

Electrochemical CO₂ reduction integrated with membrane/adsorption-based CO₂ capture in gas-diffusion electrodes and electrolytes

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Abstract

Electrochemical CO₂ reduction reaction (CO₂RR) has attracted much attention in the last decade, owing to its unique advantages such as operation at ambient conditions, coupling with renewable electricity, and producing a wide range of products and commodities. The majority of CO₂RR studies are focused on pure CO₂ as feed, while in real CO₂ waste streams, such as flue gas or biogas, CO₂ concentration does not exceed 40%. Therefore, the economic feasibility of CO₂RR and its carbon footprint are greatly limited by the CO₂ purification steps before electrolysis (\$70–100 per ton of CO₂ for CO₂/N₂ separation). In recent years, studies have exhibited the importance of this matter by integrating CO₂ capture and electroreduction in a single unit. Mostly, CO₂ capture solutions as electrolytes have been under attention, and promising results have been achieved to significantly improve the overall economy of CO₂RR. The focus on CO₂ capture-electroreduction integration can go beyond the solution/electrolyte-based CO₂ capture (e.g., amine solutions and ionic liquids) and other processes such as solid adsorption and membrane-based processes, as more efficient options, can be potentially integrated with CO₂ electroreduction in the gas-diffusion electrode design. This article aims to review the recent efforts in integrating capture and electroreduction of CO₂ and provides new perspectives in material selection and electrode design for membrane- and adsorption-based CO₂ capture-reduction integration, in addition to the analysis of the economic feasibility of this integration.

KEYWORDS

CO₂ capture-electroreduction integration, electrochemical CO₂ reduction reaction, gas-diffusion electrodes

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1 | INTRODUCTION

Excessive CO₂ emission is causing noticeable environmental issues such as climate change and ecological deterioration. This has attracted the researchers' attention around the world to urgently develop an efficient carbon utilization technology to move toward net-zero emission goals.¹⁻³ During the last 2 decades, significant progress has been made in the area of thermocatalytic, photocatalytic, and electrocatalytic conversion of CO₂ to a wide range of value-added products.^{4,5} Among these, electrocatalytic CO₂ reduction reaction (CO₂RR) has recently attracted much attention due to its capability to be coupled with renewable electricity, multiple value-added products and commodities, and ease of operation at mild reaction conditions (room temperature).^{6,7} There has been substantial advancement in the development of electrocatalysts, reactor and electrode design, and electrolytes to further tune their performance near industrially relevant conditions.⁸⁻¹⁰

Despite the remarkable progress and efforts in CO₂RR from different aspects (e.g., catalyst/electrode/ion-exchange membrane development,¹¹⁻¹³ reactor design,¹⁴ characterization techniques,¹⁵ etc.), almost all CO₂RR

studies focus on using pure CO₂ as the feed. However, real CO₂ streams, such as flue gas or biogas, are often diluted and contain less than 50% CO₂ concentration. Therefore, a costly pre-purification step will be required, which adversely affects the overall economy of CO₂ utilization. Recent analyses show that using a capture-reduction integrated route not only results in a significant reduction in energy consumption/cost but also remarkably reduces the carbon footprint.^{16,17} For example, for direct conversion of carbonate (the result of CO₂ capture in solution) to syngas, a 75% reduction in CO₂ emissions was reported as compared to that for gas-phase CO₂ electrolysis (the most common CO₂ electrolyzer studied in CO₂RR).¹⁷ Therefore, being able to directly feed the electrolyzer with the diluted CO₂ streams can reduce the operating cost associated with the carbon conversion economy.¹⁸⁻²⁰

In recent years, some studies have attempted to integrate CO₂ capture and reduction mainly via using solvent-based CO₂ capture as the electrolyte such as amine-based or ionic liquids, schematically shown in Figure 1A. As a result, innovative electrolyzers and electrode designs based on this integration have been proposed.¹⁸ However, since CO₂ is chemically captured, it

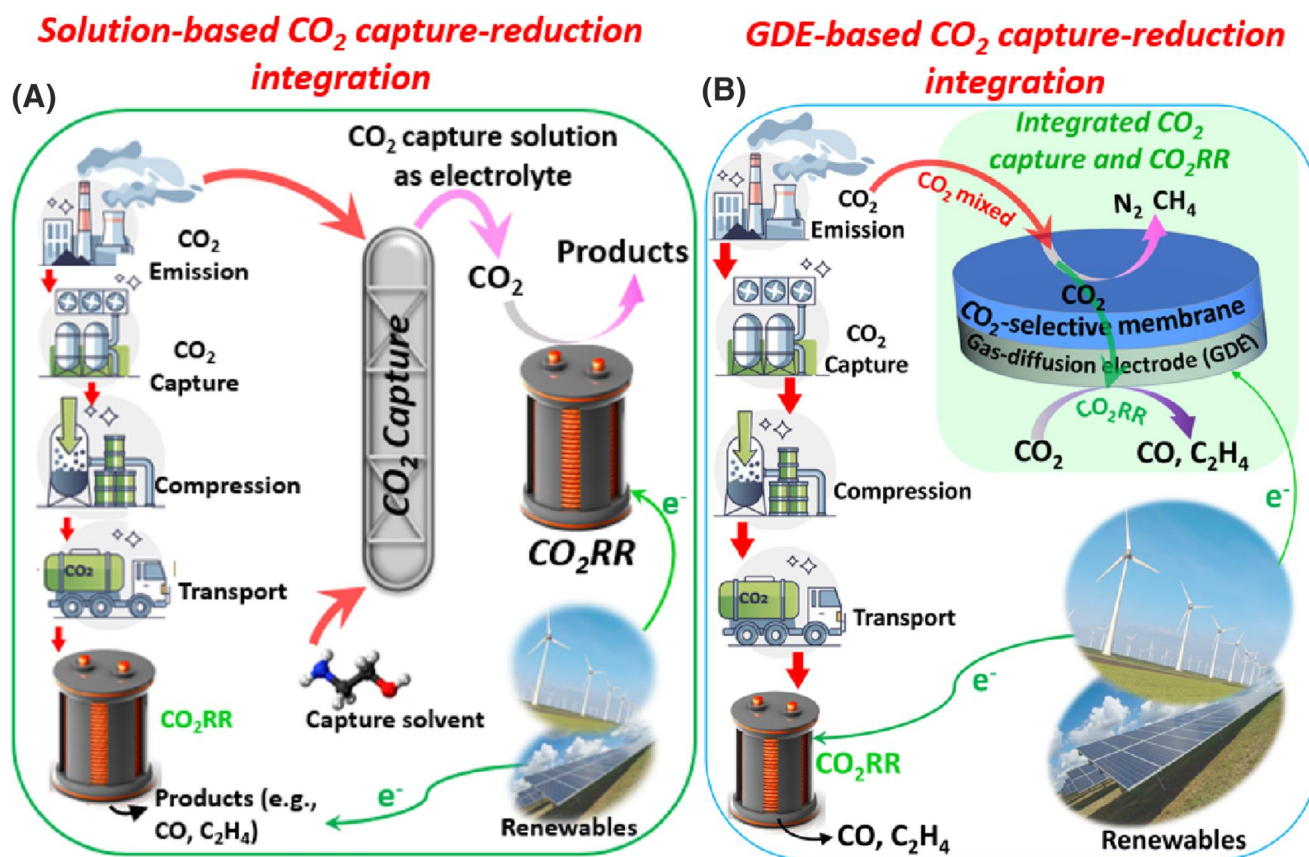


FIGURE 1 Schematic diagram of coupling (A) solution-based CO₂ capture and (B) GDE-based CO₂ capture with electrochemical CO₂ reduction reaction. The sequential route (left side in A and B) has several steps before electrolysis, as compared with the integrated route.

is hard to release and becomes available for reduction on the catalyst.¹⁹ In addition, using the capture media as the electrolyte might not be the ideal electrolyte choice for the desired product, since the effects of electrolyte type on CO₂RR performance (e.g., reaction pathway, rate of reaction, etc.) are identified and they usually suffer from low current densities.^{21,22} CO₂ electrolyzers often have a gas-diffusion electrode (GDE) where the catalyst is loaded, CO₂ is delivered, and a reaction occurs.²³ Designing and tuning GDEs is rather complicated and subject to several parameters that are out of scope and have been well reviewed in recent years.¹² Adjusting the CO₂ capture step on the GDE can open up a new avenue in the design of efficient electrodes and electrolyzers. By doing so, a solid-state CO₂ capture layer, such as membrane separation and adsorption, can be added to the GDE structure, enabling to feed diluted CO₂ streams into the electrolyzer. Unlike solution-based capture, CO₂ is not captured in the form of (bi)carbonate and is ready for the reaction without the need for exsolution.²⁴

In this perspective, we aim to showcase the possible design scenarios for integrating membrane-based and adsorption-based CO₂ capture into a GDE to feed the electrolyzer with a diluted CO₂ stream (Figure 1B). We briefly review the recent major efforts for CO₂ capture-reduction integration using solution-based designs with the key achievements, challenges, and opportunities. Then, designs for membrane-based and adsorption-based integrated systems are reviewed and potential design scenarios, material selection, and associated challenges are discussed. Further, the techno-economy analyses of CO₂ capture-reduction systems are discussed to shed light on the advantages of integrated systems. Finally, recommendations for future research based on the shortcomings of the current research are given.

