

Scalable Low-Temperature CO₂ Electrolysis: Current Status and Outlook

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ABSTRACT: The electrochemical CO₂ reduction (eCO₂R) in membrane electrode assemblies (MEAs) has brought e-chemical production one step closer to commercialization because of its advantages of minimized ohmic resistance and stackability. However, the current performance of reported eCO₂R in MEAs is still far below the threshold for economic feasibility where low overall cell voltage (<2 V) and extensive stability (>5 years) are required. Furthermore, while the production cost of e-chemicals heavily relies on the carbon capture and product separation processes, these areas have received much less attention compared to CO₂ electrolysis, itself. In this perspective, we examine the current status of eCO₂R technologies from both academic and industrial points of view. We highlight the gap between current capabilities and commercialization standards and offer future research directions for eCO₂R technologies with the hope of achieving industrially viable e-chemical production.

KEYWORDS: CO₂ electrolysis, Membrane electrode assembly, Carbon capture, Product separation, Commercialization



1. INTRODUCTION

The escalating global population and growing energy demand are seriously contributing to climate change with increased carbon dioxide (CO₂) emissions. Faced with the impending depletion of fossil fuels, the carbon capture and utilization (CCU) connected to renewable energy is receiving huge attention as an efficient method to mitigate this climate crisis where atmospheric CO₂ is directly captured and converted into value-added commodities, such as carbon monoxide, formate, methane, ethylene, and ethanol.^{1–12} The key technology enabling this field is electrochemical CO₂ reduction (eCO₂R), which has a history of decades of development. The recent application of the membrane electrode assembly (MEA)-type electrolyzer, which allows for a stack system with significantly reduced ohmic loss, has demonstrated the commercial potential of CO₂ electrolysis technology, thereby heightening interest in this field.^{13,14}

Nevertheless, there is a significant gap between the current targets in lab-scale CO₂ electrolysis and the commercialization standards. For example, given that eCO₂R can produce more than a dozen different products, most current reports prioritize the high selectivity of their target products to evaluate CO₂ electrolysis performance. However, the economic viability of CO₂ electrolysis is determined not only by product selectivity but also by applied cell voltage and stability of the overall system. Techno-economic analysis indicates that profitable

CO₂ electrolysis is achievable with a full-cell voltage below 2.5 V and a system stability of at least 5 years.¹⁵ Besides, while most lab-scale CO₂ electrolysis studies are conducted with relatively small areas (<10 cm²), scaling up CO₂ electrolysis in MEA systems must be validated through pilot-scale operations as this can lead to critical changes, such as mass transport or internal temperature.¹⁶

Furthermore, the commercialization of eCO₂R requires advancements not only in CO₂ electrolysis but also in the development and integration of all stages from carbon capturing, which captures CO₂ from the emission sources or atmosphere, to purification processes converting resulting e-chemicals from CO₂ electrolysis into final products.^{17,18} However, the absence of upstream and downstream processes in lab-scale CO₂ electrolysis studies often leads to idealized assumptions about these excluded parts. For example, in terms of reactant supply, lab-scale CO₂ electrolysis typically uses gaseous CO₂ with ultrahigh purity, while the industrial carbon capturing processes immobilize atmospheric CO₂ in liquid

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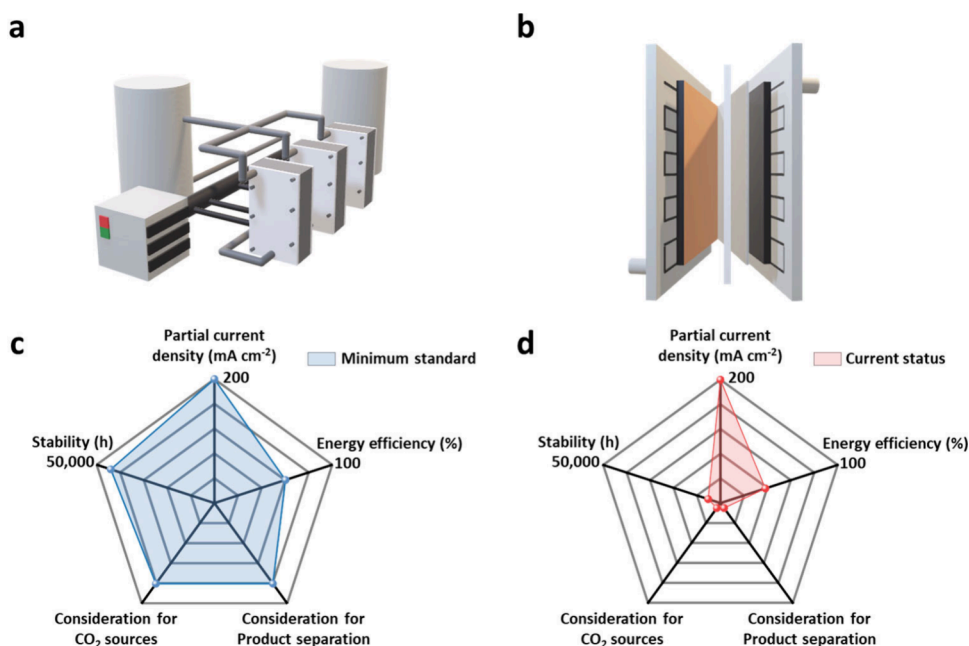


Figure 1. Illustrations of (a) an industrial-relevant eCO₂R system and (b) the current MEA system. (c) Minimum standard for commercialization and (d) current status of eCO₂R technology.

solutions using capture agents, resulting in additional costs for reactant purification unless the CO₂-containing solution is directly utilized.^{19,20} Moreover, although unreacted CO₂ is not significantly considered in determining CO₂ electrolysis performance in most lab-scale studies, this represents a substantial loss from the perspective of the CO₂ capturing process. In addition, despite the necessity of separating and concentrating the mixture of various eCO₂R products for productization, the samples obtained in lab-scale experiments are only used to evaluate the selectivity of eCO₂R system through gas and liquid chromatography.

In this perspective, we aim to present research directions for the overall eCO₂R field to bridge the gap between the current status and commercialization standards (Figure 1). As a first step, we explore the state-of-the-art progress in eCO₂R technology within MEA systems that are closest to commercialization, meeting at least one of the following criteria: a minimum partial current density of 1 A cm⁻², stability of more than 1,000 h, or pilot-scale operation. Then, we propose advancements for each component of the MEA system to achieve the commercialization target of high energy efficiency (>60%) and stability (>5 years). Finally, we address the previously overlooked upstream carbon capture and downstream product separation processes, suggesting necessary developments to ensure seamless integration with CO₂ electrolysis and the economic viability of the CCU field.

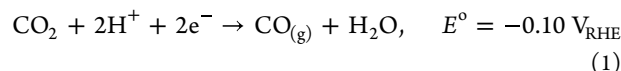
2. CURRENT STATUS OF LOW-TEMPERATURE CO₂ ELECTROLYSIS

Over the past decades, there has been significant advancement in eCO₂R technologies, including numerous studies reporting that the partial current density of their target product surpasses the commercialization benchmark (>200 mA cm⁻²) and even a few attempts to operate eCO₂R at a pilot scale. In this section, we provide a summary of the current state-of-the-art progress in eCO₂R within MEA systems, focusing intensively on the production of carbon monoxide (CO) and formic acid

(HCOOH). Since our focus in this perspective is commercialization, the investigations presented here are restricted to those that satisfy at least one of the following criteria: a minimum partial current density of 1 A cm⁻², stability of more than 1,000 h, or pilot-scale operation.

