Progress in Electrochemical CO_2 Reduction Reaction (Eco_2RR) for Multi-Carbon Product Synthesis

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Abstract. Motivated by the worldwide goal of carbon neutrality, electrochemical CO_2 reduction reaction (eCO_2RR) is an environmentally friendly technology that converts CO_2 to useful chemical products using renewalelectricity, is of significant interest both in academia and industry. Multi-carbon products (C_2^+) are expected to have clearer resource-based benefits compared with traditional CCS due to the higher energy content and value. This review outlines the recent advances of eCO_2 RR towards C_2 $^+$ products. The basic reaction mechanism is introduced first in this article, and then describes catalyst research in terms of categories (including a discussion on the dominance of copperbased catalysts), the promise of complementarity with non-copper options, and the design of tandem approaches. Besides the energy conversion efficiency, current problems of this area concerning selectivity and stability are also discussed. In the end, perspectives about industrialization pathways and future research trends are given. These developments improved greatly the performance for C_2 $^+$ products as well as the applicability of eCO_2RR systems, laying groundwork for use of dilute CO_2. The purpose of this work is to support the shift towards sustainable energy as well as contributing toward achieving global net-zero emissions, developing the green chemical industry.

1 Introduction

Achieving carbon peaking and carbon neutrality has become a global consensus. According to the 2025 report of the International Energy Agency (IEA), the global annual carbon dioxide emissions have exceeded 40 billion tons. Currently, traditional methods for the utilization and conversion of carbon dioxide mainly focus on the synthesis of low-value-added products such as carbonates, bicarbonates, and urea, or merely simple sequestration, which only offers limited benefits to economic and environmental [1]. Compared to the traditional method, the eCO_2RR can utilize renewable electricity to convert CO_2 into high-value carbon-based products, which reduces energy consumption while enhancing conversion efficiency at the same time. With the assitance of this advanced methods, the unification of environmental benefits and economic benefits will become achievable.

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In recent years, more and further breakthroughs have been achieved in the field of eCO_2RR.Depending on the multiple catalyst, the products of this technology can be primarily categorized into single-carbon (C_1) and multi-carbon (C_2^+) species. And between them, the C_2^+ products, which were derived from copper-based catalysts, mixed-metal metal-organic frameworks (MOFs), and other materials exhibit higher energy density and market value [2]. These products can be applied in fields such as fuel cells, plastic synthesis, and pharmaceutical manufacturing, thereby facilitating the transition to sustainable energy. It is projected that the associated market size will reach tens of trillions of US dollars by 2030.

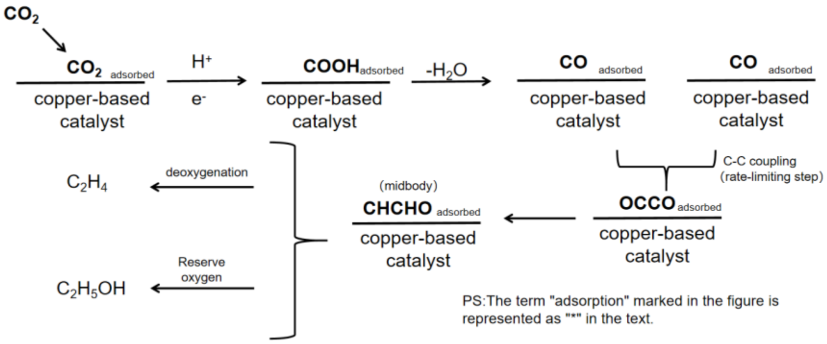
Building on an elaboration of the reaction mechanism of the eCO_2 RR, this review focuses on the research advances in eCO_2 RR catalysts, providing a systematic overview of the characteristics and research outcomes of three catalytic systems: copper-based catalysts, non-copper-based catalysts, and tandem catalytic strategies. Furthermore, it summarizes the challenges encountered in the development of eCO_2 RR and corresponding solution pathways, and concludes with a perspective on the future development of this field.