2 | ELECTROLYZERS AND ELECTRODES FOR ELECTROCHEMICAL CO₂ REDUCTION

Electrochemical CO₂ reduction reaction (CO₂RR) has advanced rapidly in the last 10 years from developing highly active/selective/stable catalysts to novel electrode/electrolyzer designs to achieve ampere-level current densities, moving toward industrial applications.²⁵ Studies focus on CO₂RR in two major designs: 1. H-cell where catalysts are coated on a substrate and CO₂RR occurs in batch mode (Figure 2A); 2. flow cell where CO₂ and other fluids (e.g., catholyte and anolyte) continuously flow to the reactor (Figure 2B). The former is used to

monitor catalysts' performance in controlled conditions, resulting in low reaction rates (i.e., current density). On the other hand, flow cells maximize the interaction between the catalyst, gaseous feed CO₂, and the electrolyte, resulting in at least one order of magnitude higher current density.²⁶ The flow cell could be catholyte-free, where humidified CO₂ is fed into the reactor, so-called membrane-electrode assembly (MEA), as described in Figure 2C. Flow cells usually employ a gas-diffusion electrode (GDE), schematically shown in Figure 2D, consisting of a gas-diffusion layer (usually carbon-based or PTFE-based) and catalyst layer, facing the electrolyte. GDEs create a high contact area for the formation of triple-phase catalyst–electrolyte–CO₂ interfaces, and recently there has been significant attention toward optimization and tuning GDEs in terms of microenvironment, hydrophilicity/hydrophobicity, catalyst layer optimization, etc.^{12,14,27}

With the technological and material-centered advances in CO₂RR, researchers have recently pointed out the economy of CO₂RR, and how the required pre-purification steps of diluted CO₂ waste streams affect its feasibility. Currently, almost all studies use highly pure CO₂ feed (>99.9% purity), while CO₂ streams are usually diluted in a mixture of gases (such as flue gas or biogas), and reaching that high purity is a considerably expensive procedure. This calls for innovative integration of CO₂ capture with CO₂RR to improve the economy of this process. CO₂ capture is rather more developed as compared with CO₂RR, and several technologies have been investigated, such as solution-based amine CO₂ capture, membrane processes, adsorption, etc. The techno-economic analysis of such integration has shown promising results. A simple analysis on CO production from CO₂RR showed that the minimum selling price could be reduced by 37% by using direct conversion compared to the decoupled route.²⁸ Another study on integrated system for CO₂ reduction to CO showed that a directly coupled CO₂ capture and electrochemical conversion could significantly reduce energy consumption (up to 44%) compared to a separated process based on the state-of-the-art gas-fed CO₂ electrolyzers.¹⁶ A great amount of this energy benefit is due to the CO₂ loss (losing CO₂ in the form of (bi)carbonates), and the development of optimized CO₂ electrolyzers without CO₂ loss can reduce this energy benefit from 44% to 26%. The majority of the studies on integrated designs are focused on solution-based CO₂ capture where CO₂ capture takes place by the catholyte. Herein, the progress and challenges associated with this integration system are briefly reviewed in the following.

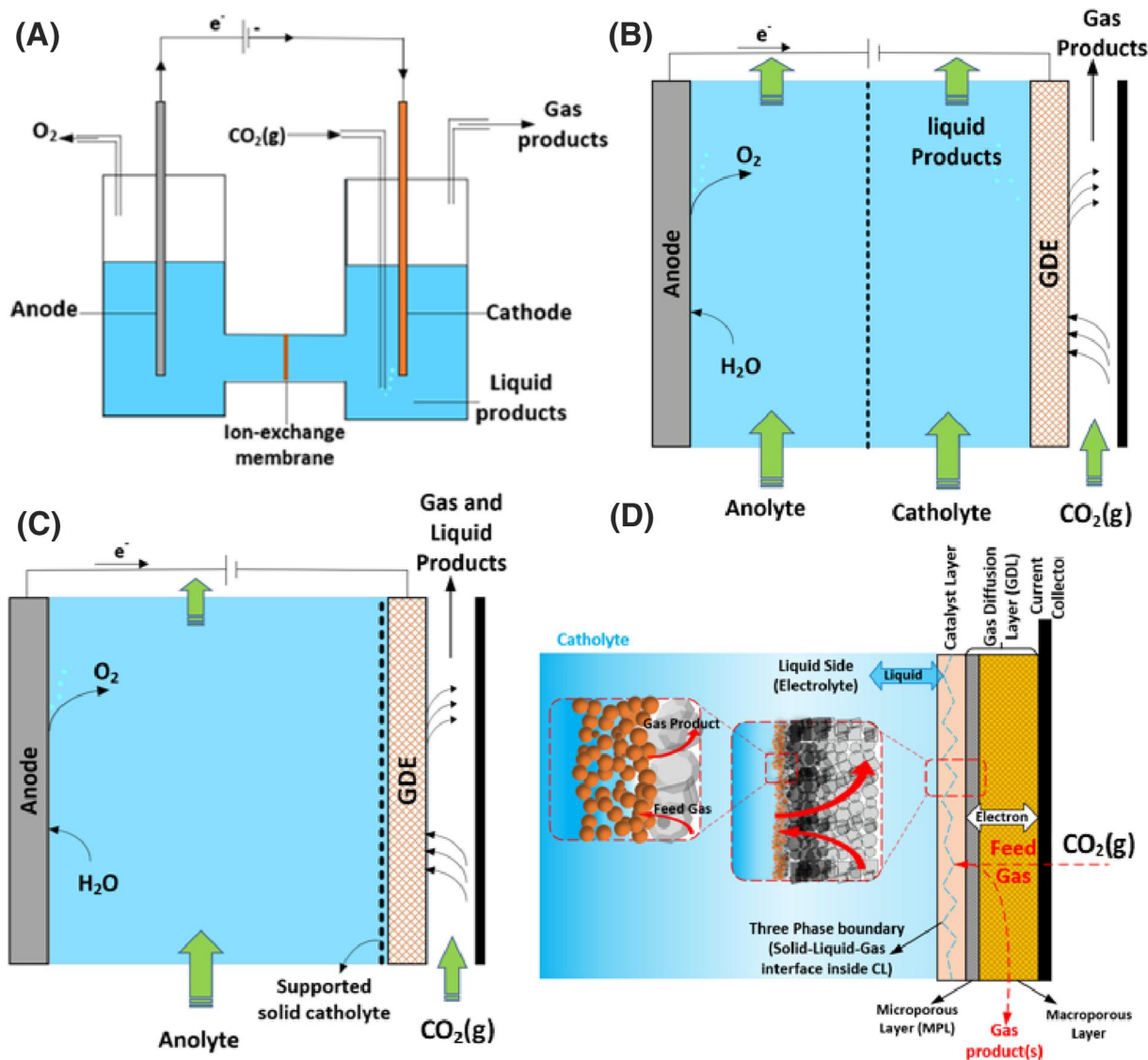


FIGURE 2 Schematic diagram of (A) H-cell, (B) GDE-based flow cell, (C) membrane-electrode assembly, and (D) different layers of a GDE. Reproduced with permission.¹²

3 | ELECTROLYTE-BASED CO_2 CAPTURE-REDUCTION INTEGRATION

The electrolyte-based CO_2 capture-reduction integration is well-reviewed in the literature.^{18,19,29–31} The recent advances in two major types: 1. Amine-based electrolyte capture-reduction; and 2. Carbonate/bicarbonate-based electrolyte capture-reduction integration are briefly reviewed in the following. The CO_2 capture mechanism of these solutions is schematically shown in Figure 3A,B.

CO_2 can be captured by diamines, alkanol amines, and their derivatives, which yield carbamate and subsequently can be electrochemically regenerated^{3,32} (Figure 3A). The schematic of using coupling amine-based CO_2 capture and using it as the catholyte for CO_2 reduction versus the decoupled CO_2 capture conversion system can be seen in

Figure 3C. Chen et al. used a 30 wt% Monoethanolamine (MEA) capture medium as the catholyte for the reduction of CO_2 using various metal catalysts.³³ Once CO_2 is dissolved in the Monoethanolamine solution, it turns into a conductive solution and is suitable for electrochemical conversion. Despite achieving faradaic efficiency (FE) as high as 60% for formate production, it was noticed that the captured CO_2 species were not converted into products and only free CO_2 molecules at a concentration of 0.03 M (dissolved CO_2) were available for CO_2RR . Therefore, choosing the right amine solution with the weaker CO_2 binding could overcome this issue. Diaz et al. reported the reduction of CO_2 to CO in switchable polarity solvents, which can also be used for CO_2 capture,³⁴ but the FE of CO did not exceed 20% as the nature of the solvent was aqueous based.