2.1. Massive and Stable E-Chemical Production

2.1.1. Carbon Monoxide (CO). Carbon monoxide (CO) is one of the simplest eCO₂R products that can be produced through a two-electron transfer (eq 1), and many eCO₂R studies targeting CO production have reported that their partial current densities (j_{CO}) already exceed commercialization standards.²¹ CO can serve as both a feedstock for various chemical processes and a component of syngas which allows for the production of long-chain carbon products by combining it with a well-established Fischer–Tropsch process.²²

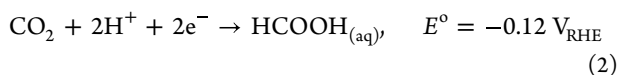


In eCO₂R, gold (Au) and silver (Ag) are well-known catalyst materials for CO production, with Ag-based electrocatalysts being more extensively utilized in state-of-the-art studies due to their cost-effectiveness, and superior stability compared to nonprecious metal catalysts.^{21,23–26} Edwards et al. achieved a j_{CO} over 1.0 A cm⁻² with 73% of FE_{CO} (@2.75 V), employing a strong alkaline electrolyte (5 M KOH) and high pressure of 50 bar.²⁷ However, while strong alkaline electrolytes can improve energy efficiency by reducing overall cell voltage, their corrosiveness may negatively affect the long-term stability of the catalyst and cell components. Under dilute alkaline conditions (0.1 M CsOH), Endrődi et al. achieved a j_{CO} of 1.0 A cm⁻² with a high FE_{CO} of 90% (@3.0 V) at ambient pressure (1 bar), and mildly elevated temperature (60 °C).²⁸ One distinctive feature of this MEA system is the utilization of the PiperION membrane, known for its high carbonate ion conductivity.²⁸ Additionally, the primary crossover species, carbonate, neutralizes the electrolyte irrespective of its initial

pH. making a carbonate-based electrolyte more appropriate than an alkaline electrolyte. Wen et al., by employing a neutral electrolyte (0.5 M KHCO₃), achieved a remarkable j_{CO} of 1.78 A cm⁻² with 92% FE_{CO} (@3.5 V), at ambient temperature and pressure (1 bar, 25 °C). Notably, an in situ CO_{2(g)}-liquid-catalyst interface was established by forced convection toward the porous electrode from an aqueous CO₂-saturated electrolyte, enhancing the transportation of CO₂, electron, proton, and product in this advanced MEA system.²⁹

In terms of stability, the best CO₂-to-CO conversions were achieved by companies. Dioxide Materials (USA) showcased their anion exchange membrane (Sustanion), performing stable electrolysis for 6 months (4,380 h) at a current density of 100 mA cm⁻², with a 98% FE_{CO} (@3.0 V).³⁰ Siemens (Germany) used a zirconium-oxide-based diaphragm membrane for consistent CO₂ electrolysis at a commercially relevant current density of 300 mA cm⁻² (@7.0–7.5 V) for 1,200 h, and demonstrated the production of butanol and hexanol with high carbon selectivity by connecting the obtained syngas from CO₂ electrolysis to a fermentation module.³¹

2.1.2. Formic Acid (HCOOH). With the growing interest in the hydrogen economy, there is an expectation of an expansion in the market size of formic acid as it can be utilized as a hydrogen carrier in addition to its conventional applications, such as a precursor to high-energy-density liquids (e.g., methanol) or fuel for power generation.^{32–35} Similar to CO, HCOOH is an eCO₂R product involving a two-electron transfer (eq 2), where Bi, Sn, In, and Pb are well-known catalyst materials for its selective production. One advantage of CO₂ to HCOOH conversion is that HCOOH is produced through a mechanistically distinct pathway from other eCO₂R products that inevitably involve CO intermediates. This enables the inhibition of CO and beyond-CO products, simplifying subsequent separation processes since formic acid exists as the sole product in the liquid electrolyte.³⁶



However, the presence of formic acid in its conjugate base form, HCOO⁻, in the alkaline or neutral environment (pK_a of HCOOH = 3.745) in which most CO₂ electrolyzers operate, necessitates the separation or acidification of the product-containing electrolyte.^{37–39} Moreover, since the crossover of anionic HCOO⁻ to the anode and its reoxidation to CO₂ in anion exchange membrane based MEA systems results in a substantial decrease in CO₂ utilization efficiency, strategies to prevent such product loss are also required.

In this regard, an acidic eCO₂R system can be an effective alternative. Fang et al. proposed acidic eCO₂R for HCOOH production, utilizing a cation exchange membrane (CEM) system with a catalyst derived from waste lead-acid batteries (cathode recycled Pb, r-Pb).⁴⁰ Given that the r-Pb catalyst, composed of lead and lead sulfate, can be readily prepared in large quantities (from kilograms to tons) from waste batteries, this system could significantly reduce the production cost of the catalyst, bringing the commercialization of e-HCOOH production closer. Furthermore, by employing a hydrogen oxidation reaction (HOR) as an alternative to oxygen evolution reaction (OER) for the anodic reaction, they were able to reduce the overall cell voltage, achieving a current density of 600 mA cm⁻² (@2.2 V) for an impressive duration of 5,200 h while maintaining FE_{HCOOH} over 90%.

2.1.3. C₂₊ Products. eCO₂R products with two or more carbons (C₂₊ products, e.g., C₂H₄, C₂H₅OH, CH₃COOH, C₃H₇OH, etc.) have high energy density, making them suitable for storing intermittent renewable electricity. In addition, the significant market size of C₂₊ products, such as C₂H₄ (120 MtC/year),⁴¹ offers further economic advantages. Nevertheless, producing C₂₊ products via eCO₂R is challenging because their mechanistic pathway involves a range of intermediates and products, making it difficult to achieve high selectivity for a specific product. This complexity necessitates multiple steps of proton-coupled electron transfer, which inevitably leads to high cathodic overpotential. Therefore, to the best of our knowledge, there have been no studies that produce C₂₊ products within MEA systems that satisfy the three criteria we have previously outlined.

To overcome such limitations, a promising strategy could be first to produce high-purity CO via eCO₂R and then produce C₂₊ products through subsequent electrochemical CO reduction (eCOR) in an eCO₂R-eCOR tandem approach. Jiao et al. successfully established an eCO₂R-eCOR tandem system consisting of a 500 cm² CO₂ electrolyzer and a 1000 cm² CO electrolyzer.⁴² In the CO₂ electrolyzer, they employed a carbon black modified Ag catalyst, achieving a j_{CO} of 320 mA cm⁻² with an 80% FE_{CO} at 3.0 V. This system was able to reduce the remaining unreacted CO₂ in the gas-phase product mixture below 10 vol %, with an additional NaOH trap used to prevent CO₂ from entering back to the CO electrolyzer. They then introduced fluorinated ethylene propylene (FEP) and carbon black reinforcement layer to the gas diffusion layer (GDL) of the CO electrolyzer and used a Cu catalyst mixed with carbon black and Nafion, achieving approximately 20% FE_{C₂H₄} and 50% FE_{CH₃COOH} at 2.3 V. Through the operation of the stack CO electrolyzer at a total current of 300 A for 125 h, they produced 98 L of acetate solution (1.2 M) with an impressive 98% purity through continuous anolyte recirculation.

2.2. Pilot-Scale MEA Electrolyzers

Despite the significant achievements in lab-scale eCO₂R studies, which commonly employ electrodes smaller than 10 cm², scaling up the dimensions of the electrode and constructing a stack system is much more complex. For example, the uniform supply of CO₂ or electrolyte to the electrode surface is not easily achieved in MEA systems with large electrode areas, emphasizing the importance of proper fluid flow channel design to alleviate mass transport issues.^{43,44} Since the CO₂ flow rate can impact the mass transfer, current density, and single-pass CO₂ conversion across the entire MEA system,⁴⁵ and considering that the performance of eCO₂R in a stack system is susceptible to gas flow or voltage distribution,⁴⁶ it is essential to optimize the flow rate and stack design according to the target products and the eCO₂R catalyst used. In addition, the pressure difference between the inlet and outlet should be precisely regulated in the stack system, as such differences may induce product or intermediate crossover.^{47,48} Besides, the internal temperature of the electrolyzer with large-area electrodes can rapidly increase at industrially relevant current densities (~200 mA cm²) due to the Joule heating effect.¹⁶ Since the elevated temperature not only alters product selectivity but also accelerates the degradation of cell components, this necessitates the development of robust catalysts, ionomers, membranes, and other cell components that can withstand increased temperatures, as well as in situ

analysis models or management techniques for continuous in-cell monitoring, which can replace post-mortem analysis.

