

Review

Open Access



Electrochemical conversion of CO₂ via C–X bond formation: recent progress and perspective

Shuaiqiang Jia^{1,2,#}, Mengke Dong^{1,2,#}, Qinggong Zhu^{3,*}, Xincheng Kang³, Haihong Wu^{1,2,*}, Buxing Han^{1,2,3,*}

¹Shanghai Key Laboratory of Green Chemistry and Chemical Processes, State Key Laboratory of Petroleum Molecular & Process Engineering, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200062, China.

²Institute of Eco-Chongming, 20 Cuinia Road, Chenjia Town, Chongming District, Shanghai 202162, China.

³Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Colloid and Interface and Thermodynamics, Center for Carbon Neutral Chemistry, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.

#Authors contributed equally.

*Correspondence to: Profs. Qinggong Zhu, Buxing Han, Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Colloid and Interface and Thermodynamics, Center for Carbon Neutral Chemistry, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Zhongguancun North First Street 2, Beijing 100190, China. E-mail: qgzhu@iccas.ac.cn; hanbx@iccas.ac.cn; Prof. Haihong Wu, Shanghai Key Laboratory of Green Chemistry and Chemical Processes, State Key Laboratory of Petroleum Molecular & Process Engineering, School of Chemistry and Molecular Engineering, East China Normal University, No. 3663, North Zhongshan Road, Shanghai 200062, China. E-mail: hhwu@chem.ecnu.edu.cn

How to cite this article: Jia S, Dong M, Zhu Q, Kang X, Wu H, Han B. Electrochemical conversion of CO₂ via C–X bond formation: recent progress and perspective. *Chem Synth* 2024;4:60. <https://dx.doi.org/10.20517/cs.2024.32>

Received: 2 Mar 2024 **First Decision:** 6 May 2024 **Revised:** 5 Jul 2024 **Accepted:** 16 Jul 2024 **Published:** 12 Oct 2024

Academic Editor: Aicheng Chen **Copy Editor:** Dong-Li Li **Production Editor:** Dong-Li Li

Abstract

With the depletion of traditional energy sources and growing environmental concerns, it is becoming increasingly urgent to develop green, low-emission renewable energy technologies to replace fossil fuel-driven methods that emit carbon dioxide (CO₂). Currently, the electrochemical production of high-value-added chemicals and fuels from CO₂ has aroused great interest from scientists. However, to make full use of CO₂ for the preparation of chemicals, it is necessary to expand the range of electrosynthesis methods, in particular by expanding reaction pathways through the reaction of CO₂ with different substrates. In general, CO₂ can form new covalent bonds with substrate molecules through the formation of C–X bonds, including C–H, C–C, C–N, C–O, and C–S bonds, which would expand the range of possible products by diversifying the reaction pathway. In this review, we focus on the research progress in electrochemical conversion of CO₂ through C–X bond formation. We start by examining fundamentals of the reactions and summarizing the reaction modes. Next, we discuss the electrosynthesis of C–X bonds (C–H, C–C, C–N, C–O, C–S) using CO₂ and different substrate molecules. Finally, (i) strategies for the



© The Author(s) 2024. **Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License (<https://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, sharing, adaptation, distribution and reproduction in any medium or format, for any purpose, even commercially, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.



design and activity optimization of catalyst materials and (ii) the future development of forming five types of bonds from CO₂ and small molecules are discussed, along with an outlook on their future research prospects.

Keywords: Carbon dioxide, electrosynthesis, C–X bonds, new covalent bonds, high-value-added chemicals

INTRODUCTION

Excessive emissions of carbon dioxide (CO₂) have been recognized as one of the main causes of global warming. With the progress of society and the development of science and technology, increasing attention has been paid to the sustainable development of carbon energy to solve the contradiction between carbon energy and CO₂ emissions. Aside from crafting strategies for mitigation and removal, CO₂ conversion to produce useful fuels/chemicals using sustainable energy is a promising route to enable a carbon-neutral cycle in modern industrial society. In 2013, the concept of “green carbon science” was first put forward by Professor Mingyuan He, which is defined as “the study and optimization of the transformation of carbon-containing compounds and the relevant processes involved in the entire carbon cycle from carbon resource processing, carbon energy utilization, CO₂ fixation, and carbon recycling to utilize carbon resources efficiently and minimize net CO₂ emission”^[1]. The design of many environmental catalytic systems and process technologies is guided by the general principles of this concept. To facilitate CO₂ capture and conversion, to date, various strategies have been developed to use CO₂ as a feedstock for chemicals and fuels, such as photochemical catalysis, thermochemical catalysis, and electrochemical catalysis, among others. Among these approaches, electrocatalysis can use renewable energy to catalytically synthesize different types of chemicals from the earth’s abundant renewable resources under mild conditions with high efficiency and selectivity^[2-5], which is the key to future new energy storage and conversion technologies^[6-10]. The activity and selectivity can be optimized by a variety of powerful tools, such as the control reaction pathways, the design of catalysts, the optimization of electrolytes, and the modulation of reaction potentials, which is expected to realize the energy and chemical de-fossilization, low carbon green, and distributed development^[11-12].

