valuable to explore the influence of the external environment on the solubility of electrolytes. For example, the temperature increase can enhance the NaHCO₃ solubility, but this requires additional energy. Therefore, the investigation of the relationship between conversion efficiency-cost-environment is necessary. Regarding cell voltage, the problem is related to the high overpotential and high energy input caused by the slow oxygen evolution kinetics, which also exist in

dual-cell systems.¹³⁰ Based on the Gibbs free energy analysis, 94.5% of the energy input is paid to the OER at the anode in a typical electrochemical CO₂ reduction reaction to HCOOH.¹³¹ In contrast, some small organic molecules have much lower oxidation potential compared with H₂O (1.23 V), such as urea (0.37 V),¹³² methanol (0.103 V),¹³¹ and glycerol (0.041 V),¹³³ etc. Thus coupling CO₂RR and organic molecules oxidation can minimize the energy consumption and promising for production high-value products at both electrodes. For example, by using methanol as the oxidation reacts, the HCOO⁻ can be produced at both the cathode and anode to achieve nearly 200% FE.^{131,134}

Achieving high performance for a single or dual electrolytic cell system is more complicated than an independent system because more parameters could affect the cell performance. For a dual electrolytic cell system, it is essential to consider the capture agent, catalyst, operation conditions (current density, potential, flow rate), and environmental conditions (pH, pressure, temperature) of both the capture cell and conversion cell. Moreover, it is necessary to construct a relationship between the current density/cell voltage (capture cell), CO₂ release rate/CO₂ inlet rate, current density/cell voltage (conversion cell), and product FE to maximize the production profit/energy cost ratio. For a single electrolytic cell system, it's crucial to consider the potential of the direct reduction of captured CO₂ (like in the form of bicarbonate) by selecting compatible catalysts and change agents, which may increase the yield by an order of magnitude. In addition, cell configuration optimization plays a critical role in improving overall energy efficiency and conversion efficiency. For example, the flow cell without using a membrane could be a good choice for the single electrolytic cell system to achieve low cost and high durability because the crossover CO₂ can be recaptured and used. For the dual electrolytic cell system, the configuration of the CO₂ capture and conversion units should also be optimized to achieve the best performance, and proper and comprehensive guidelines should be developed for configuration-performance relationships. Moreover, the purity of the released CO₂ is a significant concern for conversion efficiency and product separation. Achieving a purity of 98% is

already considered high for electrochemical capture, but impurities like O₂ may oxidize the catalyst or mix with the cathode products, causing conversion failure and changing the reaction microenvironment. Therefore, the CO₂ purity should be considered before the conversion process to select suitable catalysts that remain stable during the process and regulate the separation process accordingly.

Additionally, the previous predominant focus has been on producing CO and HCOO⁻ as the primary products, which limits the potential value of the product. C₂₊ products are more valuable due to their high energy densities, wide application, and large global market capacities.¹³⁵ However, the current technologies suffer from low selectivities toward C₂₊ production. Electrocatalysts play a key role in determining the selectivity of the final product, and most all of the catalysts currently applied for coupling CO₂ capture and electrochemical reduction are heterogeneous metals. According to current studies, the main group metals In, Sn, Bi, and Pb favor the generation of HCOO⁻ ions, while Au, Ag, and Zn favor the generation of CO, and few of them produce C₂₊ products. Cu is the only metal that produces significant amounts of C₂₊ products, such as ethylene (C₂H₄), ethanol (C₂H₅OH), and propanol (C₃H₇OH). Recent studies have demonstrated that the generation of C₂₊ products can be achieved through nitrogen modification materials and Cu-based materials (Table 2). Thus, it is feasible to design catalysts based on the above table to explore the possibility of coupling CO₂ capture and electrochemical conversion to produce C₂₊ products. Furthermore, for Cu-based catalysts, some researchers have suggested that the kinetics determining the partial current density of C₂₊ depend on the adsorption energy of the *CO intermediate and the *CO surface coverage (θ^*CO), whereas tuning of θ^*CO can induce the production efficiency of C₂₊ products.^{136,137} Hence, we suppose that segmented tandem electrodes (e.g., Ag/Cu) can be constructed to achieve stepwise conversion of CO₂-to-CO and CO-to-C₂₊.

Table 2. Recently, reported nitrogen modification and Cu-based catalysts for electrochemical CO₂ reduction to C₂₊ products

Catalyst	Electrolyte	Products	FE (%)	Potential	Ref.
Cu ₂ O/NCS	0.5 M KHCO ₃	C ₂ H ₄	24.7	-1.3 V vs. RHE	138
N-doped graphene quantum dots	0.1 M KHCO ₃	C ₂ H ₄	31	-0.75 V vs. SHE	139
N-mesoporous carbon	0.1 M KHCO ₃	C ₂ H ₅ OH	77	-0.56 V vs. SHE	140
N-doped nanodiamond/Si rod array	0.5 M KHCO ₃	CH ₃ COOH	91.8	-1.0 V vs. RHE	141
Oxygen-derived Cu	0.1 M KHCO ₃	C ₂ H ₄	60	-0.5 V vs. SHE	142
CuAg alloy	1.0 M KOH	C ₂ H ₅ OH	25	-0.7 V vs. SHE	143
Chloride-induced biphasic cuprous oxide and metallic	0.1 M KCl and 0.1 M KHCO ₃	C ₃ H ₇ OH	8.7	-	144

The coupling of CO₂ capture and conversion through electrochemical processes is emerging as a promising method for storing and using renewable electricity while preventing CO₂ from being released into the atmosphere, thus forestalling the most severe consequence of global warming. In this review, threading through the development process of this emerging field, cutting-edge intensification technologies are introduced and discussed, and some strategies to address existing problems, such as low faradic efficacy and C₂₊ chemical production, are also provided. Additionally, we propose the potential for utilizing this method to harness carbon sources in the ocean. This review will aid in the acceleration of this promising technology and contribute to addressing the global warming issue.

Supporting Information

The Supporting Information is available free of charge at <http://pubs.acs.org>.

Conflicts of interest

There are no conflicts to declare.

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Author contributions

X. Z. proposed the topic of the Review. Q. X drafted the manuscript. All authors contributed to the editing of the manuscript.

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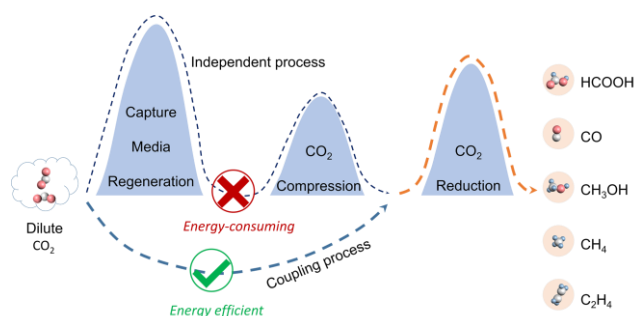
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TOC Graphic



Highlighted Quotes

1. While the process can be powered by renewable energy sources such as solar energy and wind power, the high energy demand necessitates additional facilities to

maintain a stable working temperature irrespective of light intensity and wind conditions, which may increase the process's capital cost.

2. Therefore, dual electrolytic cell systems that integrate CO₂ capture and conversion may be more attractive in the future.
3. The energy cost was only focused on driving electroreduction, which accounted for about 49.3 % of the energy cost by using the independent system.