From this point of view, pilot-scale operations with large electrode area electrolyzers and stack systems can offer valuable insights as an intermediate platform to bridge the gap between lab-scale eCO₂R studies and their industrial implementation. In a pressurized MEA system, Han et al. demonstrated consistent CO production with 93% FE_{CO} at 100 mA cm⁻² under 3 barg, regardless of electrode areas from 5 to 250 cm². Interestingly, their system employed a bipolar membrane (BPM), effectively mitigating the issue of anodic CO₂ crossover as an anionic carbonate in CO₂ electrolyzers with anion exchange membranes (AEMs), and was able to significantly improve the CO₂ single pass conversion up to 70%. Furthermore, Oh et al. successfully demonstrated a stack system that effectively connects three single MEA cells, achieving 50% FE_{C₂H₄} at 200 mA cm⁻² using a Cu-KOH catalyst, with nearly identical eCO₂R performance in terms of FE and unit cell voltage in both single cells and stack system.⁴⁶

When the pilot-scale operation collaborates with model systems, their synergistic effect can accelerate the scale-up of eCO₂R technology. Sinton et al. constructed a semiempirical model of an MEA electrolyzer, inputting operating parameters obtained from a lab-scale electrolyzer with an active area of 5 cm² to output mass and energy balances for a larger electrolyzer, then validated the model's predictions by comparing them to results obtained from a pilot-scale single MEA (800 cm²) and stack (10 × 800 cm²) system.⁴⁹ Surprisingly, their model system was able to accurately predict the outcomes in the pilot-scale operations, with a low absolute error (<16%) for most variables. This included the finding that the carbon loss through anodic CO₂ crossover, as well as the Nernstian and ohmic voltage losses in eCO₂R system, is directly related with the type of main charge carrier species (hydroxide or (bi)carbonate ion) that changes with current density. Despite the limitation of the range of current density utilized in their predictive model, where higher current density might result in unexpected issues such as cathode flooding or membrane dehydration,^{50,51} the utilization and advancement of such model systems could prove highly beneficial in scaling eCO₂R systems from lab-scale to pilot-scale and potentially to industrial implementation.

3. SCALABLE MEA-TYPE CO₂ ELECTROLYZER

To date, most eCO₂R studies have primarily focused on achieving high FE and partial current density for the target product. However, many techno-economic analyses point out that for eCO₂R to be economically viable, a minimum energy efficiency (EE) of 60% is needed (with renewable electricity price <0.04 \$/kWh), while providing steady electrolysis for an extended duration surpassing 5 years.^{15,52,53} Unfortunately, as shown in Figure 2, there has been no study that has met these standards, as achieving over 60% EE is challenging in typical MEA systems using OER as the anode reaction and the state-of-the-art stability (5,200 h) remains far below the 5-year target. We summarized the current cutting-edge achievements of eCO₂R in the MEA system for CO,^{27–31,54–64} HCOOH,^{2,40,59,65–70} and C₂H₄^{12,71–74} in Table 1. In this section, we briefly review the factors that can hinder EE and stability in each component of the MEA and propose future research directions for the commercialization of eCO₂R.

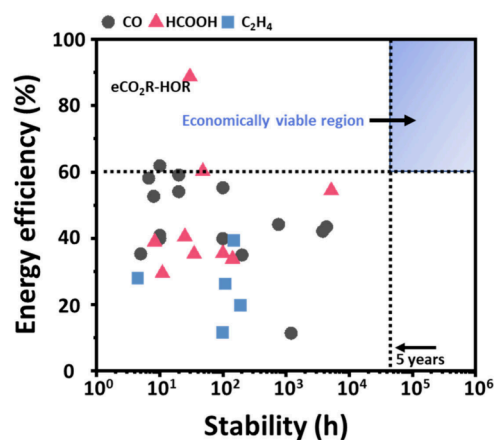


Figure 2. Current cutting-edge achievements of eCO₂R in the MEA system regarding stability and energy efficiency.

3.1. Energy Efficiency

The energy efficiency refers to the energy used to produce a specific product over the total energy consumed by the electrolysis system. As shown in eq 3, the higher EE can be achieved with enhanced selectivity for desired products at low cell voltage (E_{cell}), where EE_i and FE_i denote energy efficiency and Faradaic efficiency of the specific product, respectively.

$$EE_i = \frac{E^o}{E_{\text{cell}}} \times FE_i = \frac{E_{\text{anode}} - E_{\text{eCO}_2\text{R}}}{E_{\text{cell}}} \times FE_i \quad (3)$$

In eCO₂R, high selectivity has always been prioritized among various performance metrics due to the diversity of products. In particular, when the target eCO₂R products are CO and HCOOH, which follow relatively simple two-electron transfer pathways, high Faradaic efficiencies (>90%) are often reported.^{29,30,37,62,66,75,76} This is observed not only in lab-scale experiments but also in large-scale electrodes and pilot-scale operations, indicating significant potential for commercializing these products. Meanwhile, achieving selective production of C₂₊ products remains challenging, with the highest reported FE of C₂₊ products (e.g., ethylene) in MEA systems still around 65%.⁷³ Therefore, to accelerate the commercialization of C₂₊ products, high selectivity under industrially relevant conditions should be achieved by the collaborative efforts of fundamental research, and demonstrations on the MEA system.^{77–88}

However, E_{cell} has received much less attention compared to FE when evaluating eCO₂R performance, despite being equally crucial in determining EE. Techno-economic analysis suggests that the production cost of e-chemicals is directly proportional to the cell voltage, where E_{cell} must not surpass 2.5 V and ideally below 2 V for economical e-chemical production.^{52,53} However, to the best of our knowledge, there have been no cases that have satisfied this standard in MEA systems using OER as the anode reaction, particularly when the partial current density for the target product exceeds the commercially viable threshold of 200 mA cm⁻². This implies that achieving over 60% EE in commercializing CO₂ electrolysis requires significant efforts to lower the overall cell voltage, in addition to focusing on improving selectivity. Since the E_{cell} of the MEA system is influenced by its all components, we will discuss current issues and potential solutions for each cell component to reduce the overall E_{cell} .

Table 1. Current Cutting-Edge Achievements of eCO₂R in the MEA System for CO, HCOOH, and C₂H₄

product	catalyst	electrolyte	FE (%)	E_{cell} (V)	EE (%)	stability (h)	reference
CO	Ag	1 M KOH	98	3	43.45	4,380	30
CO	Ag	0.01 M KHCO ₃	95	3	42.12	3,800	54
CO	Ag	0.1 M K ₂ SO ₄ /1.5 M KHCO ₃	60	7	11.4	1,200	31
CO	Ag	0.01 M KHCO ₃	98	2.95	44.18	760	55
CO	Ag	0.5 M KHCO ₃	92	3.5	34.96	200	29
CO	Ag	0.1 M CsOH	90	3	39.9	100	28
CO	Au	DI	93	2.24	55.22	100	64
CO	Ni–N–C	0.1 M KHCO ₃	100	2.46	54.07	20	57
CO	Ag	1 M KOH	99	2.23	59.04	20	58
CO	CoPc-CN/CNT	1 M KOH	93	2	61.85	10	59
CO	Ag	7 M KOH	86	2.8	40.85	10	60
CO	Ag	0.01 M KHCO ₃	90	3	39.9	10	61
CO	CoPC	1 M KOH	95	2.4	52.65	8	62
CO	Zn ₂ P ₂ O ₇	1 M KOH	93.9	2.15	58.09	6.7	63
CO	Ag	5 M KOH	73	2.75	35.31	5	27
HCOOH	r-Pb	0.5 M K ₂ SO ₄	90	2.2	54.41	5,200	40
HCOOH	Sn	DI	94	3.7	33.79	142	65
HCOOH	Bi	0.1 M KOH	80	3	35.47	100	66
HCOOH	Sn	1 M KOH	95	2.1	60.17	48	70
HCOOH	SnO ₂	1 M KOH	61	2.3	35.27	35	59
HCOOH	nBuLi-Bi	PSE	90	1.35	88.67	30	2
HCOOH	Sn	2 M KOH	81	2.7	40.5	25	67
HCOOH	SnO ₂	0.4 M K ₂ SO ₄	80	3.61	29.47	11	68
HCOOH	Pb	0.5 M K ₂ SO ₄ , H ₂ SO ₄	82	2.8	38.95	8.3	69
C ₂ H ₄	Cu	0.1 M KHCO ₃	62	3.6	19.81	190	71
C ₂ H ₄	Cu	7 M KOH	70	2.4	39.38	150	72
C ₂ H ₄	Sputtering Cu	1 M KOH	65	2.85	26.23	110	73
C ₂ H ₄	Cu	0.1 M KHCO ₃	38	3.75	11.65	100	74
C ₂ H ₄	Cu(100)-rich film	0.1 M KHCO ₃	55.8	2.3	27.9	4.5	12

In an MEA system, the cathode typically comprises a catalyst layer, which includes a catalyst and ionomer, coated on a GDL.⁸⁹ Therefore, E_{cell} may increase due to ohmic losses arising from the resistance of overall cathodic components, in addition to the overpotential of eCO₂R ($\eta_{\text{eCO}_2\text{R}}$). When highly conductive GDLs made of metals or carbon ($>10^5 \text{ S m}^{-1}$) are used, the resistance from the GDL does not significantly affect the overall MEA resistance.⁹⁰ However, if hydrophobic materials like polytetrafluoroethylene (PTFE) are employed for stability enhancement, additional conductive materials (e.g., graphite layer) are necessary to reduce E_{cell} .⁷² In addition, within the catalyst layer, an excessively high or low ratio of catalyst to ionomer, which results in poor ion conductivity or poor electron transfer, respectively,⁹¹ or the use of inappropriate solvents leading to agglomeration of catalyst-ionomer composites, can cause additional ohmic losses and increase E_{cell} . Therefore, when determining the type of GDL or the composition of the catalyst ink, it is essential to consider not only the FE of eCO₂R but also its impact on E_{cell} .