2 Mechanism of electrochemical carbon dioxide reduction reaction

As shown in Fig. 1, the eCO_2RR to synthesize C_2^+ products is a multielectron and proton transfer process that mainly occurs at the surface of Cu-based catalysts. First, CO_2 molecules are first adsorbed and activated and then PCET forms the COOH* intermediate, which is further reduced to the key CO* intermediate. In this step usually two electrons are transferred and depending on the adsorption strength of the CO*, different pathways for further reactions can be selected [3].

C-C coupling is a RLS, two CO* molecules dimerize on Cu surface forming the OCCO*, with a barrier of about 0.6–0.8eV. Then OCCO* branches into sequential hydrogenation/deoxygenation pathways: the ethylene branch is OCCO* → *OCCHO → CCH → C_2H_4; the ethyl branch with intermediate species like $OCHCH_3$ or similar to form finally C_2H_5OH [4]. Operando Raman spectroscopy proved that *CO coverage is responsible for C-C coupling; meanwhile, the local environment (such as cations) could reduce the activation energy and improve the coupling ratio.

In a low CO_2-concentration environment, controlling of the rate determining step (i.e., suppression of HER, HER) dramatically increases C_2^+ selectivity and common intermediates (e.g., *CHCHO) tune the product distribution [5]. These pathways are controlled by potential, pH, and surface crystal facets, and HER competition frequently disrupts the C-C coupling process. This mechanism can be used to provide an explanation of catalyst optimization.



PS:The term "adsorption" marked in the figure is represented as "*" in the text.

Fig. 1. Mechanism of eCO_2RR.

3 Advances in catalytic materials research

3.1 Copper-based catalyst

Copper-based catalysts have their own special place among other catalysts for eCO_2RR. Starting from the late 1980s with the report that metallic Cu could be used as an efficient catalyst for CO_2 conversion into multi-carbon products, it became the only metal catalyst able to generate stably C_2^+ products in this reaction. The fundamental reason behind is that due to itsd-band electron configuration of Cu provides an intermediate strength adsorption of the *CO intermediate - necessary for C-C coupling – while all others provide C_1 as product.

In spite of these excellent lab performances, copper based catalysts are still in a very early stage for their industrialisation. Until now, large-scale commercial use is yet to be achieved worldwide due mainly to catalyst instability problems, in particular, the tendency for Cu towards surface reconstruction and degradation. Other bottle necks are a high overpotential (which undermines an energy efficient process), and the excessive complexity of the product separation step.

Nevertheless, there have been many advances despite these problems, as researchers focused more attention on the structure design and surface modification of copper-based catalysts for promoting C_2^+ formation and stability. Hefei Li prepared GB-rich Cu through an electrosynthesis method. The key idea behind this approach is that they deliberately modulated the grain boundary concentration so as to provide a greater number of CO adsorption sites, thus enabling the C–C coupling. In the case of CO electrolysis (no loss of CO_2) it reaches more than 70% FE for C_2^+, up to 400 mA/cm^2 partial current density and exceeds 500 h of stability [6]. The main advantages are that there is no carbonate precipitate formation in conventional alkaline medium (therefore increasing mass transfer efficiency); showing the universality of GBs as active sites; and offering insight into designing industrialscale FBs. Nevertheless, one important drawback is the fact that GBs stability might be subject to possible fluctuations and consequent active site passivation under long term operating conditions.

Different from the above work, Long Cheng used a silicon-doping approach. Asymmetrical Cu sites are generated by doping Si atoms into CuO. This strategy's key is to stabilize the Cu^+/Cu^0 interface and regulate the local electron density – both effects reduce the HER activity but optimize the pathway of the ethylene/ethanol synthesis reactions. In an acidic environment, this catalyst attains a C_2^+ FE of 84.7% while offering tunable ethylene selectivity at a current density of ~300 mA/cm^2 [7]. Major benefits from the system are: good affinity to acid media (direct treatment of industrial flue gas at a low level of CO_2 content); enhanced atom utilization and decreased Cu loading through doping; and the experiment verification of the fact that heteroatom doping is favorable for intermediates' stabilization. Yet crucial issues remain: inhomogeneous doping that can lead to lotto-lot variability; and potential Si leaching at high current densities, which limits the catalyst's lifetime.