Electrosynthesis, as an efficient and environmentally friendly synthesis method, employs electrons as redox reagents^[13-14]. In CO₂ fixation, coupling CO₂ with small molecule compounds or organic compounds by electrochemical methods has recently been promoted as an environmentally friendly and sustainable synthesis technique^[15-19]. In general, CO₂ can form new covalent bonds with substrate molecules through the formation of C–X bonds, including C–H, C–C, C–N, C–O, and C–S bonds, which would enrich the reaction pathway and produce various chemicals [Figure 1]. During the electrosynthesis, the inert CO₂ molecule must first be adsorbed and activated on the catalyst surface because CO₂ is a stable molecule and breaking or hydrogenating one of the oxygen atoms of CO₂ is needed for its utilization in electrochemical C–X bond formation reactions. The activated CO₂ molecules subsequently combine with the X source to form intermediates. Through the transfer of electrons and protons, C–X bonds can be constructed to produce the final product. Among various reaction routes for CO₂ conversion, the C–H bond is constructed from the hydrogenation of CO₂ to produce CO, CH₄, HCOOH, and C₂₊ products which have been intensively investigated. However, studies on the construction of C–C, C–N, C–O, and C–S bonds are still limited and achieving high efficiency and selectivity remains a great challenge. Therefore, designing efficient electrochemical systems for the formation of different C–X bonds is highly desired^[20-21].

This paper reviewed the recent advances in the electrosynthesis of C–X bonds (C–H, C–C, C–N, C–O, C–S) using CO₂ and substrate molecules, including the electrochemical C–H bond formation for hydrocarbon/carbohydrate, electrochemical C–C bond formation for carboxylation of CO₂, electrochemical C–N bond

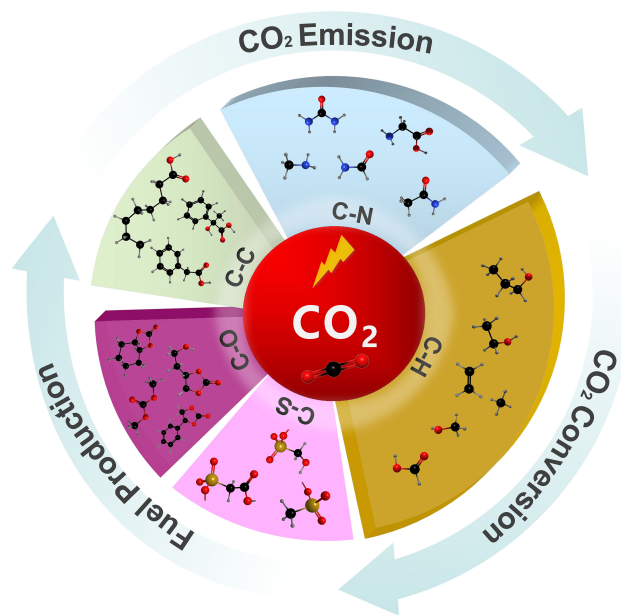


Figure 1. Sustainable fuel and chemical production through the formation of C-H, C-C, C-N, C-O, and C-S bonds.

formation for organic nitrates synthesis, electrochemical C-O bond formation for cyclic carbonates and dimethyl carbonate (DMC) and electrochemical C-S bond formation for sulfonates^[22-23]. Recent developments, prospects, and challenges in electrochemical CO₂ utilization, and the fundamentals of electrocatalytic reactions on the initial activation of CO₂ and product selectivity will also be described. Finally, improvement strategies for the shortcomings of electrocatalytic CO₂ coupled organic reactions and outlooks on their future research prospects are proposed^[24].

FUNDAMENTALS OF ELECTROCATALYTIC REACTIONS

The electrochemical CO₂-catalyzed reaction is capable of using various substrate molecules to prepare advanced products in addition to the direct conversion of CO₂ and water into carbon-containing chemicals^[25-28]. Typically, [Figure 2A](#) and [B](#) can represent the construction of C-H bonds between water and CO₂, which are reduced to a one-carbon product and a multi-carbon product, respectively. [Figure 2C](#) can represent the construction of C-N and C-S bonds between CO₂ and N (S)-containing small-molecule compounds, and [Figure 2D](#) can represent the form of the reaction that forms C-C and C-O bonds.

According to the different electrocatalytic reaction pathways, there are generally two types of reaction modes.

One is the tandem reaction mode. The use of desorbed intermediates as local self-sufficient sources for following reactions is also of great research interest and value, which can be electrocatalytic or thermodynamically spontaneous. This tandem reaction concept has the obvious advantage of allowing more complex chemicals obtained by single-step electrocatalytic reactions and simplifying the synthesis process by avoiding the separation of intermediates, thus showing higher economic attractiveness. The concept of tandem reactions, as reviewed by Tang *et al.*, can broaden the application of electron utilization to more complex chemicals that cannot be obtained by one-step electrocatalytic reactions^[29]. Inspired by this, Peng *et al.* discovered that double sulfur vacancies on copper hexagonal sulfide serve as effective electrocatalytic centers, stabilizing CO* and OCCO* dimers and facilitating the coupling of CO-OCCO to produce C₃