Moreover, in typical CO₂ electrolysis coupled with OER as the anodic reaction, the thermodynamic potential required by both sides of the reactions ranges from 1.02 to 1.35 V depending on the target product,⁴¹ indicating that the overpotentials of eCO₂R ($\eta_{\text{eCO}_2\text{R}}$) and OER (η_{OER}) must be minimized to achieve a desirable E_{cell} of below 2.5 V. In this context, developing eCO₂R catalysts that can reduce $\eta_{\text{eCO}_2\text{R}}$ while maintaining high selectivity is essential. Promising strategies for designing highly active catalysts include single-atom catalysts to enhance the initial proton-coupled electron transfer,^{56,92} dopant introduction,^{6,93} oxide-derived Cu-based

catalysts to facilitate C–C coupling (particularly for C₂₊ products).^{4,94}

However, despite the extensive research on OER, there have been only a limited number of studies focused on the development of OER electrocatalysts in eCO₂R-relevant environments, especially in MEA systems.^{95–101} In particular, given that a near pH-neutral local anodic environment is created due to the crossover of a high flux carbonate, the development of highly active OER catalysts in such neutral environments is necessary to reduce η_{OER} .¹⁰² Meanwhile, as an alternative to addressing the challenge of OER in a neutral environment, one approach to achieve a lower E_{cell} is to utilize alternative organic compound oxidation reactions (e.g., glycerol oxidation) with lower thermodynamic potentials compared to OER.¹⁰³ Besides, when utilizing alternative oxidation at the anode to coproduce value-added chemicals, targeted by cathodic eCO₂R at the same time, it is possible to attain a maximum FE of up to 200%.¹⁰⁴ Nevertheless, organic compound oxidation in anode with multiple products inevitably requires product separation process, which can be more severe when the crossover of eCO₂R products occurred through the ion-exchange membrane. Moreover, the gradual decrease in the concentration of organic compounds during electrolysis may lead to reduced activity of the anodic reaction, although this can be mitigated by periodic reactant supplementation. Therefore, to effectively contribute to reducing E_{cell} , operational conditions that carefully balance the trade-off between the activity and reactant conversion are required when considering alternative anodic reactions to OER.

Furthermore, the low conductivity of the membrane used in CO₂ electrolysis (4.5–10 S m⁻¹) contributes a significant portion to the overall cell's ohmic loss.⁹⁰ Therefore, to improve the low conductivity of the membrane, it is necessary to optimize its chemical composition to increase ion exchange capacity and enhance its water uptake properties to facilitate ion transfer.^{105–110} Additionally, the inevitable interfacial losses between the cathode, membrane, and anode in MEAs produced via manual pressing contribute significantly to the overall E_{cell} in addition to ohmic losses, where strategies from analogous water electrolysis, such as hot pressing, catalyst-coated membranes, and direct membrane deposition, could be adopted to minimize these interfacial losses.

3.2. Stability

Since each component of the CO₂ electrolysis system is intimately interconnected, damage to a single component can lead to the failure of the entire system. Therefore, to achieve our target stability of over 5 years, balanced development of all MEA components is required. Generally, the stability of an MEA system encompasses both the mechanical and chemical stability of the components, as well as stable electrolysis performance. Thus, we have considered both types of stability.

To efficiently produce the desired target product, eCO₂R catalysts are designed with appropriate surface engineering, which induces structural characteristics such as defects,¹¹¹ grain boundaries,¹¹² facets,^{12,113} and confinement,^{1,114} as well as chemical properties like oxidation states.^{4,6} However, structures with high catalytic activity generally have high surface energy, resulting in lower thermodynamic stability compared to bulk or flat surfaces.¹¹⁵ Consequently, during the eCO₂R, active sites can dissolve and then agglomerate, forming an inactive catalyst surface with low electrochemical active surface area,¹¹⁶ which further decreases the electrolysis performance.¹¹⁷ Additionally, cathodic potential applied to the eCO₂R catalyst or residual O₂ in the inlet can change the chemical properties of catalyst during the reaction.^{118–121} Therefore, developing eCO₂R catalysts that can maintain their initial characteristics is necessary. Promising strategies include forming continuous interconnected networks based on metal nanoparticles,^{122,123} using surface capping ligands^{124,125} to prevent the loss of metal active sites and structural changes, or introducing modifier elements with significantly different electronegativity or orbital occupancy into the elements constituting the active site through alloying⁴ or doping⁶ to maintain chemical properties during the reaction, as this method allows electrons to migrate in a single direction continuously.

The GDL serves as the conduit for the reactant (CO₂) and gaseous products. Therefore, the failure of the GDL can lead to the mass transfer issue to the catalyst layer. Flooding is the most common phenomenon induced by physical or chemical failure of GDL, where the electrolyte infiltrates the GDL, rendering it nonfunctional as a conduit. Although using PTFE with high mechanical and chemical stability as a GDL can effectively prevent flooding, the trade-off between this improved stability and the low conductivity that may result in energy efficiency losses needs careful consideration. However, permanent damage to typical carbon-based GDLs can result from physical cracks or the formation of salts due to carbonation between CO₂ and OH⁻ in the electrolyte,⁴⁸ while the electrowetting effect from cathodic voltage can weaken the hydrophobicity of the GDL.¹²⁶ To prevent physical cracks to

the GDL, the pressure difference between the inlet and outlet of gas-phase channel in the MEA system should be minimized,^{47,48} as well as the pressure balance on both sides of the GDL by adjusting the flow rates of the anolyte and CO₂.¹²⁷ Besides, strategies such as applying alternating current voltage during the reaction or flushing DI water through the catalyst layer to remove carbonate salts before they cause permanent damage to the GDL¹²⁸ can be utilized to mitigate damage caused by carbonation.

Meanwhile, there have been only a few anode catalysts developed specifically for CO₂ electrolysis, as it has been assumed that long-developed alkaline water oxidation catalysts could be directly applied for the anodic reaction. However, due to the high flux of carbonate crossover along with the continuous proton release from OER, a stable anodic catalyst that can survive in the near pH-neutral local anodic environment of an MEA system needs to be developed. Besides, given that the most common nonprecious metal anodic catalysts, such as Ni-based catalysts, can easily dissolve in neutral electrolytes,¹²⁹ it is important to enhance their stability in commercially relevant CO₂ electrolysis environments with strategies such as alloying or developing transition metal chalcogenides and phosphides.^{130–132} Moreover, if organic compound oxidation is employed as the anodic reaction to lower the E_{cell} , this will lead to more severe damage on anode catalyst as the anodic environment becomes more complex. In this context, incorporating a reference electrode into the existing MEA system could serve as an in situ diagnostic tool for deconvolution of the electrochemical performance of anode catalysts in the commercially viable device. While a significant disparity exists between the typical aqueous three-electrode setup and the local anodic environment in commercial CO₂ electrolysis systems, this reference electrode-integrated MEA system is expected to bridge this gap, facilitating the rapid and accurate development of stable anodic catalysts suitable for CO₂ electrolysis under industrially relevant environment.^{102,133,134}