Such advances significantly improve the applicability of Cu catalysts and also demonstrate that interface tuning plays an essential role in controlling catalytic properties. However, the economic viability and industrial scale-up ability of such approaches still need to be enhanced. Going forward, we anticipate that combining computational screening with in-situ characterization will continue to lead to new advances, thus enabling scale-up from bench-top to industry-ready outcomes.

3.2 Non-copper-based catalysts

Although most successful catalysts for eCO_2RR toward C_2^+ products are based on Cu, non-Cu-based catalysts also play important roles in this area. With the utilization of low-cost precursors and new types of active sites, these catalysts cleverly overcome some intrinsic shortcomings of copper-based systems (copper shortage, possible toxicity, and high overpotential—while aiming for the C-C coupling through either heterointerface or cascade reaction mechanism. Non-copper based catalysts rapidly developed from 2023 to 2025, greatly enriching the catalyst variety of this field, which can provide significant support to enable cost-effective, sustainable CO_2 use options.

Jiayi Huang prepared a Sn-Bi bimetal site catalyst, which is mainly based on constructing a Sn-Bi heterojunction to realize the cooperative adsorption of CO intermediate by two sites and then induce C-C coupling, thus enabling acetate-based or ethanol-selective routes. The catalyst attains a C_2^+ FE of ~42% (with acetic acid being the main product) in alkaline flow cell under ~200 mA/cm^2 current density [8]. The most notable benefits over the copper-based counterpart are low-cost and earth-abundant Sn/Bi raw material with simplified synthesis. Besides, which it can also suppressed the HER competition (enhancing the atomic economy). Despite this important achievement, severe restrictions remain: moderate C_2^+ selectivity; and Bi leaching under acidic conditions that induces the stability loss and therefore limits their use for direct flue gas treatment.

Zhongze Bai prepared an industrial-potential SACs, Fe-N-C, which has the main idea that Fe single atom is anchored on N-doped C(N-C) and forms Fe-N4 coordination site; this will modulate the d-band center of Fe, thus stabilizing the transition state of C-C coupling. For CO_2 electroreduction, the catalyst enables C_2^+ product formation (ethanol is the major product) on the N-C framework with a C_2^+ FE of 40%, a current density of ~180 mA/cm^2, and a stability of more than 200 h [9]. This process has a very high atom economy, close to 100% in ideal cases; the reagents used are non-precious metal containing and all cheaply available or abundant elements; and the adjustable support provides good structural stability with great economic advantage. The number of active sites in the reaction system are low, leading to a rather low current density. Thirdly, the carbon support will be oxidized easily at higher potential and cause the system performance to decrease significantly after a long period of time.

Daniel Moreno has created an extremely novel abiotic- biotic hybrid system. The key to its novelty is to break through the limitation of inorganic material, bringing the enzymatic reaction into the reaction system of this field. After electrochemical generation of C_1 intermediates, that are enzymatically cascaded to C_2^+ products. The total yield of the system is increased about 35% and displays a C_2 selectivity higher than 75%, and holds for weak assumptions [10]. The merit of this strategy lies in that the biological enzyme has high specificity and it may greatly decrease the difficulty for C-C coupling. Combined with the effective input from electrochemistry, the reaction system reaches a synergistic effect and greatly improves the catalytic activity. In addition, the reaction occurs at room temperature in mild conditions, where we use less energy. But it also presents disadvantages, like for example the high sensitivity of enzymes against pH or impurities that will cause their deactivation; the difficulty in system integration, which requires a multi-chamber design; and the high price tag for producing large quantities of enzymes and immobilizing them, which is a barrier to scaling up.