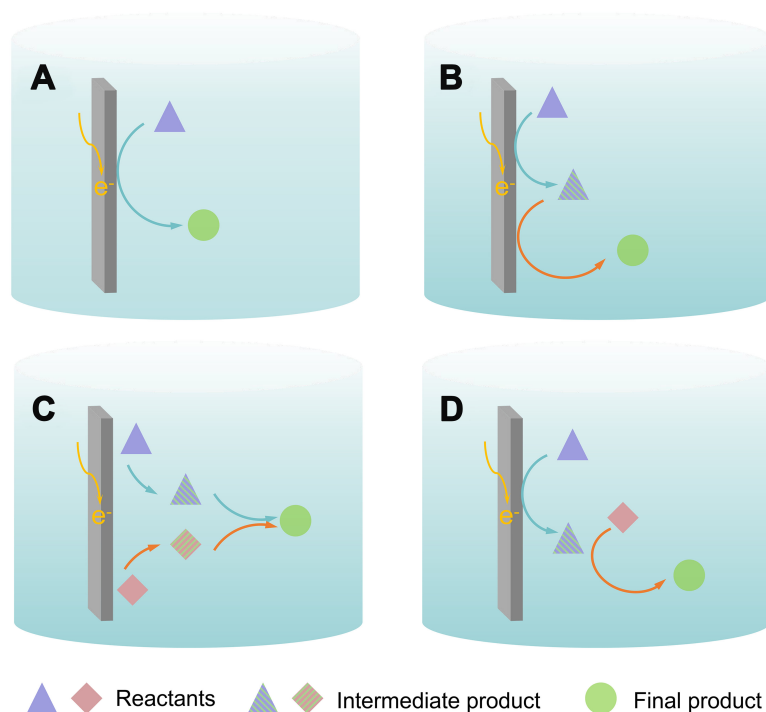


Figure 2. Different electrocatalytic reaction pathways. (A) Illustration reactions of $a \rightarrow d$; (B) Illustration reactions of $a \rightarrow b \rightarrow d$; (C) Illustration reactions of $a + c \rightarrow d$; (D) Illustration reactions of $a \rightarrow b$, $b + c \rightarrow d$. a and c: reactants; b: intermediate or intermediate product; d: final product.

compounds [Figure 3A]^[30]. In another study of the CO_2 electrocarboxylation reaction, ketones are first reduced by two-electron transfer at the cathode, and then further converted to carboxylates by coupling with CO_2 [Figure 3B]^[31]. It is also a typical pathway for a tandem reaction.

The other is the coupling reaction mode. The electrocatalytic CO_2 conversion reactions can potentially derive new chemistries by simultaneous activation of small molecules other than CO_2 at the active site of the catalyst to increase activity and alter selectivity, which can be achieved by adjacent active reaction sites and coupling reactions^[32-34]. Wu *et al.* recently proposed a possible coupling reaction pathway for the electrocatalytic synthesis of methylamine^[35]. This pathway integrates the electrochemical reduction of CO_2 ($\text{CO}_2\text{-RR}$) and nitrate ($\text{NO}_3\text{-RR}$) [Figure 3C]. First, $\text{CO}_2\text{-RR}$ and $\text{NO}_3\text{-RR}$ can occur independently to form formaldehyde (HCHO) and hydroxylamine (NH_2OH) intermediates, respectively. Then, formaldoxime is produced by nucleophilic NH_2OH attack on HCHO and then reduced to N-methyl hydroxylamine. Finally, methylamine is obtained by further reduction of N-methyl hydroxylamine. It is noteworthy that the key to the generation of the C–N bond is the condensation of NH_2OH and HCHO intermediates from $\text{NO}_3\text{-RR}$ and $\text{CO}_2\text{-RR}$, respectively.

INTEGRATED ELECTROCATALYTIC REACTIONS

C–H bond formation

The generation of C–H bonds occurs during the CO_2 reduction reaction ($\text{CO}_2\text{-RR}$) with multiple proton-electron transfer steps that yield carbon-based products. A typical CO_2 electrolysis usually involves a multi-electron/proton transfer process: (i) CO_2 adsorption and activation on electrolyte/electrode interface; (ii) additional electron/proton transfer to produce the desired product; and (iii) release of the product into the