The ion-exchange membrane in an MEA system can be damaged by pressure, joule heating, and chemical corrosion.^{135,136} Specifically, the low mechanical and chemical stability of AEMs poses a significant challenge in the eCO₂R operations within the MEA system. Currently available commercial AEMs were originally developed for electro dialysis and generally exhibit chemical stability up to pH 10.¹³⁷ However, even when using a neutral anolyte, the local pH at the cathode-AEM interface can exceed pH 11 due to the generation of OH⁻ at the cathode during eCO₂R, leading to damage of the AEM.¹³⁸ Furthermore, AEMs designed for electro dialysis are vulnerable to alcohols such as methanol, ethanol, and propanol,¹³⁷ exacerbating stability issues when targeting alcohol production. However, although CEMs can provide improved mechanical and chemical stability compared to AEMs, solutions must be developed to address the acidic cathode environment due to the H⁺ transfer from the anode. Therefore, there is an urgent need to develop membranes specifically tailored for eCO₂R applications. In this regard, leveraging accelerated stress testing (AST) protocols, which have been used in membrane development for fuel cells,^{139,140} is a promising approach for eCO₂R as well. By subjecting eCO₂R membranes to independent, short-term, high-intensity exposures of chemical (ion and product/intermediate concentration), thermal (temperature), and mechanical (stress) factors that could potentially degrade the membrane, it is

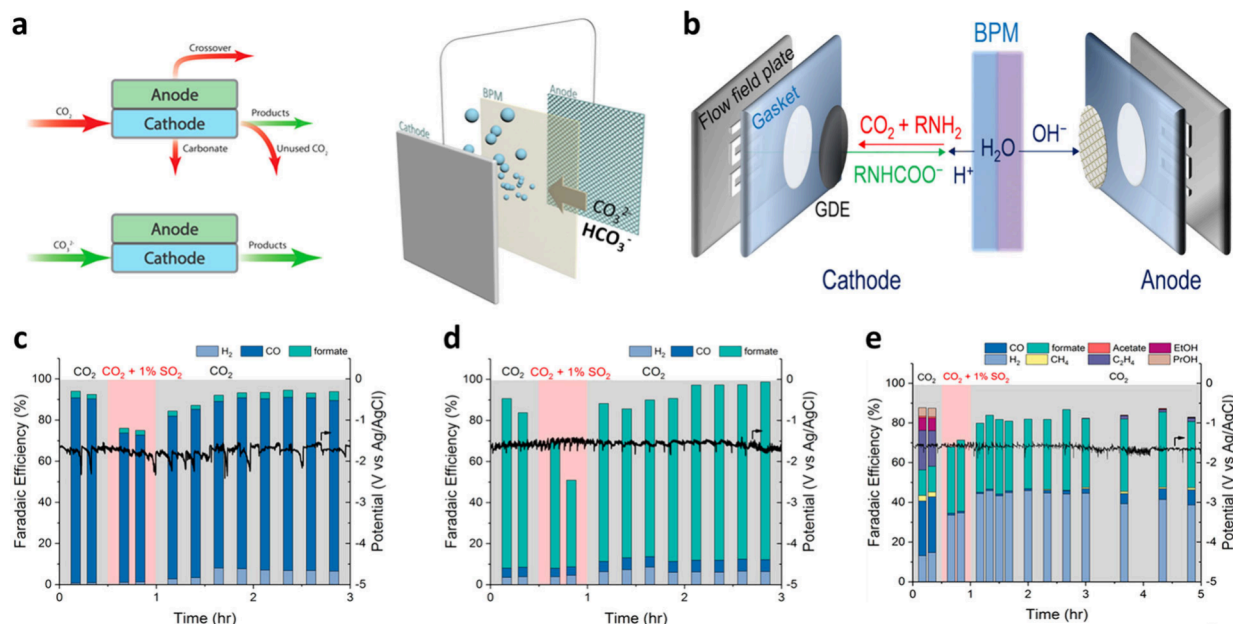


Figure 3. Considerations for scenarios that directly connect eCO₂R with the carbon capture process. (a) Carbon loss mechanisms in a CO₂ electrolysis cell with gas-fed CO₂ (left) and illustration of the BPM for the in situ generation of CO₂ through the local acidification of (bi)carbonate (right). Reproduced from ref 145. Copyright 2019 American Chemical Society. (b) Schematic illustration of the in situ CO₂ generation using BPM from the carbamate ion. Reproduced with permission from ref 152. Copyright 2022 Royal Society of Chemistry. (c) Impact of SO₂ in the flue gas on the electrolysis using the (c) Ag, (d) Sn, and (e) Cu catalysts. Reproduced from ref 162. Copyright 2019 American Chemical Society.

possible to identify parameters that need reinforcement for stability enhancement, and suggest the future research direction.

4. CO₂ SOURCES

Over the past few decades, most research on eCO₂R has used refined gaseous CO₂ as a reactant. Although this conventional scenario of separating the carbon capturing process from CO₂ electrolysis offers flexibility by allowing the captured CO₂ to be used in other fields besides CO₂ electrolysis, this approach inevitably requires energy-intensive capturing agent regeneration and CO₂ purification processes, which greatly reduce the economic viability of CCU. Hence, there is a growing need for a new scenario where CO₂ immobilized in the capture agent is directly electroreduced instead of being purified. Although several pioneering eCO₂R studies have been conducted in this regard, there still exists a discrepancy between the industrial carbon capturing process and the current status. In this section, we discuss the three possible sources of CO₂, including direct air capture (DAC), amine-based chemical capture, and flue gas conversion, along with the factors that need to be considered when integrating them with eCO₂R.

4.1. Direct Air Capture (DAC)

DAC is a method capable of directly capturing CO₂ from the atmosphere, regardless of a specific emission source. In contrast to other carbon capture methods that can only be applied in locations with high CO₂ concentrations (e.g., factory smokestacks) to achieve “carbon neutrality,” DAC can be implemented anywhere to capture CO₂ that has already been emitted into the atmosphere, thus moving toward “carbon negativity”. DAC is a long-developed technology and has a higher technology readiness level (TRL) compared to CO₂ electrolysis. More than 20 companies, including AirCapture (USA), Climeworks (Switzerland), Carbon Engineering (Canada), and Soletair Power (Finland), have successfully

completed large-scale pilot operations and are collectively capturing a total of 11,000 tons of CO₂ annually. Although specific conditions differ by company, a typical DAC process generally consists of two major loops. In the first loop (loop 1), CO₂ captured through an air container is fixed in an aqueous alkaline solution (e.g., KOH), where it exists in the form of carbonate (CO₃²⁻). For example, in the case of Carbon Engineering, a 2 M KOH initial aqueous alkaline solution is employed until the OH⁻ concentration drops to 0.68 M, resulting in a solution containing 2.00 M K⁺, 0.68 M OH⁻, and 0.66 M CO₃²⁻ after the first loop.²⁰ Although this solution still retains some capacity to capture additional CO₂, the lowered capturing efficiency due to the chemical equilibrium makes it applicable only for high CO₂ emission sources, such as flue gas.¹⁴¹ Therefore, to fully utilize the advantage of DAC being location-independent, it is preferable to directly use this solution as a reactant in the eCO₂R system, instead of further CO₂ capturing. Moreover, while a typical second loop is used to concentrate the obtained solution into high-purity CO₂ through multiple chemical steps requiring high temperatures and pressures,²⁰ direct utilization of immobilized CO₂ in eCO₂R allows the replacement of loop 2, where the substitution of high-temperature, high-pressure processes with ambient conditions makes this integration more promising.¹⁸

Nevertheless, to directly integrate DAC with eCO₂R, several additional considerations need to be addressed. Since direct electroreduction of CO₃²⁻ is not feasible, in situ generation of CO₂ by reacting CO₃²⁻ with H⁺ is necessary. Typically, a bipolar membrane (BPM) is employed for this purpose, where reverse bias is applied to induce water dissociation (WD) reactions to produce H⁺ and OH⁻ ions (Figure 3a). H⁺ ions are then transported toward the cathode to facilitate local acidification of CO₃²⁻ to convert it into gaseous CO₂, which then can be used as the reactant.¹⁴² However, BPM, which

consists of a CEM and an AEM with a bipolar junction between them, inevitably leads to higher ohmic and interfacial losses compared to monopolar membranes.^{143,144} Moreover, since two H⁺ ions are required to convert CO₃²⁻ into CO₂ via local acidification, the in situ CO₂ generation step becomes rate-limiting for the entire system.¹⁴⁵ Therefore, to increase the overall reaction rate, it is crucial to enhance the production rate of H⁺ ions through the development of BPMs with superior WD capabilities. As an alternative to BPM, employing CEM and HOR could potentially facilitate local acidification.¹⁴⁶ However, it is important to consider the changes in fluid dynamics at the anode when the reactant transitions to the gaseous phase. Furthermore, the additional process for producing H₂ as a reactant not only incurs additional costs for the entire process but also results in significant CO₂ emissions, which could cancel out the effort toward achieving carbon negativity.