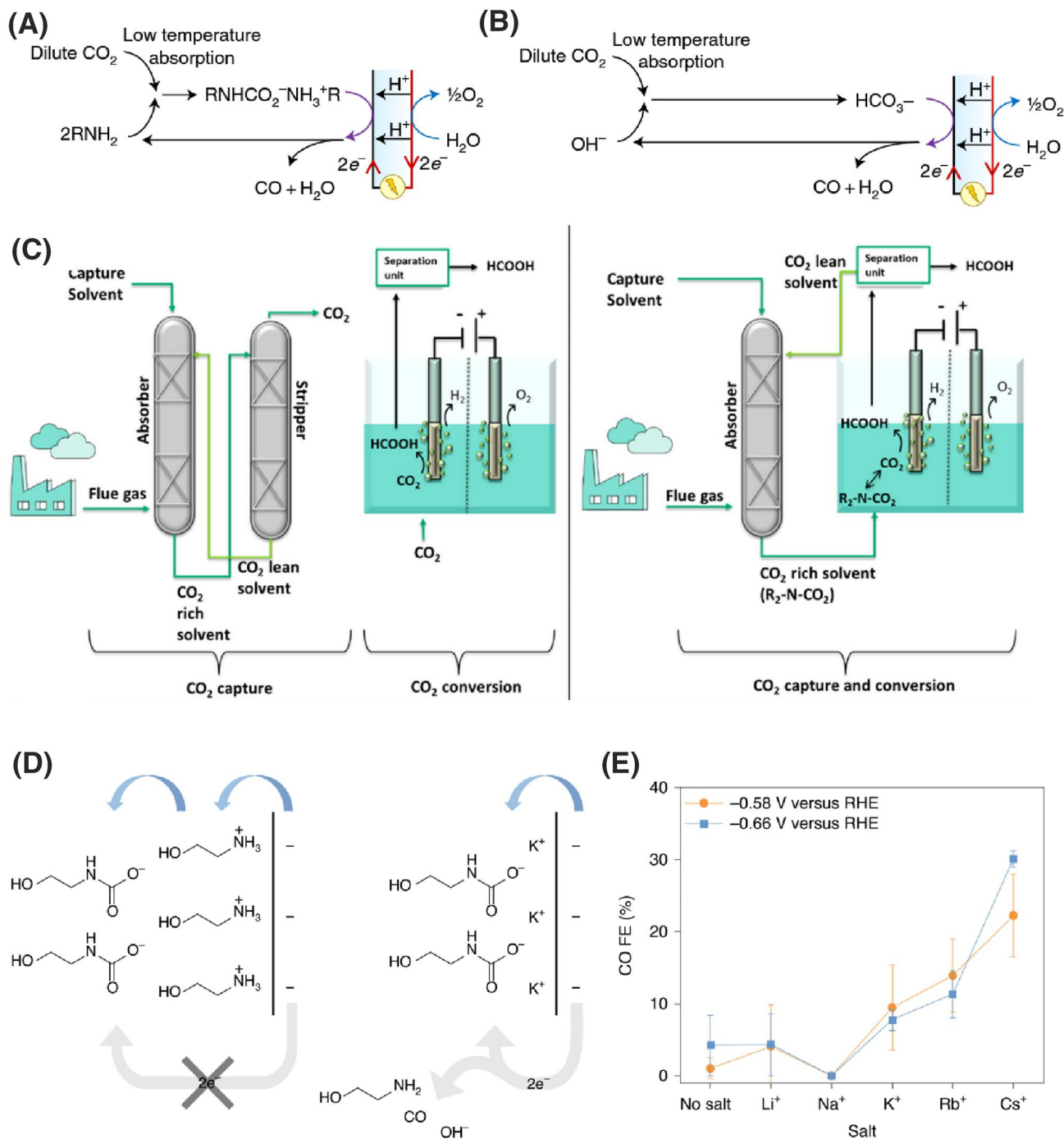


FIGURE 3 Integrated CO₂ capture and electrochemical reduction via using (A) amine-based and (B) carbonate/bicarbonate-based capture agents as the electrolyte. Reproduced with permission.¹⁹ (C) Schematic diagram of separated and coupled CO₂ capture and conversion. Reproduced with permission.³⁶ (D) Interfacial structure near the electrode surface: MEA-CO₂ electrolyte (left), MEA-CO₂ with alkali salt electrolyte (right). (E) FE for different alkali cation salt solutions in the MEA electrolyte at the applied potentials of -0.58 V and -0.66 V versus RHE (reverse hydrogen electrode). Reproduced with permission.³⁵

Lee et al. recently reported 72% FE for CO production at an applied current density of 50 mA cm⁻² by tailoring the electrochemical double layer of MEA solution by using alkali cations.³⁵ They suggested that by addition of K⁺ cations (through mixing KCl with MEA) an interfacial electron transfer mechanism will take place, as

illustrated in Figure 3D, promoting heterogeneous electron transfer and leading to improved conversion of amine-CO₂ to CO. They also determined that CO₂ captured by MEA was the source of CO production via isotopically labeling CO₂. The effect of cation size (Figure 3E) showed that cation serves to improve the

adsorption energy of reactants by increasing the strength of the electric field, and Cs^+ with the smallest hydrated ionic radius had the best performance as compared with larger cations, such as Li^+ and Na^+ , which barely produced any products. Pérez used a mixture of chemical and physical CO_2 absorption solvents (mixture of 2-amino-2-methyl-1-propanol and propylene carbonate) as electrolytes and reported up to 50% FE of formate with carbon conversion of approximately 30% carbon conversion.³⁶ One interesting finding of this study was the effect of temperature on the release of the captured CO_2 , and by increasing the temperature from 20 to 75°C the reaction rate toward formate formation is inclined by a factor of 10. Since for industrial-scale electrolyzers the electrolyte temperature increases due to ohmic losses, this heat, which is usually perceived as a negative point, can aid in boosting the rate of CO_2 release/conversion.

Bicarbonate/carbonate is the product of CO_2 capture by inorganic hydroxides (e.g., KOH), and studies have recently shown that bicarbonate/carbonate can be reduced to CO_2RR products.^{17,37–45} This occurs through local acidification and local generation of molecular CO_2 ((bi)carbonate + H^+ → CO_2 + H_2O), and the captured CO_2 is converted into the desired products in a reactor shown in Figure 4A. Berlinguette et al. have developed several designs for conversion of bicarbonate into formate and CO, often with using a bipolar ion-exchange membrane to supply the required protons for the mentioned local acidification.^{38,42,43,46–49} However, bipolar ion-exchange membranes require a high voltage to dissociate water into H^+ and OH^- (Figure 4B); therefore, they designed a bicarbonate electrolyzer working with Nafion cation exchange membrane and sourcing H^+ from H_2 oxidation in the anode (Figure 4B, left). In doing so, a CO partial current density of 220 mA cm^{-2} at a voltage of merely 2.3 V was achieved.⁴⁶ Comparing the techno-economy of using H_2 oxidation and Nafion membranes with using a bipolar membrane or gas-phase CO_2RR with anion exchange membranes, exhibited the profitability of this design with less capital and operation costs, and higher net present value in the long term.⁴⁶

One challenge of (bi)carbonate reduction is insufficient CO_2 access due to inefficient generation of aqueous CO_2 from bicarbonate. Wen et al. recently designed a gas-diffusion electrode to expedite sufficient CO_2 access from CO_2 exsolution through a flow-through configuration, where bicarbonate is pushed to the electrode.³⁹ The convection by electrolyte pushing through and localized pressure decrease resulted in the release of CO_2 capture in the form of gas bubbles, which were subsequently reduced to CO (Figure 4C). This design achieved a maximum current density of 3.37 A cm^{-2} with an Ag-based catalyst, and they scaled-up to $4 \times 100 \text{ cm}^{-2}$

electrolyzer stack, and a record-breaking CO production rate of 90.6 L h^{-1} was reported. One issue of bicarbonate reduction is its limited recapture capacity of the unreacted CO_2 , resulting in the dilution of the gaseous product with CO_2 . Sargent et al. reported that carbonate reduction produces high-purity gaseous products.^{17,37,50} They explored this design with both bipolar membrane (coupled with alkaline water oxidation⁵⁰) and cation exchange membrane (with acidic water oxidation³⁷) and achieved the product with an H_2/CO ratio in the industrially relevant range (1–2) and less than 400 ppm CO_2 .

4 | MEMBRANE- AND ADSORPTION-BASED CO_2 CAPTURE-REDUCTION INTEGRATION

So far, the efforts regarding the integration of CO_2 capture and reduction have mainly focused on using an electrolyte with CO_2 capture capability, as reviewed. However, this comes with several challenges such as: 1. Low current density as compared with gas-phase CO_2RR , 2. The difficulty of processibility of many CO_2 capture solutions such as ionic liquids. Moreover, the capture and reduction steps need to be separate, meaning that the CO_2 capture solvent will be subsequently used in the electrolyzer. A method by which CO_2 capture can be coupled with gas-phase CO_2RR on a gas-diffusion electrode (GDE) can take advantage of high current density in gas-phase CO_2RR as well. There have been significant advances in membrane-based and adsorption-based CO_2 capture methods in terms of material development^{51,52} and economic performance,⁵³ which make them the optimal option. In both membranes and adsorption, CO_2 capture occurs on a solid platform, making it possible to couple the capture step with gas-phase CO_2RR , if the CO_2 -selective membrane or CO_2 -selective adsorbent layer is on the gas-diffusion electrode (GDE), as schematically described in Figure 5.