Even though the selectivity to produce C_2^+ is usually less than 50%, which are still lower than those obtained in Cu-based, they present some attractive features such as such as low cost, environmental benignity, and mild reaction condition, which makes them have great development potential and industrialization prospects. At present, all these non-copper-based C_2^+ syntheses have been limited at the lab stage mainly due to the low total efficiency and unsatisfactory stability preservation. However, their intrinsic benefits can still offer insightful lessons and industrialization blueprints in the eCO_2RR towards C_2^+ products area.

3.3 Tandem catalyst strategy

At the same time, by making use of the complementarity between copper-based catalysts and non-copper-based catalysts, a new type of catalytic mode was put forward and verified. Xinyang Gao's team designed a tandem catalyst strategy based on the integration of Ag/Au-based highly efficient CO-generation module and Cu-based C-C coupling module. This device offers an unprecedented improvement of the total C_2^+ selectivity and current density with great potential to bridge the gap between laboratory research and industrial implementation in the field of eCO_2RR.

Taking the Ag-Cu cascade electrolyzer system as an example. This system builds an Ag-Cu heterogeneous interface, where Ag sites preferentially reduce CO_2 to form CO intermediates, which then overflow to adjacent Cu sites for C-C coupling, achieving dynamic reconstruction. This system achieves over 80% C_2^+ FE on gas diffusion electrodes with a current density of 500 mA/cm^2, and significantly improved stability [11]. The advantage of this method lies in breaking down the originally complex path, increasing the local concentration of *CO and suppressing the competition of HER, making it suitable for high-current industrial conditions; and through interface regulation, the product distribution is optimized. However, the interface stability is sensitive to potential, prone to phase separation, and Ag is expensive, making industrialization difficult, and further exploration of cost reduction paths is still needed.

Table 1 presents three representative catalyst examples and their performance characterization data. Through the intuitive data, it can be concluded that copper-based catalysts have a relatively high efficiency in the generation of multi-carbon products, and they also have good current density and stability, with all data being in the middle range among the three. The performance of the reaction system of non-copper-based catalysts is average, but they have low costs. The advantage of cost performance determines that they have a good industrialization prospect. The tandem catalytic strategy shows very excellent performance, but it faces practical challenges such as high costs and high technical thresholds, and still requires further technological breakthroughs by scientists.

Table 1. Performance Metrics of Three Representative Catalysts.

Type of catalyst	**Example**	**C_2^+ products**	**FE (%)**	**Current Density (mA/cm^2)**	**Stability (h)**
Copper-based [6]	GB-richCu	C2H4	70	400	500
Non-copper-based [9]	Fe-N-C	C2H5OH	40	180	200
Tandem strategy [11]	Ag-Cu cascade	C2H5OH	80	500	800

4 Current challenges

Despite enormous strides taken toward rational catalyst design and better mechanistic insights into eCO_2RR-mediated C_2^+ formation which represents the industrial embodiment of this field of study, there is still an array of related issues that have been slowing down its advancement due to the complexity involved with such reactions. The breadth of dynamic catalyst behavior, as well as limitations in systems engineering— all of which together constrain improvements to system-wide performance.

Firstly, low selectivity and activity are currently the most urgent bottleneck that needs to be broken through. As a limiting factor, the C−C coupling has a high barrier, which results in a FE to the C_2 products often less than 80% and complicated product distributions (often mixtures of several C_2^+ ions). In contrast, the HER dominates especially in acidic media and/or at low concentrations of CO_2 feed, which decreases CUE even more. Further, mass-transport limitations of dilute CO_2 sources exacerbate activity degradation, because intermediate coverage on the catalyst surface is not sufficient to drive effective C−C coupling. This difficulty stems from the fact that exquisitely precise regulation of adsorption equilibria at the catalyst−electrolyte interface is needed—while grain boundary engineering has shown some promise toward alleviating this problem, selective production of only one highly valuable product with overwhelming dominance over other products is still out of reach.