Generally, many studies assume that the remaining catholyte after DAC-coupled eCO₂R is reused in the capture process, thereby completing the overall capture-and-conversion loop. However, the catholyte, which gradually becomes more acidic due to the local acidification process, has a low CO₂ capture efficiency and its direct utilization in the capture process may reduce the CO₂ capture fraction to below 1%.¹⁴⁷ The introduction of an additional electrodialysis unit can raise the pH of the catholyte to complete the loop, but this can increase both capital and operational costs.¹⁴⁸ Therefore, when establishing an environmentally and economically viable DAC coupled eCO₂R process, careful consideration, including a life cycle assessment of the entire process, will be essential.

4.2. Amine-Based Chemical Capture

Amine-based chemical capture is one of the wet absorption methods used in postcombustion CO₂ capture within various carbon capture and storage (CCS) technologies.¹⁴⁹ Unlike the dry absorption method, which stores CO₂ in solid form, wet absorption is more suitable for integration with eCO₂R electrolyzers as it stores CO₂ in liquid form. Amines can be categorized into primary, secondary, and tertiary amines. Primary and secondary amines directly react with CO₂ to store it as carbamate ions (RMHCOO⁻), whereas tertiary amines react with water to form OH⁻, thereby indirectly store CO₂ as bicarbonate through carbonation.¹⁵⁰ While the ability of primary and secondary amines to form carbamate ions provides relatively faster kinetics for CO₂ capture reactions and allows operation under lower CO₂ partial pressures, storing CO₂ as carbamate ions involves strong C–N bonds, which require high overpotentials for C–N cleavage when integrated with CO₂ electrolysis. Conversely, tertiary amines, which indirectly capture CO₂, are rarely used in CCS processes due to their low capture efficiency but offer the advantage of requiring less electrical energy in subsequent CO₂ electrolysis.¹⁵⁰

When utilizing reactants in the form of carbamate fixed by primary or secondary amines in CO₂ electrolysis, there are two main approaches. The first approach involves adding additives, such as alkali cations, to the CO₂-captured carbamate solution. These additives can destabilize the strong C–N bond in carbamates, allowing carbamate to directly participate in eCO₂R as a reactant, rather than merely serving as an additional anion to enhance the conductivity of the electrolyte.^{17,151} However, implementing a local acidification using a BPM, similar to the DAC-integrated eCO₂R system, could be

employed as an alternative approach.¹⁵² In this case, the H⁺ generated from the BPM can react with the carbamate ion (RMHCOO⁻) to produce CO₂ and RNH₂, allowing the cathode catalyst to utilize the in situ generated CO₂ as a reactant (Figure 3b). Since the overall process will be heavily dependent on the C–N bond cleavage step, efficient local acidification through the development of BPMs will be essential, as discussed in Section 4.1.

When utilizing tertiary amines, CO₂ is captured in the solution in the form of bicarbonate, also allowing for the in situ CO₂ generation strategy by using BPMs (Figure 3a).¹⁵³ Since bicarbonate does not have the strong C–N bond as carbamate, the energy required for in situ CO₂ generation is much lower compared to when utilizing primary or secondary amines. However, the slow CO₂ capture kinetics of tertiary amines result in a longer time needed to fix sufficient amounts of CO₂, making these capturing agents suitable only for sources with relatively high CO₂ concentrations,¹⁵⁰ such as flue gas, and necessitating further research to enhance their CO₂ capture efficiency.

Furthermore, it is worth noting the high affinity of amines for metals, which can lead to the formation of amine-metal complexes when amine-containing solution contacts with cathode catalysts.^{154,155} Since high concentrations of amines are used to maximize carbon capturing efficiency during the carbon capture process,¹⁵⁶ it is crucial to develop eCO₂R catalysts that can mitigate the binding between amines and metals when directly employing amine-containing solution.

4.3. Flue Gas

Directly utilizing flue gas as a CO₂ source presents a promising strategy to bypass the energy-intensive CO₂ purification process where industries such as coal-fired power plants, iron and steel manufacturing, and cement production, which emit substantial amounts of CO or CO₂, can serve as potential emission sources for this approach. Compared to DAC and amine-based chemical capture, which utilize liquid-captured carbon sources, the direct conversion of flue gas can use gaseous reactants, allowing the use of typical eCO₂R MEA electrolyzers, although the numerous impurities contained in the flue gas, aside from the required reactants (CO₂/CO), must be pretreated.

Among the impurities present in flue gas, the most electrochemically active species are SO₂ and NO_x (NO, N₂O, etc.). Since their thermodynamic reduction potentials are more positive than those of eCO₂R, a high concentration of these impurities will divert the input power to side product formation rather than eCO₂R, significantly reducing the current efficiency for e-chemical production. Therefore, desulfurization and denitrification processes must be performed prior to flue gas conversion. With the current technology, desulfurization and denitrification processes can generally remove about 90% of SO₂ and 80% of NO_x, leaving approximately 100 ppm of residual SO₂ and NO_x in the outlet.^{157,158} Fortunately, the reduced NO_x concentration achieved through denitrification does not significantly affect the eCO₂R reaction.^{159,160} However, due to the high affinity of sulfur for metals, even trace amounts of SO₂ can easily poison the catalyst active sites, reducing the overall activity, selectivity, and stability of the reaction (Figure 3c–e).¹⁶¹ In particular, SO₂ poisoning may cause permanent damage to Cu-based catalysts, which are considered the only element capable of producing C₂₊ products (Figure 3e).¹⁶² Therefore, when