There are mainly 2 types of GDEs developed for CO_2RR based on the gas-diffusion layer (GDL). For conventional carbon-based GDLs (Figure 5A), the CO_2 -selective layer can be coated on the CO_2 side of the GDE; however, since most carbon-based GDLs have irregular large pores on their gas side (unlike the catalyst layer side that comes with a smooth microporous layer), it might be necessary to have a gutter layer as a smooth substrate for a uniform CO_2 -selective layer, as can be seen in Figure 5A. This is a common practice in fabrication of gas separation membranes since it is necessary to keep the selective layer as uniform as possible.⁵⁴ Recently, hydrophobic polymeric-based (usually PTFE-based) GDLs have been used for CO_2RR due to their robust stability under cathodic

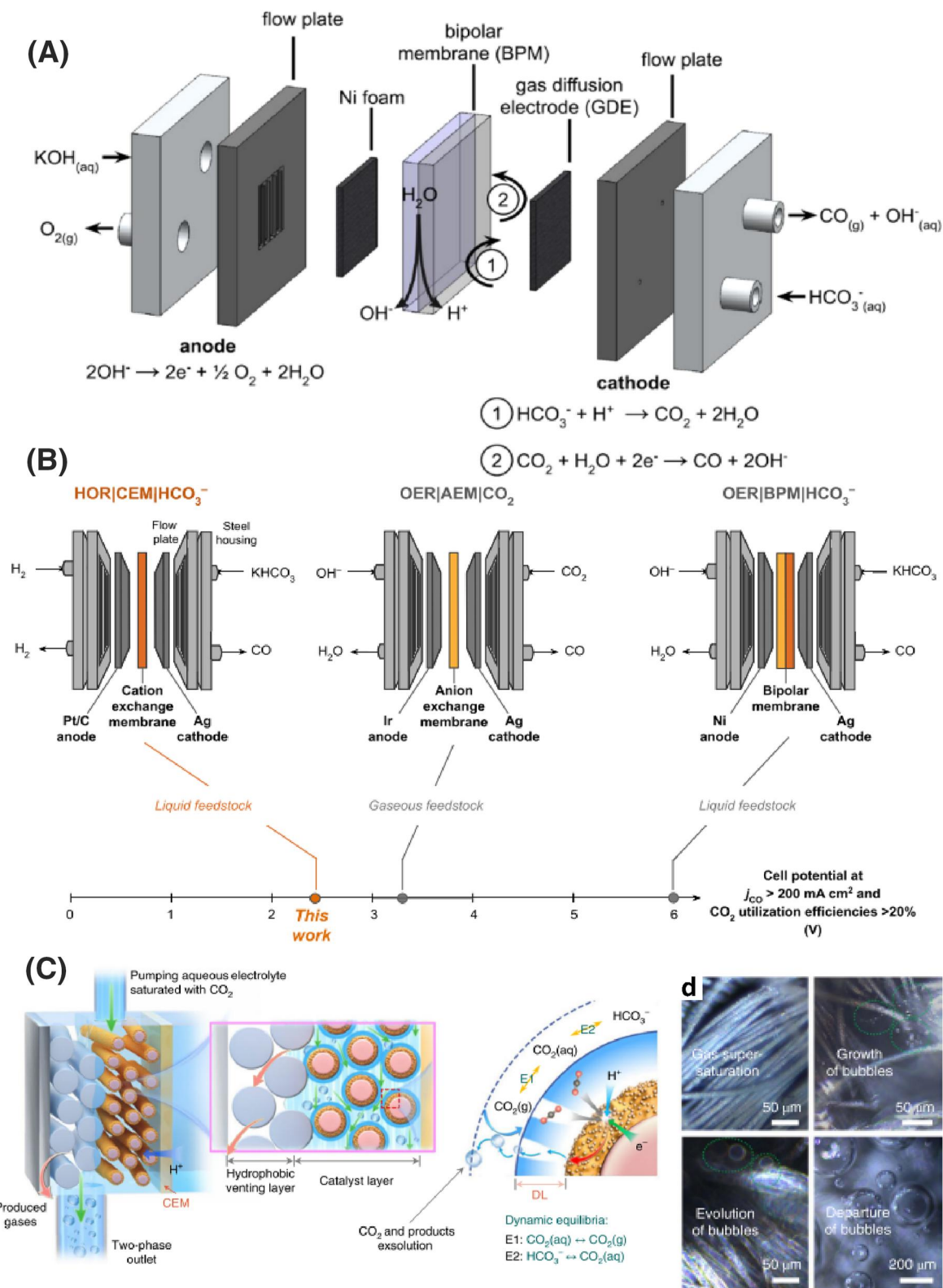


FIGURE 4 (A) Schematic diagram of the liquid-fed bicarbonate electrolyzer containing a Ni foam anode, bipolar membrane (BPM), and silver cathode gas diffusion electrode (GDE), CO is produced at the cathode GDE by a chain reaction: (1) conversion of HCO_3^- to CO_2 by acid–base equilibrium and (2) electrochemical CO_2 conversion into CO. Reproduced with permission.⁴³ (B) Schematics of prototypical CO_2 to CO electrolyzer configurations: KHCO_3 reduction with H_2 oxidation using a cation exchange membrane (left), gas-phase CO_2 RR (middle), and KHCO_3 reduction with water oxidation using a bipolar ion-exchange membrane (right). Reproduced with permission.⁴⁶ (C) Illustration of CO_2 exsolution from the dynamic equilibria via pumping CO_2 -saturated catholyte throughout a porous electrode. (D) Photographs of the formation procedures of gas bubbles due to gaseous CO_2 and product exsolution with the fibers of the electrode. Reproduced with permission.³⁹

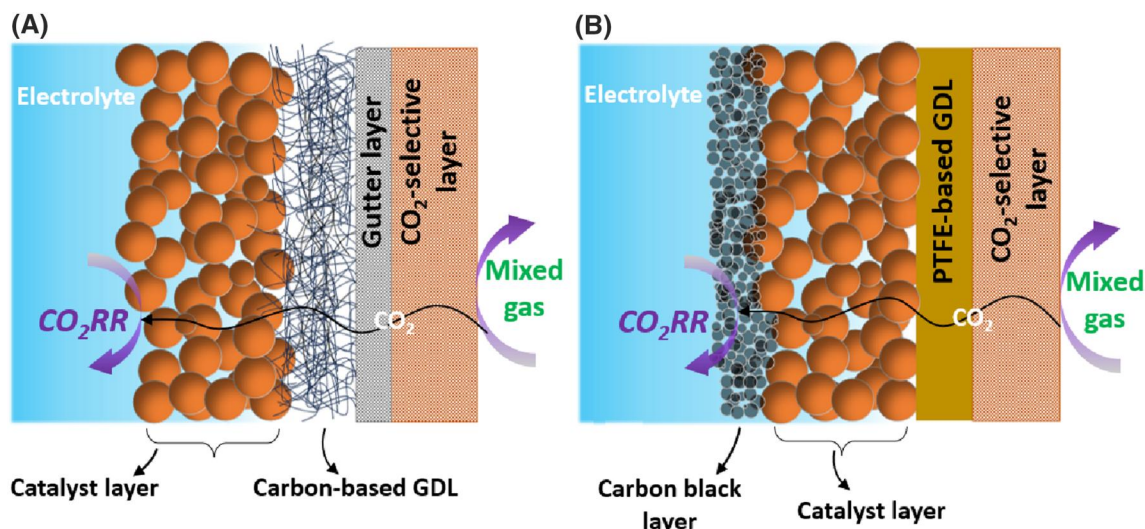


FIGURE 5 Schematic diagram of scenarios for a GDE-based integrated system via loading a membrane-based or adsorption-based CO_2 -selective layer on (A) carbon-based and (B) PTFE-based gas-diffusion electrodes in a flow-cell CO_2 electrolyzer.

conditions and resistance to flooding.⁵⁵ In this case, a carbon black layer is coated on the catalyst layer to act as the current collector (Figure 5B). Considering the type of the selective PTFE GDL a gutter layer might not be required because PTFE substrates with uniform microporous layers on both sides are commercially available. In addition, the CO_2 -selective layer could be sandwiched between the PTFE and catalyst layer as well.

The CO_2 -selective layer could be a CO_2 -selective membrane with a high affinity to permeate CO_2 as compared with other gases such as N_2 or CH_4 . Membranes for CO_2 capture are usually made of organic (polymers), inorganic (ceramic), or a combination of them, so-called mixed-matrix membrane.⁵⁶ In addition to using membranes for CO_2 capture from flue gas and biogas, membranes have the potential for CO_2 direct air capture as well.^{57,58} The membrane could be coated on the GDE via different methods such as solution casting, spraying, electrospinning, etc.⁵⁹ There are many comprehensive reviews on membrane types, materials, and their mechanism; therefore, the full description of their properties (such as solution-diffusion, filtration, etc.) is out of scope here.^{60,61} Similarly, the selective layer could be made of adsorbent with high affinity for CO_2 capture, such as metal-organic framework (MOF), silica, graphene-based materials, and metal oxide.⁶² By mixing CO_2 adsorbents with polymers with high CO_2 affinities, mixed-matrix membranes could be prepared.⁶³ In the following, the few recent efforts in this regard and the perspectives for future designs are discussed.