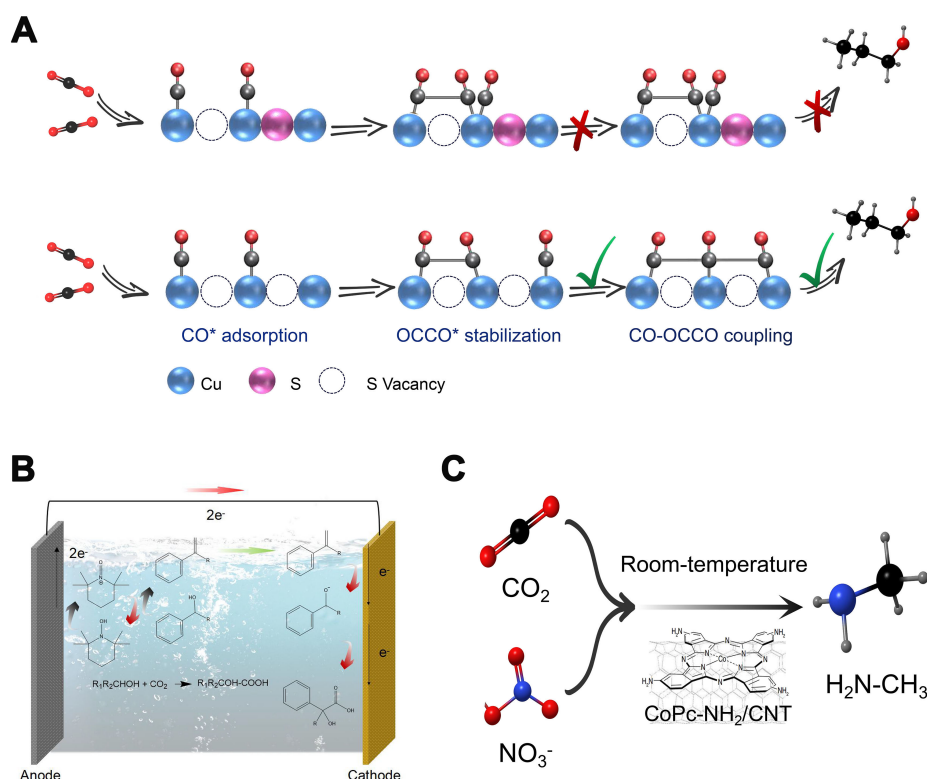


Figure 3. Typical tandem reaction and coupling reaction modes. (A) Mechanism of *n*-propanol formation on adjacent CuS_x-DSV, showing the dimerization of CO–CO followed by CO–OCCO coupling; (B) Electrosynthesis of α -hydroxy acids through the electrocatalytic coupling of alcohols and CO₂; (C) Cascade electrocatalysis of methylamine from CO₂ and NO₃⁻. CuS_x-DSV: CuS_x double sulfur vacancy.

electrolyte. Therefore, both electrocatalysts and electrolyte are pivotal for designing efficient electrochemical devices^[36-38]. Generally, various electrocatalysts have been utilized in CO₂ electrolysis, ranging from homogeneous to heterogeneous catalysts. Homogeneous catalysts dissolved in the electrolyte, generally organic or organo-metallic complexes, such as metal pyridine, and metal porphyrins, usually promote CO₂ reduction coupling by facilitating the transfer of electrons and protons^[39]. In contrast to homogeneous electrocatalysts, heterogeneous electrocatalysts are more concerned. Electrocatalysts are typically solid materials, with the reaction predominantly taking place at the interface between the electrolyte and the catalyst. Up to date, various electrocatalysts (e.g., Au, Ag, Pd, Co, Bi, Cu, Fe, Sn, carbon-based materials, *etc.*) have been explored^[40-46], and a wide range of products have been generated^[47-49].

As shown in Figure 4, electrochemical CO₂RR involves the transfer of multiple protons and electrons, which involves diverse pathways. CO₂ can undergo reduction to yield a variety of products comprising both single- and multiple-carbon compounds, including carbon monoxide (CO), methane (CH₄), methanol (CH₃OH), formate (HCOO⁻), ethylene (C₂H₄), ethanol (C₂H₅OH), and propanol (C₃H₇OH), among others. There are three types of bonding steps in the CO₂RR route: oxygen hydrogenation, carbon hydrogenation, and carbon-carbon coupling^[50-53]. Hydrocarbonation often occurs during the evolution of intermediates and the formation of products^[54-56]. By calculating the relevant intermediates, the resulting hydrogen (H₂), HCOO⁻, and hydrocarbon moieties can be distinguished^[57]. The key factors affecting the distribution of these three products are the H* binding energy, the HCOO* binding energy, and possibly the *CO binding energy. The reduction potential of CO₂ is typically more negative than the hydrogen evolution potential. At extremely

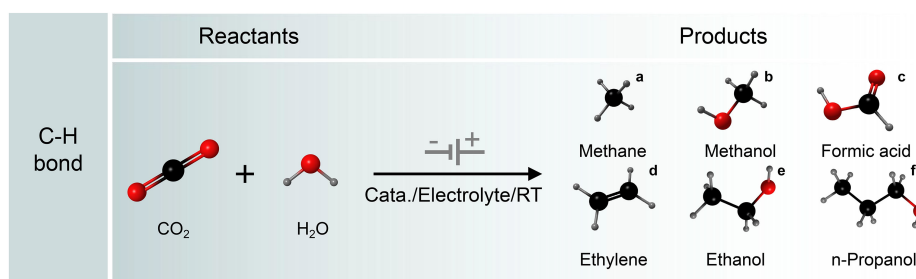


Figure 4. C–H bond formation by electrocatalytic reaction of CO₂ and H₂O.

negative potentials, the hydrogen evolution reaction (HER) tends to take precedence. Therefore, it is crucial to tailor catalyst characteristics to suppress the HER and enhance the multiple proton and electron transfer processes, enabling precise control over electrocatalysis for the targeted product.

Up to now, significant endeavors have been dedicated to enhancing the efficiency and specificity of CO₂ reduction, ranging from the advancement of catalysts to the design of electrolytes and electrolyzers. Among them, designing robust electrocatalysts with self-supported nanostructures and desired features is very important to improve the catalytic ability of CO₂RR.

Numerous reports have demonstrated the excellent catalytic properties and potential of carbon-based materials for CO₂RR [Figure 5A]^[58]. However, the active sites of the catalysts have been the focus of debate. Currently, various forms of nitrogen species (e.g., pyridinic N, pyrrolic N, and graphitic N) doped in carbon materials, carbon atoms surrounding the nitrogen dopants, and carbon atoms with topological structural defects are considered to be the active sites for CO₂RR. Therefore, to develop highly active carbon-based catalysts, it is necessary to identify the active sites of the catalysts. Kondo *et al.* suggested that in the CO₂RR process, the carbon atoms adjacent to pyridinic N can act as Lewis base sites to adsorb CO₂, which makes the reduced carbon atoms the active sites for CO₂RR^[59]. However, Guo *et al.* showed that the acidic CO₂ molecules can only adsorb on the pyridinic N sites, and the Lewis base sites for CO₂RR are generated by pyridinic N rather than graphitic N. Therefore, pyridinic N is considered as the active site for CO₂RR^[60].