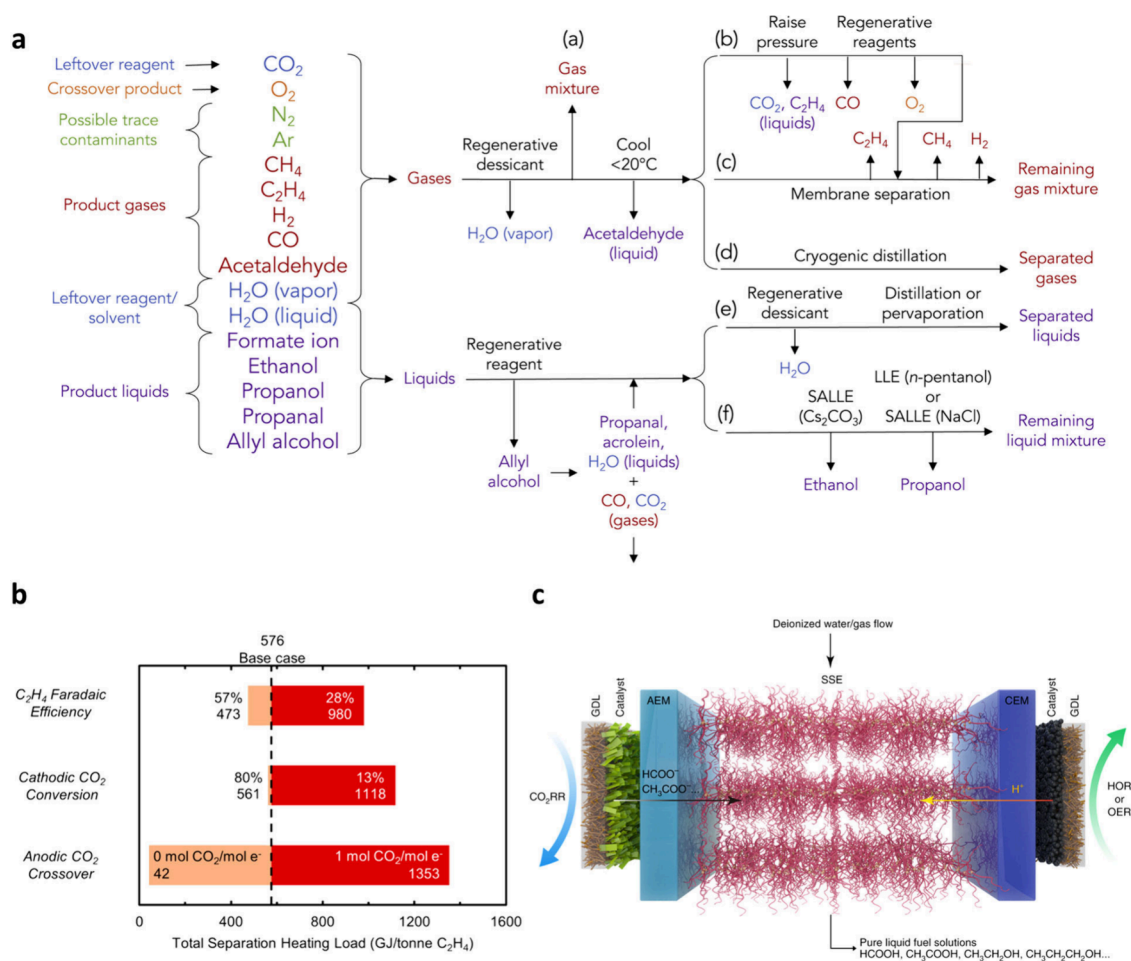


Figure 4. Considerations for the product separation processes. (a) Possible separation approach for a mixture of eCO₂R products, reagents, and contaminants. Reproduced with permission from ref 174. Copyright 2018 Elsevier. (b) The impact of unreacted CO₂ on the product separation cost. Reproduced from ref 173. Copyright 2021 American Chemical Society. (c) Illustration of porous solid electrolyte (PSE) used to concentrate liquid products. Reproduced with permission from ref 66. Copyright 2019 Springer Nature.

directly converting flue gas to C₂₊ products, strategies are necessary for Cu-based catalysts to survive in sulfur environments, such as introducing a passivation layer to block SO₂ access to the catalyst.

In addition to SO₂ and NO_x, O₂ can occupy as much as 14% (e.g., cement production industry) of the flue gas.^{163,164} Although O₂ does not directly cause catalyst degradation like SO₂, its positive reduction potential (oxygen reduction reaction, $E^\circ = 1.23 \text{ V}_{\text{RHE}}$) compared to the eCO₂R can consume most of the electricity input in the electrolyzer, even in trace amounts.¹⁶⁵ Given that the solubility of O₂ in water (1.22 mM) is much lower than that of CO₂ (33.4 mM), increasing the hydrophilicity near the catalyst to prevent ORR could be considered.¹⁶⁶ However, this approach might lead to GDL flooding during long-term operation. Therefore, despite the additional refining costs, a practical approach could involve implementing a deoxygenation process before introducing flue gas into the electrolyzer. Alternatively, restricting the application to industries like iron and steel, where flue gas contains minimal O₂ (<1%), could also be viable.

Since flue gas features low reactant concentrations, developing eCO₂R electrocatalysts with high activity and selectivity under low CO₂ partial pressures is crucial for direct conversion of flue gas. For instance, inert nitrogen (N₂), which is predominant in the composition of flue gas, ranges from

about 5% to 47% in iron and steel industries,¹⁶³ and even higher in other emission sources up to 80%.^{167,168} In addition, the high concentration of CO in flue gas could be beneficial as it can contribute to the reaction as a key intermediate when targeting C₂₊ products; however, when targeting CO or formate, it serves only as a diluting factor for the reactant CO₂, similar to N₂. Recognizing this challenge, there have been a few studies focused on addressing eCO₂R under low CO₂ partial pressure conditions.^{169–171} However, these studies have primarily focused on producing C₁ products, and there have been no successful cases yet of producing C₂₊ products from CO₂ concentrations diluted to less than 10%.

Consequently, we propose three criteria to consider when directly adopting flue gas as a reactant. First, prioritize emission sources with low O₂ concentrations to minimize power loss. Second, target C₁ products for emission sources with high N₂ concentrations. Third, in the case of flue gas with a high concentration of CO, such as blast furnace gas or basic oxygen furnace gas in the iron and steel industry,^{163,172} aim to produce C₂₊ products using Cu-based catalysts while also considering the additional impact of SO₂ in this scenario.

5. PRODUCT SEPARATION PROCESS

The ultimate goal of CO₂ electrolysis is to economically produce high-purity e-chemicals, making the separation and

concentration processes of the eCO₂R product crucial, although these have been overlooked in most eCO₂R studies. Since over a dozen products can be produced through eCO₂R,⁴¹ separating the target product is not straightforward, and numerous energy analyses predict that the cost of separation and purification may exceed the cost of electrolysis if the concentration of products in the outlet is low.^{52,173} In this regard, the technology to concentrate individual products from the outlet is necessary and detailed strategies will vary depending on the characteristics of each product (Figure 4a). In this section, we aim to discuss the separation strategies of e-chemicals categorized into gas and liquid phases, and provide our viewpoint on considerations for future research.

5.1. Separation of Gas Product

The mixture of gas-phase products commonly contains unreacted CO₂ and water vapor. Therefore, the mixture gas from the outlet should first pass through CO₂ adsorbents to recover unreacted CO₂ and desiccants to remove water vapor.^{173,174} However, since the regeneration process of CO₂ constitutes a significant portion of the entire separation process, it is necessary to develop strategies to maximize single-pass CO₂ conversion (Figure 4b).^{173,175} To increase single-pass CO₂ conversion, it is necessary to minimize both the unreacted CO₂ that forms a mixture with gas-phase products and the loss of CO₂ through carbonation. In typical MEA systems that utilize pure CO₂ as the reactant, reducing the CO₂ flow rate is a common strategy to decrease unreacted CO₂.^{74,176,177} However, excessively low CO₂ flow rates may promote competing reactions such as HER, necessitating careful optimization.⁷⁴ Furthermore, the loss of CO₂ through carbonation can be mitigated by conducting electrolysis in an acidic environment. In an ideal scenario where H₃O⁺ is used as the proton source, carbonate formation is inhibited, and the (bi)carbonate formed at high current densities is regenerated into CO₂ in the bulk electrolyte before passing through the membrane. Nonetheless, the lower FE and higher E_{cell} compared to neutral or alkaline eCO₂R require improvement. Promising strategies include developing catalysts with enhanced CO₂ adsorption^{178,179} or utilization of neutral buffer layers to mitigate acidic conditions near the catalyst surface.^{180,181} However, when directly converting immobilized CO₂ in solution through DAC and amine-based chemical capture, unreacted CO₂ remains in the captured solution,¹⁵³ which is advantageous for gas-phase product separation. Conversely, in the direct conversion of flue gas containing high levels of impurities, additional process units might be required.

After removing unreacted CO₂ and water vapor, the remaining gaseous eCO₂R products, such as CO, CH₄, and C₂H₄, along with H₂ produced by HER, must be separated and concentrated, considering their specific properties. Furthermore, the gas-phase product mixture originating from the anode side contains not only high concentrations of O₂ but also CO₂ that has been reoxidized after crossover through the membrane. Additionally, gas-phase product crossover may occur due to leakage within the MEA system.¹⁷⁴ Therefore, when designing the separation process, it is crucial to adequately consider not only eCO₂R but also the products generated from the anode reaction. Typical gas-phase separation steps include cryogenic distillation, pressure/temperature-swing adsorption (PSA), and membrane-based separation, where the appropriate method depends on the

target product to be separated.¹⁷⁴ For example, cryogenic distillation could be promising for separating C₂H₄, as C₂H₄ (169 K) has a higher boiling point compared to other gas-phase products such as CO (81.5 K) and H₂ (20.4 K) at 1.013 bar.¹⁷³

5.2. Separation of Liquid Product

The typical MEA system for CO₂ electrolysis operates with the circulation of liquid electrolytes (anolytes), and the liquid-phase products generated by eCO₂R are present within the electrolyte in a diluted state. Regardless of the type of membrane used in an MEA system, all liquid-phase products can crossover through electro-osmotic drag or diffusion.^{182,183} This crossover is particularly notable when using an AEM under neutral and alkaline conditions, as products existing in anionic forms such as formate and acetate can migrate more extensively due to the electric field effect.¹⁸⁴ For example, in an MEA system using an AEM, approximately 75% of the produced ethanol has crossover to the anolyte when electrolysis is conducted at a current density of 100 mA cm⁻², resulting in an anolyte ethanol concentration of roughly 0.05 wt %, where the liquid-phase products in the anolyte can undergo reoxidation back to CO₂, potentially causing further losses of products.¹⁸²

Furthermore, although the adjustment of the volume of the electrolyte might increase the liquid product concentration to some extent, there remains a significant disparity between the concentrations achieved at the lab scale and those required to meet industrial purity standards. For example, in commercialized bioethanol production, ethanol with a concentration of 10 wt % is typically found at the outlet,¹⁸⁵ suggesting that a minimum target concentration of about 10 wt % ethanol should also be set for e-ethanol production. Moreover, the cost of concentrating dilute products in the electrolyte through subsequent separation processes far surpasses the price of e-chemicals themselves, making this scenario economically challenging.^{174,186} Therefore, a strategy is needed to sufficiently concentrate the liquid products from eCO₂R to achieve high purity before entering the separation process.