Kibria et al. fabricated permselective mixed-matrix MOF-based GDEs for direct conversion of CO_2 from flue gas (Figure 6A).²⁸ Doing so, the mixture of CO_2 selective metal-organic framework (CALF-20) and Nafion

was cast on the gas side of an Ag-sputtered GDE, and due to the affinity of CO_2 with the MOF, CO_2 diffusion is higher than that for N_2 and O_2 (Figure 6B), resulting in favorable CO_2 permselectivity. Mixed-matrix membranes are favorable gas separation membranes since the fabrication of a uniform and robust layer of MOF (or other standalone inorganic membranes) is challenging; therefore, the polymer binder can bring strength to the CO_2 selective layer.⁵⁶ This GDE, as the first attempt to couple membrane CO_2 capture with CO_2 reduction on a GDE, was tested for gas-phase CO_2 reduction to CO (Figure 6C). For such a design, the properties of the membrane can affect the electrochemical performance of the cell, since the membrane is meant to provide sufficient CO_2 for the reaction. For this mixed-matrix membrane, loading of MOF higher than 7 mg cm^{-2} led to blocking the pores of the gas diffusion layer; therefore, a significant drop was seen in FE of CO (Figure 6D). Considering that the flue gas contents oxygen and humidity, the tests were also performed with 15% CO_2 , 4% O_2 , and 100% relative humidity in N_2 balance, as seen in Figure 6E. Although missing FE was noticed due to the parasitic oxygen reduction reaction at relatively lower overpotentials for both AgPTFE GDE (without membrane) and PGDE (with membrane), but for higher overpotentials the permselective membrane showed negligible loss of FE due to high affinity of the membrane with CO_2 rather than O_2 . The existence of humidity in the feed gas also led to generally lower FE of CO, since the polar nature of water will typically mean much stronger physisorption in the pores than for carbon dioxide, minimizing CO_2 adsorption.⁶⁴ However, this adverse effect was less severe for the GDE with permselective membrane, owing to the elevated hydrophobicity

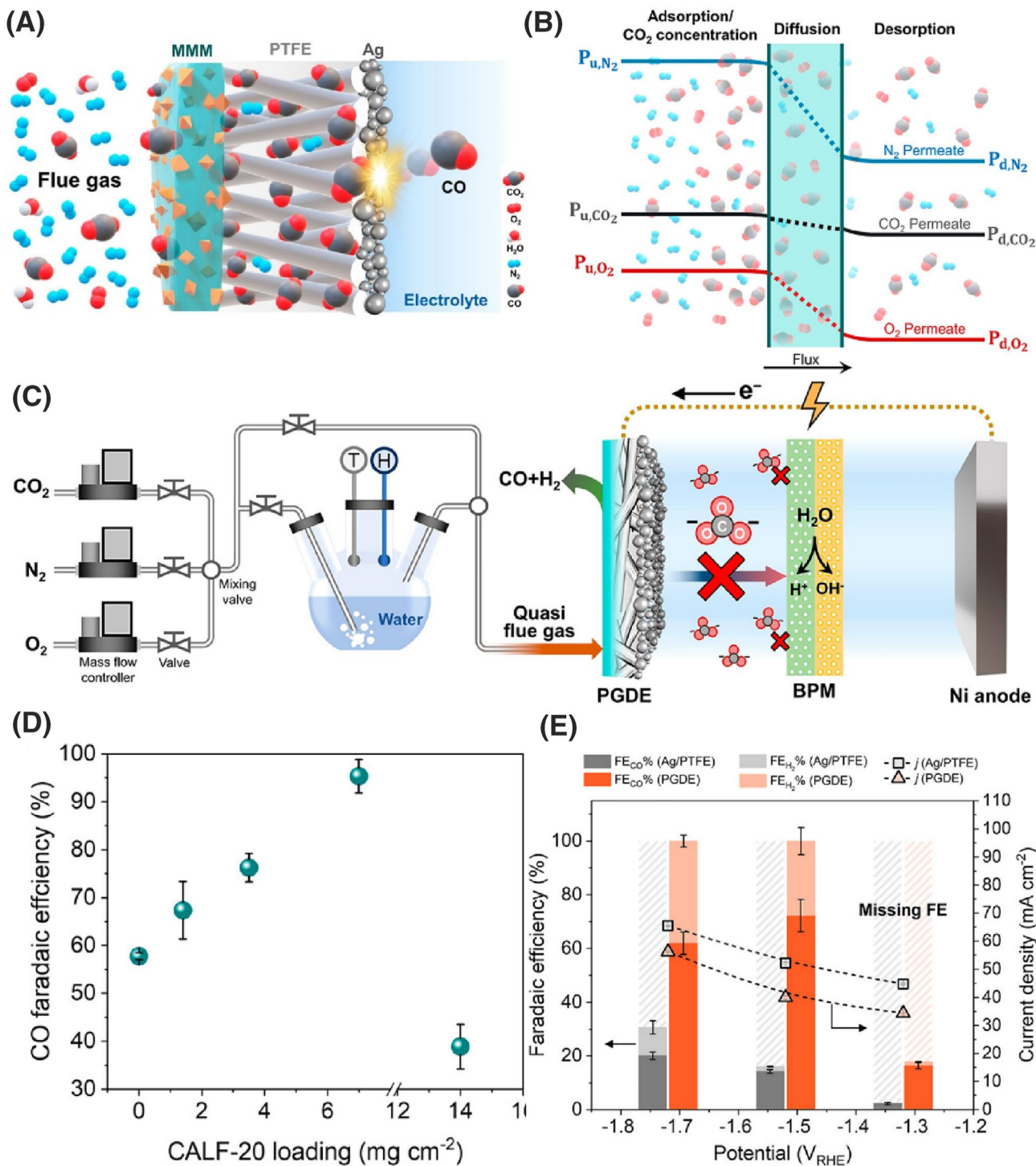


FIGURE 6 (A) Schematic diagram of coupling CO₂ capture and reduction on a GDE with a CO₂-selective layer, and its advantages to eliminating steps such as compression and transport before conversion. (B) Schematic diagram of coating a mixed-matrix membrane (MMM) on an Ag-coated PTFE GDE for selective permeation of CO₂ into the catalyst layer. (C) Diffusion difference between CO₂, N₂, and O₂ through the MMM with MOF, higher diffusion of CO₂ results in higher CO₂ permeation. (D) Schematic diagram of making quasi-flue gas with controlled CO₂/N₂/O₂ content and humidity to directly feeding to the gas-phase CO₂RR electrolyzer. (E) Effect of the content of CALF-20 as the CO₂-selective MOF in the membrane matrix on the CO₂-to-CO performance. (F) Effect of O₂ on the electrochemical performance the Ag/PTFE GDE (no membrane) and PGDE (permselective GDE with the membrane). Reproduced with permission.²⁸

of CALF-20, which mitigates the humidity impact on CO₂ to permeate through the MMM layer.²⁸

PTFE-based GDLs are preferred since they provide a smooth substrate for defect-free membrane coating. In addition to the mixed-matrix membranes, both polymeric and inorganic membranes for the fabrication of CO₂-selective GDEs can be developed. For example, polymeric membranes made from *Polymers of Intrinsic Microporosity (PIM)* are known for their high CO₂ permeation selectivity^{65,66}; in addition, these polymers can tune the electrochemical properties by providing multiphase interfaces,⁶⁷ and their benefits for improving CO₂ reduction has been also reported.⁶⁸ Other polymeric membranes such as poly (ether-b-amide) (PEBA) and polyimide are also promising choices as they are often used for CO₂ capture purposes.^{69,70} Porous inorganic membranes for CO₂ capture have also developed significantly in the past, and several types of membranes such as microporous silica, amine-functionalized mesoporous, ionic liquid membranes based on mesoporous alumina and silica, zeolite and MOF membranes have been fabricated.⁷¹ Unlike polymeric membranes where the CO₂ capture mechanism is based on solution-diffusion, inorganic membranes have an adsorption route for the materials with high CO₂ uptake, or a diffusion mechanism where separation occurs based on the size of gas molecules (molecular sieving). Therefore, achieving high CO₂ selectivity/flux with inorganic membranes is feasible; however, having uniform inorganic membranes without any defects or pinholes is challenging since unlike polymeric membranes, with a connected network polymer, inorganic membranes tend to have voids between the inorganic particles, deteriorating the separation selectivity.⁷²

Nam et al. fabricated Cu-sputtered PTFE GDE augmented with an MOF layer with high adsorption capacity for CO₂ in gas-phase and MEA-type cells.⁷³ The MOF layer was sandwiched between the Cu and PTFE layer, as shown in Figure 7A. MOFs with different CO₂ adsorption abilities were used to improve the FE of ethylene. Compared with the GDE without the PTFE layer with 43% FE of ethylene at 200 mA cm⁻², the addition of the CO₂-phil MOF layer led to 50% at 1 A cm⁻² (Figure 7B), over 5-fold increase in the production of ethylene. One interesting finding of this study was the dual function effect of the MOF, wherein the Cu-based metal part was incorporated in the CO₂RR, while the organic ligands provided high CO₂ capture capability. However, this study only tested the GDEs with pure CO₂; therefore, investigating their performance with mixed gas can be useful. The MOF-augmented GDEs were tested in MEA cells and reported a 2.7-fold improvement in the C₂H₄ production rate compared to the system without any MOF layer, as seen in Figure 7C. It has been found that for the MEA design, the

optimal condition was where the MOF layer was as an underlayer (under the catalyst layer), while for the alkaline electrolyzer, the best results were when the MOF layer was over the catalyst layer. This shows that the performance of the MOF adsorbent layer is relevant to the microenvironment differences between the flow cells and MEA electrolyzers, that is, the absence of electrolyte, water vapor, and CO₂ supply from the backside of GDE, and site difference where CO₂RR occurs in GDE.⁷⁴ The long-term test of a 5 cm² GDE also showed stable operation in terms of cell voltage and the FE of ethylene (Figure 7D), indicating the efficiency of the adsorbent layer to stably provide CO₂ for the catalyst layer.