Secondly, insufficient catalyst stability prevents long-term operation of the reaction system. Cu based catalysts tend to dynamically restructure and rapidly degrade at high current density, while for the others, problems like migration of active sites or oxidation of supports can occur (non-copper based).Carbonate precipitation at high pH causes electrode fouling while acidic conditions speed up the electrode corrosion – leading to common lifetime of a few hundred hours ,well below industrialization requirements, which is mainly due to the irreversibility of redox cycling and pH gradient effects on the electrochemical system; even in the case of tandem approaches to decouple reaction paths, interface instability is challenging to entirely overcome.

At the same time, poor energy efficiency and large overpotential limit the economical viability of this process: Multi-electron transfer steps require large overpotentials, leading to overall energy efficiencies often lower than 50%, which is mainly due to the loss of mass and heat transfers in intermediate hydrogenation. In addition, this problem is synergistically reinforced by inadequate selectivity. HER competes with electron consumption and overpotential feed of dilute CO_2, as well as mass transport resistance. Although the latter two are at least in part amenable to mitigation by microenvironment engineering, the inputs to the system will continue to be driven by cheap renewables (electricity); and overall, the current cost of the technology is still higher than conventional petrochemical pathways.

Last but not least are scale-up and economic barriers to industrializing this technology. Severe reaction conditions, low performances, and high costs hamper both its deployment in an industrial context and its insertion within a socio-economic path. With all its significant promise and revolutionary advantages, overcoming the above issues is key in order for the technique to be practically implemented and thus realize its general social benefit.

All together, we observe that there is also a cascade between the different problems as primary issues of selectivity and activity result in secondary issues related to stability and efficiency, which then cascade to become economic and scale-up barriers. Further progress will likely depend critically upon interdisciplinary efforts like applying in-situ characterizations toward better understanding mechanisms. AI-aided catalyst screening, and systems integration innovation— all with an aim to unlock the commercial potential of eCO_2RR.

5 Future technological development

eCO_2RR for the preparation of C_2^+ as a key technology for carbon neutrality will focus on a systematic transformation from laboratory to industrialization in the future, with significant breakthroughs expected before 2030.

In the first phase (2026–2030), catalysis design will focus on multilevel optimization. Cu-based catalysts will achieve higher C_2^+ selectivity/stability via surface/interface engineering and heteroatoms doping, aiming to achieve FE ≥ 90% and a stability time of ≥ 5000 hours by 2030, initially meeting industrialization requirements. Meanwhile, non-copper-based materials and tandem coupling strategies will be expanded to reduce costs and precisely control product distribution. Thirdly, we shall apply the aid of artificial intelligence (AI) for aiding both the HTS and ML prediction of the intermediate adsorption, accelerating the rate of technological iteration and innovation, and in conjunction with operando characterization for enhanced understanding of dynamics.

In the second stage (2030-2040), system integration will likely be the development focus here with optimized MEAs or flow electrolyzer reaching an industrial grade current density and direct conversion from a low concentration CO_2; meanwhilethis technology will be tightly integrated with DAC and renewable energy for a local carbon cycle loop. The hybrid system is expected to enable production of a higher value product thus increasing economic competitiveness. Via TEA and LCA, the scale-up of the system.

6 Conclusion

The studies of eCO_2RR for C_2^+ product synthesis have made significant progress in catalysts design and system optimization, mechanism-guided catalyst systems laying down the foundation to realize high selectivity, low overpotential, and improved energy efficiency. But the majority of existing techniques are still at the laboratory level with overlapping issues such as low selectivity, low thermal cycling durability, slow kinetics (mass transfer), or cost that prevents commercialization.

Looking ahead, eCO_2 RR is expected to move towards industrialization in 2030. The future direction of research will likely extend into the production of C_3^+products (e.g., (propanol), whereas coupling to DAC and renewable electricity will allow us to build closed-loop carbon cycles–a key technical enabler towards the net-zero emission goal. Considering the wide scope of applications for CO_2 utilization through eCO_2RR, it will require continued government attention and global cooperation to further enable the development of this technology into a scalable solution that transitions discoveries at bench scale into commercialization and deployment.

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