Metal-based catalysts are often the most common electrocatalysts in the CO₂RR. Typically, the diverse transition metals yield distinct primary products as a result of their varying affinities towards the intermediates *COOH and *CO. Bagger *et al.* classified more than ten metals through more detailed calculations of the adsorption energy correlations of species such as H*, *COOH, HCOO_B*, and *CO^[61]. The study found that: (1) Pt, Pd, and Ni have great adsorption energy on H* and *CO; thus, HER becomes the dominant one; (2) Metals such as Au and Ag, which have CO as the main product, have weak adsorption energy for H*, *COOH, and *CO, *etc.*, and *CO has the opportunity to desorb from the surface to produce gas-phase CO products. At the same time, it is also their weak adsorption of intermediate *COOH that makes the production of CO on these metals require a certain overpotential. To reduce the overpotential (enhance *COOH adsorption) while maintaining high CO-producing activity (maintain *CO adsorption), measures are needed to break the linear relationship between *COOH and *CO adsorption energies^[62-64]; (3) Sn, Pb, Hg, and other metals with formic acid as the main product tend to have the weakest adsorption of H*, while they also have weak adsorption of *CO and *COOH and moderate adsorption of HCOO_B*; (4) Cu has relatively moderate adsorption of both H* and *CO which makes *CO neither too easily desorbed from the surface to produce gas-phase CO products, nor too strongly adsorbed on the surface to become toxic, but has the opportunity to be further reduced to hydrocarbons or polycarbonate products [Figure 5B].

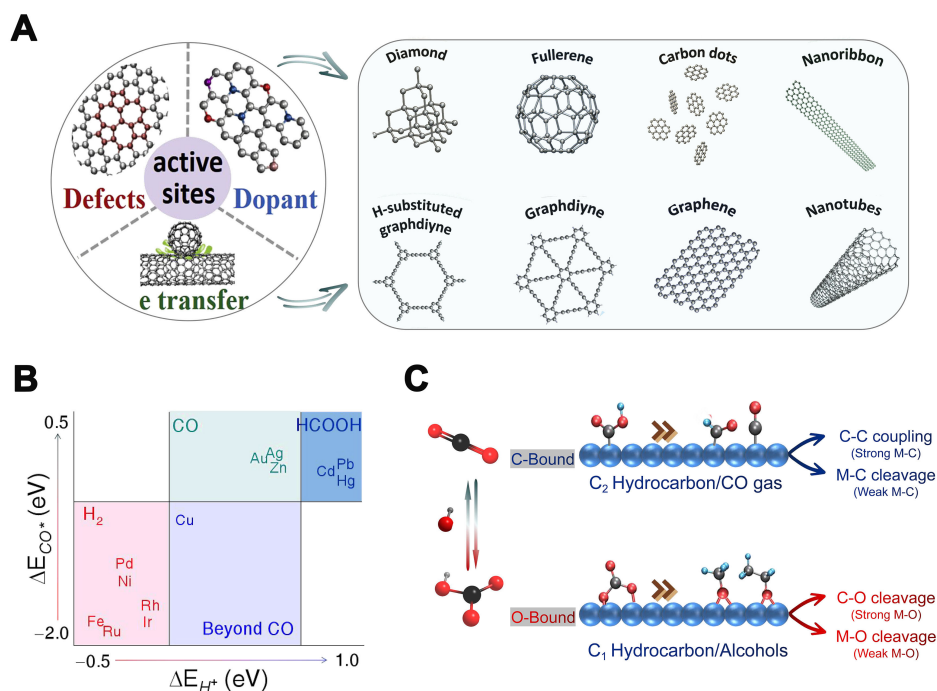


Figure 5. (A) Design of effective catalytical active sites in carbon-based metal-free electrocatalysts; (B) The adsorption energies of the CO and H intermediates on diverse metals and the predominant products of CO₂RR on them; (C) The impact of surface-bound carbon and oxygen reaction intermediates on the selectivity of CO₂RR products. CO₂RR: CO₂ reduction reaction.

Katayama *et al.* further clarified the surface reaction properties of metal catalysts [Figure 5C]^[62]. They deduced that when the metal has a propensity to bond with carbon rather than oxygen, intermediates such as *CO, *CHO, and *carboxylate are readily formed on the metal surface. In contrast, if the metal tends to bond with oxygen, the adsorption of carbonates in easily formed states occurs. The different binding types will affect the formation of C–H bonds, which, in turn, will lead to the eventual formation of CO, C₂ products, *etc.* of intermediate species adsorbed on the carbon end, while intermediate species adsorbed on the oxygen end eventually form C₁, alcohols, *etc.*

Recent advancements have also focused on achieving industrially significant performance by optimizing gas diffusion electrodes (GDEs) in flow reactor systems, in addition to investigating reaction pathways^[65]. A gas diffusion layer (GDL) and a catalytic layer (CL) are the key components of a GDE. The porous architecture enhances the rapid transport of CO₂ to the interface between the gas, electrolyte, and catalyst via the rear of the GDL. Polymers/binders are usually used to coat the powder electrocatalyst on the GDL as the catalyst layer. In this device, CO₂ electrolysis occurs at the gas-liquid-solid three-phase interface.