Liu et al. recently fabricated GDEs made of a series of silver cluster-based metal-organic framework for simultaneous CO₂ capture and reduction to CO from simulated flue gas (15% CO₂ in N₂).⁷⁵ MOFs with amine groups, which are known for capturing and enriching CO₂ conditions from simulated flue gases under wet conditions, with high porosity selectively capture CO₂ and the clusters of silver reduce it to CO. The results in terms of FE of CO and CO partial current density shown for pure CO₂ and simulated flue gas exhibited that the existence of amine groups for CO₂ capture is necessary to achieve comparable performance when flue gas is used (Figure 7E,F). Whereas, for other MOFs without the amine moiety, this trend was not observed when using flue gas. Considering the versatility of MOFs, this strategy can be applied to other metal clusters for other products of CO₂RR from flue gas.

Solid adsorbents for CO₂ capture have been well-reviewed in the literature.⁷⁶⁻⁷⁸ For the design of an adsorbent layer on a GDE, it is important to develop solid adsorbents with high CO₂ adsorption capacity and selectivity, and other parameters such as kinetic rate, active porosity and surface area to adsorb, and tolerance to moisture and impurities need to be considered.⁷⁹ In addition, having adsorbents with high interaction with CO₂ could lead to saturation of the adsorbent layer and CO₂ will not be available for reduction; therefore, the bonding between CO₂ molecules and the adsorbent cannot be very strong, meaning that rational design of adsorbents with optimal interaction with CO₂ is required to develop efficient GDEs with an adsorbent layer.

5 | TECHNO-ECONOMIC BENEFITS OF INTEGRATED CO₂ CAPTURE-REDUCTION SYSTEMS

Due to the need for integration of CO₂ capture and reduction, there have been several attempts in recent years to evaluate the energy and techno-economy of coupling CO₂ capture and conversion. Li et al. analyzed

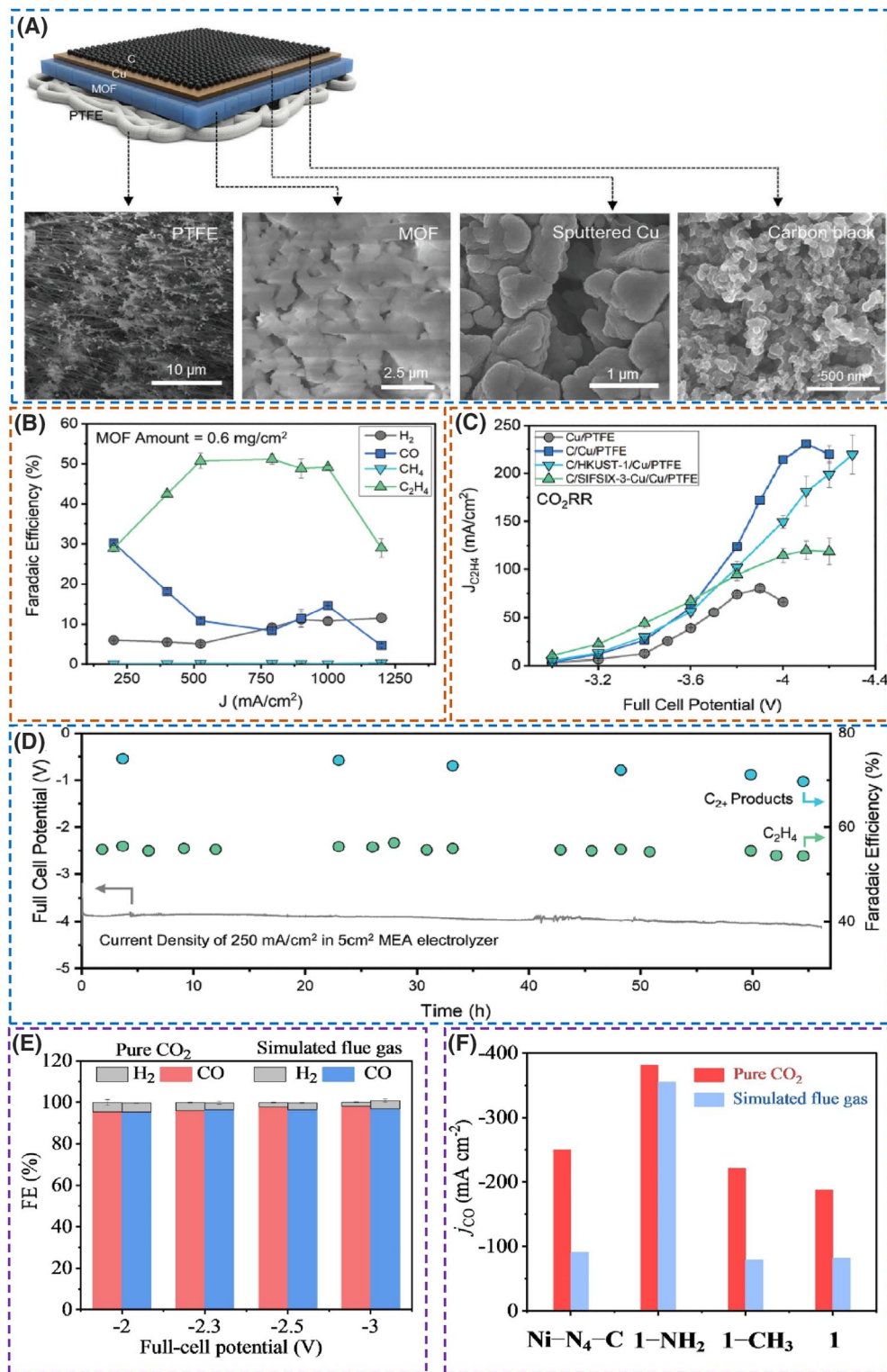


FIGURE 7 (A) Schematic diagram of MOF-augmented GDE components (C/Cu/MOF/PTFE) and the corresponding SEM images. (B) Performance of MOF-augmented GDE at different current densities, HKUST-1 is the MOF for GDE fabrication. (C) Partial current density of C_2H_4 in MEA electrolyzer with MOF-augmented GDE and 0.1 M KHCO_3 anolyte. (D) CO_2RR stability of C/HKUST-1/Cu/PTFE in MEA electrolyzer with 0.1 M KHCO_3 anolyte. Reproduced with permission.⁷³ (E) Comparison of CO selectivity for silver cluster 1-NH₂ catalyst measured in CO_2 atmosphere and simulated flue gas. (F) Comparison of current density of various GDEs measured under pure CO_2 atmosphere and simulated flue gas. 1 is $[\text{Ag}_{12}(\text{S}^t\text{Bu})_8(\text{CF}_3\text{COO})_4(\text{bpy})_4]$, 1-CH₃ is $[\text{Ag}_{12}(\text{S}^t\text{Bu})_8(\text{CF}_3\text{COO})_4(\text{bpy}-\text{CH}_3)_4]$, 1-NH₂ is $[\text{Ag}_{12}(\text{S}^t\text{Bu})_8(\text{CF}_3\text{COO})_4(\text{bpy}-\text{NH}_2)_4]$, and Ni-N₄-C is single-atom catalyst Ni-N₄ sites. Reproduced with permission.⁷⁵

the energy efficiency of sequential and integrated CO₂ capture and electrochemical conversion with amine-based solution as the electrolyte for CO production in three different scenarios (optimistic, baseline, and pessimistic, as shown in Figure 8A).¹⁶ They reported that the coupled system could potentially reduce 44% of energy consumption and 21% of energy cost versus a sequential process based on the state-of-the-art gas-fed CO₂ electrolyzers (similar to Figure 2B), if the integrated electrolysis performs in the optimistic scenario and has a high single-pass conversion efficiency to achieve the CO₂ lean state of the amines. In the sequential route, the energy consumption is shown to be dominated by CO₂ electrochemical conversion to produce CO (CO₂ electrolysis + generation of (bi)carbonate). However, for the baseline scenario, the integrated route is not more efficient than the separated route, due to the high electrical energy consumption, as shown in Figure 8B. These results suggest that future research should be directed toward enhancing the faradaic efficiency and cell voltages at industrially applicable current densities to reduce the energy of the overall process otherwise, the sequential route remains favorable. This is also emphasized by looking at the poor performance of the integrated system in the pessimistic scenario.

Tian et al. recently developed a 2D steady-state multiphysics model to analyze the effects of the flue gas components on the direct electrochemical electrolysis of flue gas and found out that at the normal atmospheric temperature and pressure flue gas electrolysis is dominated by the H₂ evolution reaction (>90% FE).⁸⁰ However, increasing the pressure to 20 atm will eliminate the adverse effects of diluted feed and the FE of CO₂RR will be even greater than that with pure CO₂, as can be seen in Figure 8C. Therefore, pressurization could be an option to achieve high-performance CO₂RR with flue gas, as it improves/homogenizes the dissolved CO₂ concentration, and relieve the local high temperature in the catalyst layer, which is caused by the increasing current density and SO₂ partial pressure in the flue gas. The comparison of cumulative present value between the pure CO₂ electrolysis system and flue gas electrolysis system also showed that the flue gas electrolysis takes 2 years to achieve a turnaround, whereas purified CO₂ electrolysis takes 4 years (Figure 8D). Over 20 years, the net present value for flue gas electrolysis showed to be 1.5 times that of purified CO₂ electrolysis, indicating the profitability of considering direct electrolysis of CO₂ from the diluted sources.