In order to concentrate the liquid product, utilizing a porous solid electrolyte (PSE) proposed by Wang et al. offers a promising strategy (Figure 4c).^{2,66} In this novel MEA system, the PSE is located between the AEM on the cathode side and the CEM on the anode side, capturing the liquid-phase products that pass through the AEM. Specifically, anionic products such as formate and acetate can combine with H⁺ ions generated from the anode to reform their original molecular forms, such as formic acid and acetic acid, within the PSE layer. These products are then concentrated by the continuous flow of inert gas (N₂) passing through it. Using this novel system, state-of-the-art eCO₂R liquid products with remarkably high concentrations have been achieved, with 49 wt % for formic acid and 13 wt % for alcohols, demonstrating the effectiveness of this MEA design.^{2,66,65,182} However, despite the promise of PSE for liquid product separation, the MEA system consisting of AEM/PSE/CEM inevitably suffers from high interfacial losses, resulting in relatively low energy efficiency compared to typical MEA systems. Therefore, further investigation is needed to develop strategies to minimize the E_{cell} of this novel MEA system.

Meanwhile, integrating the eCO₂R system with the carbon capture process requires several considerations depending on the capture method. For example, when directly converting

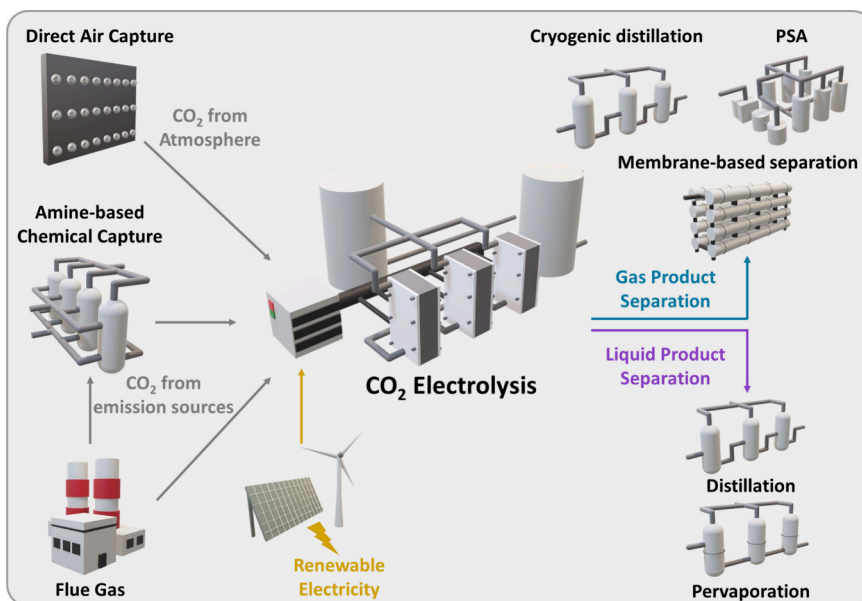


Figure 5. Schematic illustration for the overall process of the eCO₂R technology, including CO₂ source (left), CO₂ electrolysis (middle), and product separation (right).

CO₂ immobilized in solutions via DAC or amine-based chemicals, it is important to separate unreacted CO₂, which exists in the form of carbamate or (bi)carbonate in the liquid electrolyte, as well as the high concentration of remaining capturing agents such as amines. Furthermore, if the eCO₂R system directly utilizes flue gas with high impurities, effective methods may be required to remove highly water-soluble impurities such as SO₂.

The concentrated liquid product exiting the outlet of the eCO₂R system can be further refined for productization through additional separation processes including distillation and pervaporation.¹⁷⁴ As with gas phase products, a rational design of the separation process is essential to reduce the overall process cost, while also considering the materials used in the process unit, especially when dealing with corrosive eCO₂R products such as formic acid. For instance, distillation columns used for separating liquid products typically operate at high temperatures, where formic acid is known to be corrosive to stainless steel in particular.¹⁸⁷ This corrosion of process units not only disrupts the stable operation of the entire process but also release metal cations to induce the decomposition of formic acid, decreasing the overall yield of the process.¹⁸⁸ Hence, careful consideration of the characteristics of the possible products at the outlet is crucial when selecting materials for separation units. Furthermore, if the process is designed to simultaneously separate the gas phase and liquid phase outlet for minimal separation steps, the high partial pressure of the gas phase products can cause vacuum destruction of the distillation column, leading to corrosion of the process unit by the corrosive liquid phase products. Therefore, when designing a separation process, all possible failure factors should be considered, while pilot-scale operations can provide valuable information for identifying any overlooked issues during the process design.

6. SUMMARY

In this perspective, we discussed future research directions aimed at bridging the gap between the standards necessary for the commercialization of eCO₂R technology and its current

status from three perspectives: CO₂ electrolysis, CO₂ sources, and product separation (Figure 5). As a first step, we explored the most advanced state-of-the-art progress in eCO₂R technology within the MEA system reported to date. This exploration highlights the exciting progress made in leveraging successes achieved in lab-scale operations toward recent pilot-scale operations, aiming to pave the way for commercial-scale applications. At the same time, it reveals that even the state-of-the-art lab-scale achievements significantly diverges from the standards required for commercialization. Awareness of this gap emphasizes the need for a balanced development in eCO₂R, which has focused heavily on achieving high selectivity and production rates. To bridge this gap, we have evaluated the fundamental hurdles in achieving high energy efficiency and stability in CO₂ electrolysis. Faced with these issues, we have identified potential impediments in each component of the MEA system and proposed strategies to overcome them. Then, to enhance overall economic viability, we reviewed scenarios for directly utilizing CO₂ immobilized in capture agents without purification or converting CO₂ from emission sources, with a special emphasis on examining the distinct properties of captured CO₂ via DAC and amine-based chemical capture and the potential threats posed by impurities in flue gas. Finally, the critical role of product separation processes in achieving the ultimate goal of productizing high-purity e-chemicals from eCO₂R products is emphasized. We concluded that concentration and separation methods must be tailored to the specific characteristics of each eCO₂R product, and potential equipment damage should be thoroughly considered during the process design. In addition, techno-economic analysis has played a crucial role in assessing the current status of the technology and suggesting development directions from a commercial standpoint in all parts of eCO₂R technology covered in this perspective. However, many existing techno-economic analyses focus only on specific parts of eCO₂R technology, assuming no economic losses in other areas. We believe that a comprehensive techno-economic analysis considering all parts of eCO₂R technology is necessary to serve as an accurate evaluation metric for achieving

commercialization. We hope that this perspective will stimulate future research efforts addressing the previously overlooked aspects of eCO₂R technology and believe that combining these efforts with the extensive knowledge accumulated over the past decades will accelerate the commercialization of eCO₂R.

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[§]H.L. and S.K. contributed equally to this work. Y.K. supervised the project. CRediT: **Hojeong Lee** conceptualization, investigation, methodology, validation, visualization, writing - original draft; **Seontaek Kwon** conceptualization, methodology, visualization, writing - original draft; **Namgyoo Park** writing - review & editing; **Sun Gwan Cha** writing - review & editing; **Eunyoung Lee** writing - review & editing; **Tae-Hoon Kong** writing - review & editing; **Jihoo Cha** writing - review & editing; **Youngkook Kwon** conceptualization, funding acquisition, project administration, supervision, writing - review & editing.

Notes

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