In order to enhance the CO₂RR activity under high current conditions, diverse strategies have been employed to design the gas diffusion assembly. In a representative study, de Arquer *et al.* integrated ionomer with catalyst particles to enhance the diffusion of CO₂ to the active catalyst surface, resulting in CO₂ electrolysis to ethylene at the current density of 1 A·cm⁻²^[66]. The electrolysis was conducted in 7 M KOH electrolyte, leading to an ethylene partial current density of 1.3 A·cm⁻² with a cathodic energy efficiency of 45%. The results show that the catalyst ionomer bulk heterojunction (CIBH) consists of a metal and an ultra-thin ionomer layer with hydrophobic and hydrophilic properties, which separates the transport of gas, ions, and electrons. Recently, Li *et al.* used quaternary ammonia poly(ether ether ketone)

(QAPEEK)-containing carbonyl groups as a bifunctional electrolyte for CO₂RR^[67]. The results show that the ionomer has ionic conductivity, which can activate CO₂ at the catalyst-electrolyte interface and promote the production of ethylene. At a cell voltage of 3.54 V, the partial current density of ethylene was 420 mA·cm⁻² without any electrolyte consumption, which meets the requirements for industrial-scale production. In another study, Endrödi *et al.* developed a poly (aryl piperidinium)-derived anion exchange membrane (PiperION) with enhanced carbonate conductance for the CO₂RR to CO^[68]. Utilizing a PiperION membrane in a membrane electrode assembly (MEA) resulted in a current density of more than 1 A·cm⁻² for CO production. These works provide theoretical guidance for the industrial application of CO₂ as a substrate for electrochemical reactions.

As shown in [Table 1](#), to facilitate a more intuitive comparison and understanding for the readers, we have summarized some representative CO₂ reduction reactions on nanostructured catalysts.

C–C bond formation

As the key skeleton of organic compounds, C–C bonds are one of the most common chemical bonds in organic compounds^[15-17,92]. Among the many products of CO₂ conversion, carboxylic compounds are a very important class of compounds that are the basic structural units of many functional molecules, natural products, and biologically active substances, as well as important chemical products and industrial raw materials^[93,94]. Therefore, the synthesis of carboxylic acids and their derivatives by electrocarboxylation of CO₂ is of great importance [\[Figure 6\]](#). In recent years, the method of CO₂ carboxylation by the electrochemical drive has received increasing attention and has undergone development. Electrochemical synthesis of carboxylic compounds by constructing C–C bonds will provide a new way for the green and sustainable advancement of the chemical industry^[14,95-98].

In recent years, there has been a growing focus on research into electrocarboxylation, a process that utilizes CO₂ as a feedstock. Under mild conditions, the carbon negative ions generated by the electroreduction of organic substrates can trap CO₂ in the system, which, in turn, generates organic carboxylic compounds with multifunctional groups and higher added value^[99-104]. For example, CO₂ can react with olefins or alkynes to generate organic carboxylic acids through electroreductive addition reactions^[99,100]. Aromatic ketones, whose C=O double bonds are conjugated with aromatic rings, are more likely to gain electrons on the electrode surface for electroreduction and carboxylation reaction^[101,102]. On silver electrodes, organic halides can undergo electrocarboxylation reactions with CO₂ to generate carboxylic acid compounds^[103]. In addition, aromatic imine compounds can also react with CO₂ to form carboxylic acid compounds, but the yields of such electrocarboxylation reactions tend to be low because they are inherently less stable and easily consumed by hydrolysis^[104].

Generally, in a CO₂ carboxylation reaction, the substrate usually carries polar covalent bonds or unsaturated patterns such as C–C double bonds, C–C triple bonds, carbonyl groups, imine patterns, and aromatic rings [\[Figure 7A\]](#). The electrochemical carboxylation reaction with CO₂ generally proceeds via the following two possible pathways [\[Figure 7B\]](#). The first pathway is the direct electroreduction of CO₂ to form a CO₂ radical anion followed by a subsequent conversion to an acid [\[Figure 7C\]](#). As a typical example, Zhang *et al.* reported that the unactivated skip dienes could be electrochemically carboxylated with CO₂ to obtain valuable dicarboxylic acids. Control experiments and theoretical studies indicate that CO₂ first undergoes a single electron transfer (SET) reaction to be reduced to its radical anion, followed by a slow radical addition reaction with the unactivated alkenes. Finally, the unstable alkyl radical is reduced to carbanions with nucleophilic properties, which are then coupled with CO₂ to give the desired product^[16]. The other pathway is the electroreduction of the substrate to form a carbon ion or radical anion, followed by a carboxylation

Table 1. C₁-C₃ compound (CH₄, formate, CO, C₂H₄, EtOH, acetic acid, and *n*-propanol, etc.) production from CO₂RR