Lee et al. recently conducted a comprehensive techno-economic analysis and life-cycle assessment on three CO₂ utilization techniques for syngas production,

one being integrated CO₂ capture-electroreduction by using triethylamine as the capture and electrolyte in electrolysis, which is called reaction swing absorption (RSA).³ The schematic of this process as compared with gas-phase CO₂RR and reverse water gas shift reaction (RWGS) as two conventional pathways can be seen in Figure 9A. RSA consists of chemisorption, pressurization, and CO₂RR processes. The captured CO₂ via triethylamine in the form of bicarbonate is pressurized into a membrane electrode assembly. The integrated route shows significantly better performance compared with RWGS or gas-phase CO₂RR in terms of carbon footprint (here it is called global warming potential (GWP), meaning how much of CO₂ is produced per kg of syngas production) (Figure 9B). The current status is related to having the mix of fossil fuels and renewables as energy sources, whereas for the optimistic form only renewables (solar and wind) are used. Considering the optimistic energy source for RSA, the cash flow charts (considering capital expenditure (CAPEX) and operating expenditure (OPEX)) show an earlier positive value in the long term as compared with the other two routes, indicating the profitability of this integrated method (Figure 9C).

6 | OUTLOOK AND FUTURE STUDIES

In this perspective, the recent advances and progress in the integration of CO₂ capture and electrochemical reduction were discussed. Despite the high interest in this integration and economic incentives, more studies need to be focused on this route toward the industrial application of CO₂ capture-reduction systems. As briefly reviewed, the majority of studies use CO₂ capture solution as the electrolyte for this integration. Along with the efforts to improve the performance of electrolyte-based capture reduction systems in terms of current density and cell voltage, more promising results can be potentially achieved if membrane-based or adsorption-based CO₂ capture is coupled with a reduction in gas-diffusion electrode design step. This could even eliminate the need for any chemical CO₂ capture, which is done by CO₂ capture solvents; therefore, captured CO₂ is readily available to be reduced on the catalyst layer. We proposed designs for this integration for two major carbon-based and PTFE-based diffusion layers. Herein, further recommendations for future research works are summarized (Figure 10):

1. Testing GDEs with various CO₂ concentration feeds and impurities.

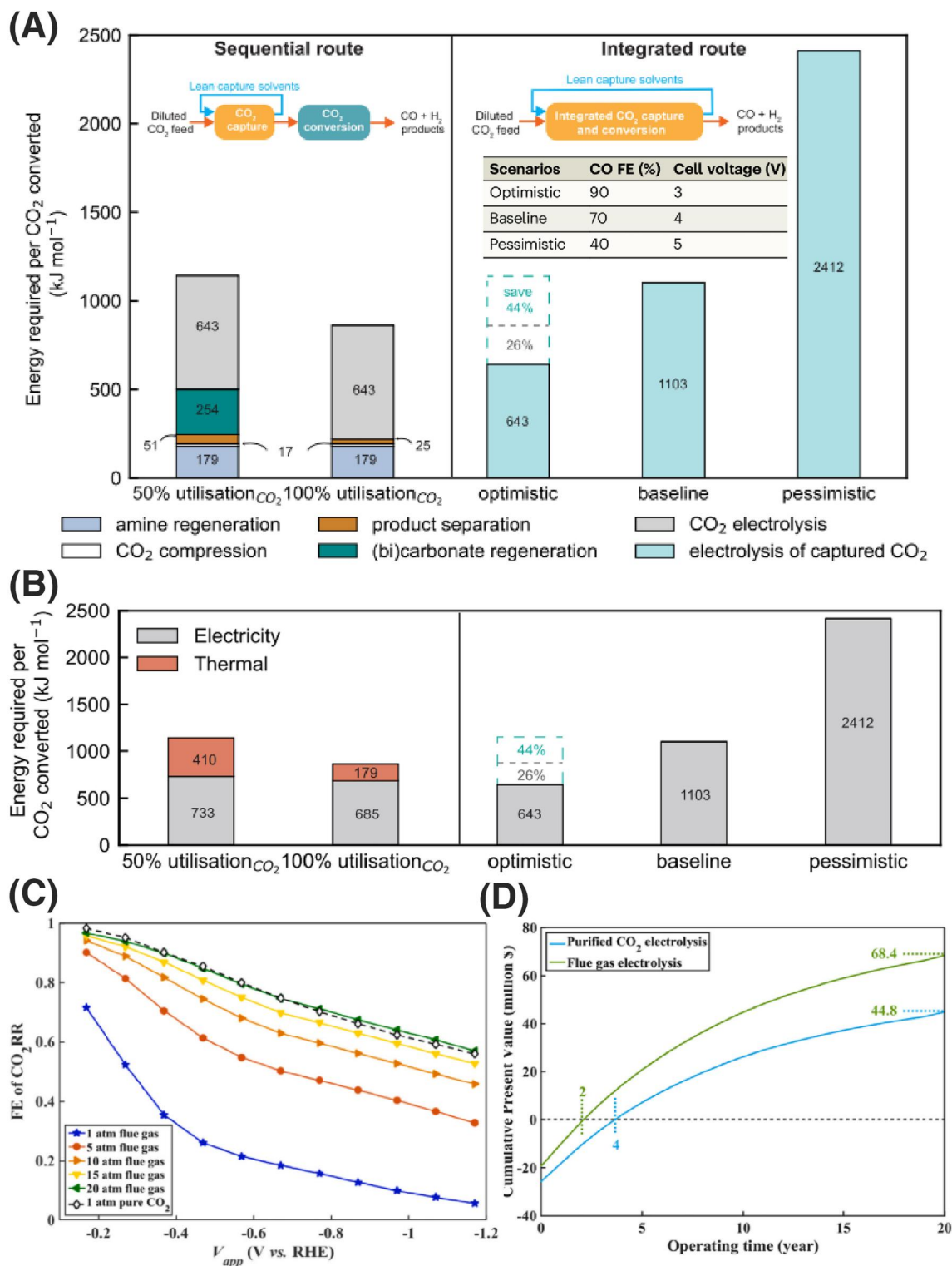


FIGURE 8 (A) Overall energy consumption. (B) Thermal energy and electricity consumption in different scenarios. Reproduced with permission.¹⁶ (C) The effect of pressurization on the FE of CO₂RR with flue gas as the feed. (D) Comparison of Cumulative present value between pure CO₂ electrolysis system and flue gas electrolysis system. Reproduced with permission.⁸⁰

To fully understand the performance of CO₂-selective GDEs, GDEs need to be tested with mixed gases with real compositions, where CO₂ concentration is usually around 40% biogas or less than 20% in flue gas, and impurities

such as Oxygen, NO_x, and SO_x exist.⁸¹ This can shed light on the effects of concentration and impurities in the long-term stability of GDEs for both CO₂ capture and reduction. Further efforts should be made to test the GDEs/