Substrate	Product	Electrode	Electrolyte	Current density/mA·cm ⁻² or potential/RHE	FE/%
CO ₂ , H ₂ O	CH ₄	Cu/CeO ₂ @C ^[69]	1 M KOH	172	80.3
CO ₂ , H ₂ O	CH ₄	Cu/CeO ₂ ^[70]	1 M KOH	300	67
CO ₂ , H ₂ O	CH ₄	CuNCN-500 ^[71]	1 M KOH	300	66.3
CO ₂ , H ₂ O	CH ₄	Cu SA/F-GDY ^[72]	1 M KOH	241	72.3
CO ₂ , H ₂ O	CH ₄	Cu SAs/GDY ^[73]	1 M KOH	247	81
CO ₂ , H ₂ O	Formate	MIL-68(In)-NH ₂ ^[74]	0.5 M KHCO ₃	108	94.4
CO ₂ , H ₂ O	Formate	TMP-CH ₃ -MCOF ^[75]	0.5 M KHCO ₃	33.5	95.6
CO ₂ , H ₂ O	Formate	CPs@V ^[76]	0.5 M KHCO ₃	6.87	90.1
CO ₂ , H ₂ O	CO	Cu/In NWS ^[77]	0.1 M KHCO ₃	4.2	93
CO ₂ , H ₂ O	CO	Bimetallic Cu/In ^[78]	0.1 M KHCO ₃	17	92
CO ₂ , H ₂ O	CO	Zn ₁ Ni ₄ -ZIF-8 ^[79]	1.0 M KHCO ₃	57.9	96.5
CO ₂ , H ₂ O	CO	Cu/Zn-CP-1-30 ^[80]	0.5 M [Bmim]PF ₆ / MeCN	165.5	94.3
CO ₂ , H ₂ O	C ₂ H ₄	Cu-[CF ₂] _n -5-CP ^[64]	0.1 M CsI	23.8	67.3
CO ₂ , H ₂ O	C ₂ H ₄	MOF CuPz ₂ ^[81]	0.1 MKHCO ₃	12.4	70.2
CO ₂ , H ₂ O	C ₂ H ₄	Cu-dimethyl-pyrazole ^[82]	0.1 M KCl	10.0	70.7
CO ₂ , H ₂ O	C ₂ H ₄	CuPOF-Bpy/Cu ₂ O@CNT ^[83]	0.5 M KHCO ₃	31.2	71.0
CO ₂ , H ₂ O	C ₂ H ₄	CuO/Ni SAs ^[84]	1.0 M KOH	811.5	54.1
CO ₂ , H ₂ O	EtOH	Cu/C-0.4 ^[85]	0.1 M KHCO ₃	-0.7 V	91
CO ₂ , H ₂ O	EtOH	Cu-DS ^[86]	0.1 M KHCO ₃	70	52
CO ₂ , H ₂ O	EtOH	Cu ₂ S _n -X ^[87]	0.5 M KHCO ₃	-0.3 V	73.3
CO ₂ , H ₂ O	Acetic acid	PcCu-TFPN ^[88]	0.1 M KHCO ₃	11.3	90.2
CO ₂ , H ₂ O	Acetic acid	NDD/Si RA ^[89]	0.5 M NaHCO ₃	0.54	77.3
CO ₂ , H ₂ O	Acetic acid	Cu(I)/BN-C ^[90]	25 mol% [Emim]BF ₄ and 75 mol% water	11.1	80
CO ₂ , H ₂ O	<i>n</i> -propanol	Cu ₂ O/Cu ^[91]	0.1 M KHCO ₃	6.8	12.1

CO₂RR: CO₂ reduction reaction; RHE: reversible hydrogen electrode; FE: Faradaic efficiency.

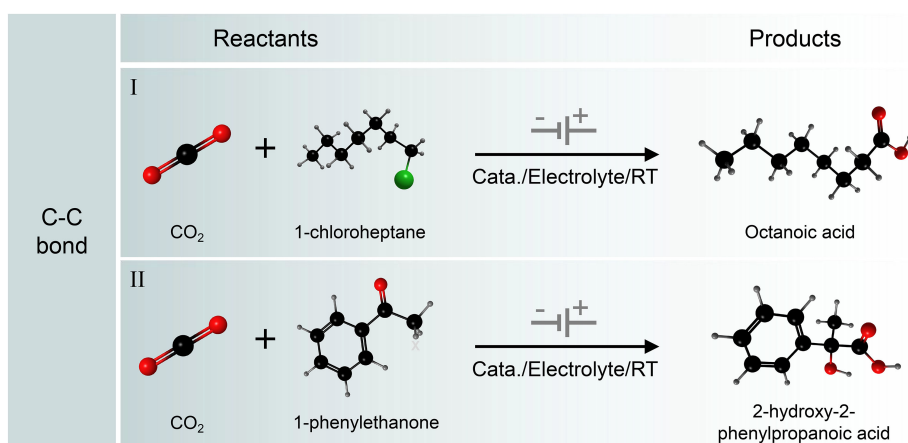


Figure 6. Electrocatalytic C-C coupling reactions. (I) Scope of aryl halides or alkyl halides; (II) Electrochemical CO₂ fixation to unsaturated organic compounds.

which reduce the selectivity of the target products, and the current research generally suffers from the carboxylation product yield. On the other hand, many of the reactions require the use of co-catalysts, which complicates the electrochemical reaction system and is not conducive to the separation and purification of the products. Meanwhile, this reaction is typically conducted in non-aqueous organic solvents, and the evaporation of significant quantities of these solvents also leads to environmental pollution and substantial waste. Therefore, it is of great significance to design cheap and effective electrocatalytic materials and green catalytic systems to improve the reaction efficiency.

As shown in [Table 2](#), we have summarized some representative examples of CO₂ and substrate electrolysis through the construction of C–C bonds, and provided a detailed comparison of relevant parameters such as catalysts and yields among different reactions.