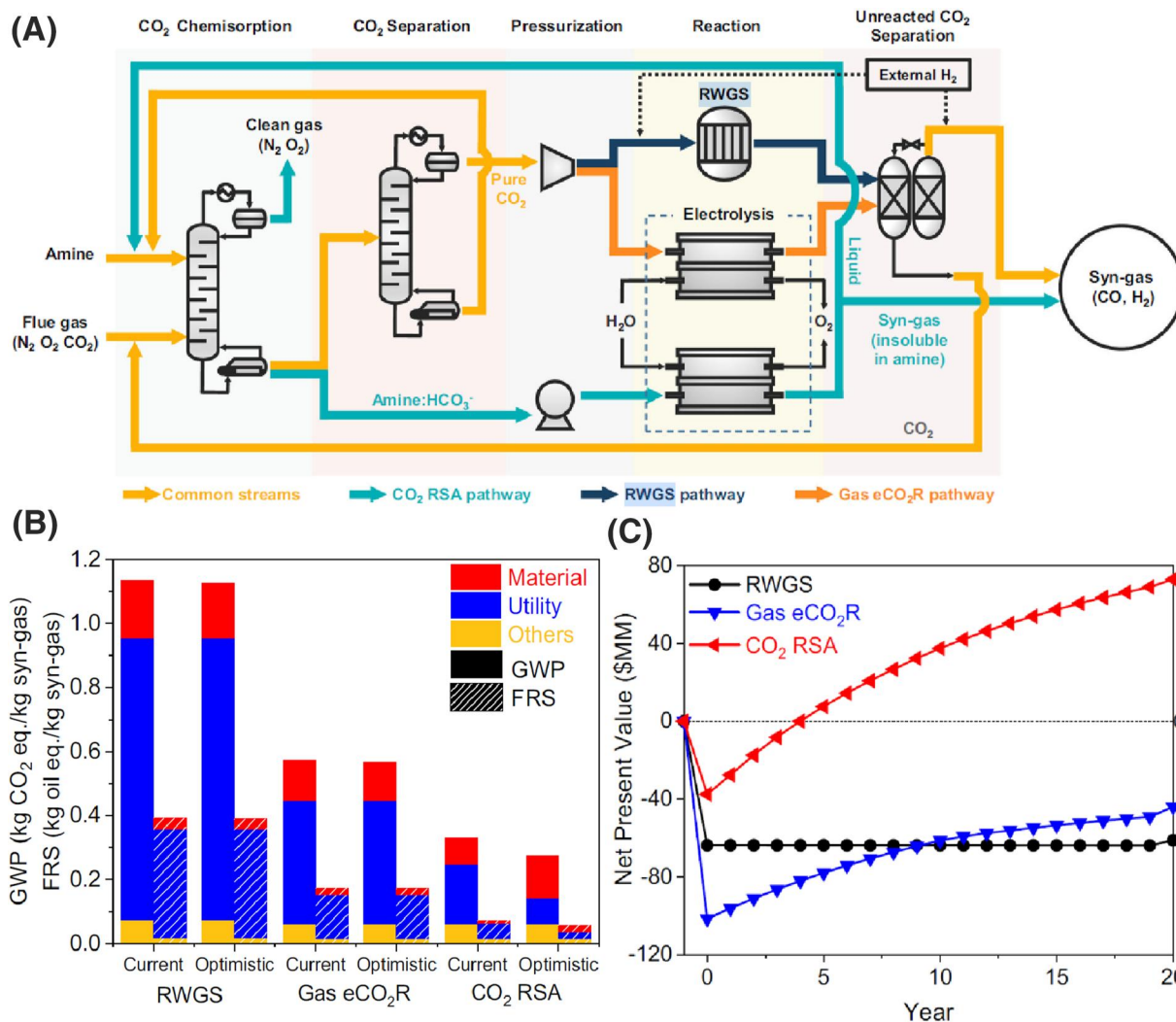


FIGURE 9 (A) Schematic diagram comparing the integrated CO₂ capture–reduction pathway and reaction swing absorption (RSA), with other pathways. RWGS stands for reverse water gas shift reaction. The RSA pathway exhibits a simple process configuration, retains the highest portion of electricity, and is capable of providing a viable CO₂ capture–utilization solution. (B) Life-cycle assessment results for three processes: RWGS, gas-phase CO₂RR and integrated CO₂ capture–reduction, GWP stands for global warming potential, and FRS stands for fossil resource scarcity. (C) Cash flow charts for an optimistic scenario with a selling price of \$0.8/kg syngas for three scenarios. Reproduced with permission.³

electrolyzers with the diluted CO₂ streams with the industrial compositions to analyze which impurities can affect the system the most and what steps need to be taken to improve the stability of the systems in these cases. There are membranes and adsorption systems that are designed to work with corrosive feeds (e.g., NO_x and SO_x)^{82,83}; therefore, having a CO₂-selective layer that hinders passing these impurities can protect the catalyst layer which is usually sensitive and poisoned in these cases.

2. Material selection criteria for the CO₂-selective layer.

The studies using adsorbents or membranes in the GDEs do not consider parameters such as selectivity and

permeability based on the amount of CO₂ required for the desired reduction. For example, for having higher current densities, a higher amount of CO₂ is needed and this needs to be matched with the separation properties of the selective layer and feed composition (e.g., permeability and selectivity parameters). In addition, the bonding/interaction between CO₂ molecules and the adsorbent layer should not be very strong to lead to saturation and inactivation. Considering the feed gas composition, and the desired feed concentration for the reaction, the right CO₂-selective materials for the membrane/adsorption layer can be developed. This is an important step for designing CO₂-selective GDEs. This area could learn massively from relatively well-established membrane gas separation and adsorption literature for the desired

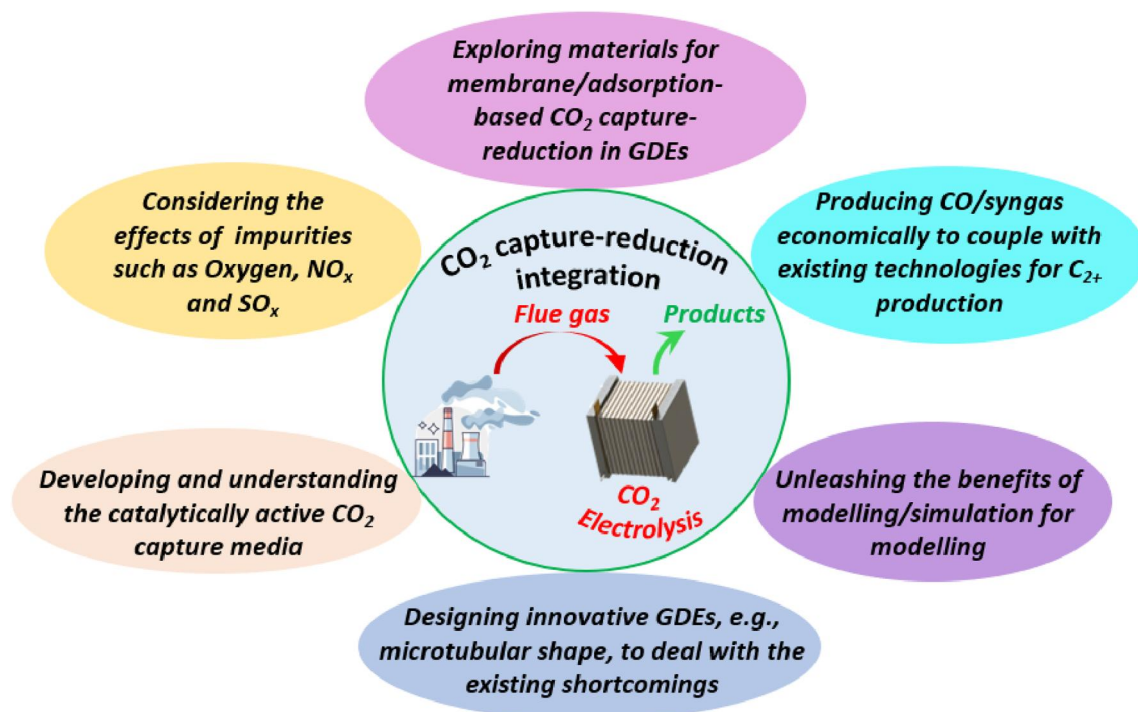


FIGURE 10 Future research directions in CO₂ capture-reduction systems.

separation and compatibility with the reduction reaction.^{84,85} Due to the immense literature available in this area, machine-learning models can be trained to provide guidance in the synthesis/selection of CO₂-selective layer to meet the criteria required for the reduction reaction.⁸⁶

3. Focus on benign and environmentally friendly production of syngas.

For carbon capture-utilization technology, if syngas as the product of an endothermic reaction can be produced economically, it is possible that this integrated technology can be industrialized because the downstream processes are exothermic and well-established. Analyses show that the production of syngas accounts for the highest proportion in terms of cost and energy consumption³; therefore, having an eco-friendly and cost-effective production of syngas from CO₂ can change the paradigm for chemical processes. So far, electroreduction of solution-based (carbonate/bicarbonate) to syngas needs high over potential and therefore more research and studies are required to further make carbonate/bicarbonate reduction economical.³¹ Paying more attention toward the membrane/adsorption-based capture step could potentially lead to more efficient syngas production compared with the solution-based route. In parallel with the efforts for syngas production, other products can be also considered. Most studies have focused on CO/syngas or formate formation, while production of C₂₊ products

is more economical with a larger market size.⁷ Whether C₂₊ products can be produced from solvent-based capture-reduction route or not, needs further investigations in terms of the catalytic pathway, but membrane- and adsorption-based routes are more promising in this regard since the captured CO₂ is not converted into (bi)carbonate and direct reduction is possible.

4. More focus on modeling/simulation and economic analyses

Along with advanced engineering, modelling of CO₂ capture-reduction both in terms of technological phenomena (e.g., reaction pathways, catalyst stability/performance) and economic analysis could greatly benefit from the integrated design. For a GDE-based integrated system, the interface of the selective layer and catalyst layer and then transport phenomena in the interface can affect the overall performance of the system. Modelling/simulation of the intermediates' transport and mass transfer resistance in between the layers can greatly smooth the path for the following research in this direction.

5. Designing novel electrodes with CO₂ capture-reduction

Electrode design is the heart of the reduction process where the reactions occur and interfaces are made.

Besides planar GDEs with the commercially available carbon-based gas-diffusion layers, other configurations such as microtubular (or hollow fiber) GDEs, with a much higher active surface area to volume ratio, can be also explored.^{87–93} Conventional planar GDEs are in a flow-by gas delivery regime, whereas developing flow-through electrodes makes it possible to maximize the interaction between the gas and capture media, therefore, increasing the amount of CO₂ captured for electrochemical reduction.^{38,43}

6. Better understanding of the CO₂ capture media

Most studies use bicarbonate as the capture medium for CO₂ capture-reduction systems,^{42,46} and recently some studies have attempted to use carbonate directly.^{17,50} There are some contradictions in the literature regarding the catalytic inactivity of carbonate and whether it can be reduced to products.⁴⁹ Therefore, exploring the evidence for the active components in (bi)carbonate and possibly developing more active CO₂ capture media could enhance our knowledge of the process.

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CONFLICT OF INTEREST STATEMENT

There is no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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