C–N bond formation

Compounds containing nitrogen have been applied extensively in chemical synthesis, medicinal chemistry, agriculture, and aerospace industries. Therefore, the development of efficient electrocatalytic C–N coupling strategies is of great significance for the production of organic nitrogen compounds. The combination of electrochemical CO₂ with N₂ reduction reaction (NRR), which utilizes the earth's abundant small molecules N molecules (N₂, NO, NO₂⁻, NO₃⁻, *etc.*), is a viable approach to obtain valuable organic nitrogen compounds^[109–111]. Electrocatalytic synthesis of nitrogen-containing chemicals can utilize green energy by decomposing water to provide protons under mild conditions of ambient temperature and pressure. It involves the adsorption, activation, and dissociation of inexpensive CO₂ and nitrogen-containing compounds, facilitating the construction of C–N bonds and the generation and desorption of urea molecules. It is one of the viable alternatives to conventional processes with considerable economic viability and environmentally friendly sustainability. However, the limitation of this technology resides in the competition between the C–N coupling reaction and the reduction reactions of CO₂ and N-containing small molecules, as well as HER. Driving both electrochemical reduction reactions (CO₂RR/NRR) in the same electrochemical system to selectively produce the C–N coupling products is more difficult] [[Figure 8](#)]^[112–115]. However, this approach offers significant advantages over currently reported industrial synthetic routes^[116–118].

To address the problem of C–N bond co-activation, Chen *et al.* pioneered a new method to prepare urea by electrochemically coupling CO₂ and N₂ in water. The electrocatalyst used in this method consists of PdCu alloy nanoparticles attached to TiO₂ nanosheets with oxygen-rich vacancies. The yield of urea was 3.36 mmol·g⁻¹·h⁻¹ at a Faradaic efficiency (FE) of 8.92% in a flow cell. The experimental results indicated that N₂ is activated by binding to the catalyst surface and by the reduction of CO₂ to CO. The generated CO* and *N=N* are exothermically coupled to produce *NCON* intermediates, which are further reduced to urea under reducing conditions [[Figure 9A](#)]^[119]. In another example, it is reported that in NO₂⁻-integrated electrocatalytic CO₂ reduction, only those electrocatalysts that promote CO₂⁻-CO and NO₂⁻-NH₃ reduction can produce urea^[120,121]. The *CO and *NH₂ intermediates are obtained from the co-reduction of NO₃⁻/NO₂⁻ and CO₂. The C–N bond of urea was then constructed via the successive interconnections of the generated intermediates. Specifically, the first C–N bond in urea (i.e., *CONH₂) is constructed by coupling *CO and *NH₂; the second C–N bond in urea is formed by the combination of *CONH₂ and *NH₂ [[Figure 9B](#)]^[122,123]. Yuan *et al.* also demonstrated that the use of non-precious-metal Bi–BiVO₄ and BiFeO₃/BiVO₄ heterojunctions could efficiently electro-synthesize urea from CO₂ and N₂^[124]. The FEs of urea exceeded 10% with both catalysts. Among them, the heterojunction structure stands out for its distinct capability to expedite localized charge redistribution. This, in turn, facilitates targeted adsorption and activation of N₂ and CO₂ molecules within specific electrophilic and nucleophilic regions of the catalyst, thereby enhancing urea selectivity.

Table 2. Selected examples of electrolytic conversion of CO₂ and substrate by constructing C–C bonds

Substrate	Electrode	Catalyst	Electrolyte	Solvent	Current or voltage	Yield
	(-)Pt-Ni(+) ^[105]	/	TBAI	DMF	8 mA	75%
	(-)Ni-Mg(+) ^[106]	Co(OAc) ₂ PPh ₃	TBAPF ₆	DMF	10 mA	59%
	(-)Ag NPs-Mg(+) ^[103]	/	TEAI	MeCN	5 mA	98%
	(-)C-Pt(+) ^[107]	/	TBAPF ₄	DMF	4.5 V	70%
	(-)C-Zn(+) ^[96]	NiBr ₂ DME dmbpy	LiClO ₄	NMP	8 mA	70%
	(-)C-C(+) ^[92]	/	TEAI	DMF	10 V	70%
	(-)SS-Mg(+) ^[101]	/	TEAI	MeCN	1.2 mA	41%
	(-)Ni-Al(+) ^[104]	/	TBAB	DMF	10 mA	68%
	(-)Ni-Al(+) ^[108]	/	TBAB	DMF	10 mA	70%
	(-)Ni-Al(+) ^[100]	/	TBAB	DMF	10 mA	84%
	(-)C-C(+) ^[93]	/	TEAI	DMF	10 V	76%
	(-)Pt-Mg(+) ^[17]	/	TBAI	DMF	10 mA	94%
	(-)Ni-Al(+) ^[16]	/	TBAI	NMP	12.5 mA	78%
	(-)Fe-Zn(+) ^[98]	Cu(OTf) ₂	TEAI	NMP	5 mA	72% (C5)
	(-)Fe-Pt(+) ^[98]	/	TEAI	NMP	6 mA	85% (C4)
	(-)GF-GF(+) ^[15]	/	TEAI	DMF	20 mA	87%
	(-)Nb-Zn(+) ^[95]	/	TBAPF ₄	NMP	15 mA	82%

TBAI: Tetrabutylammonium iodide; DMF: *n,n*-dimethylformamide; DME: 1,2-Dimethoxyethane; TBAPF: tetrabutylammonium hexafluorophosphate; TEAI: tetraethyl ammonium iodide; MeCN: acetonitrile; TBAB: tetrabutylammonium bromide; NMP: *n*-methylpyrrolidone.

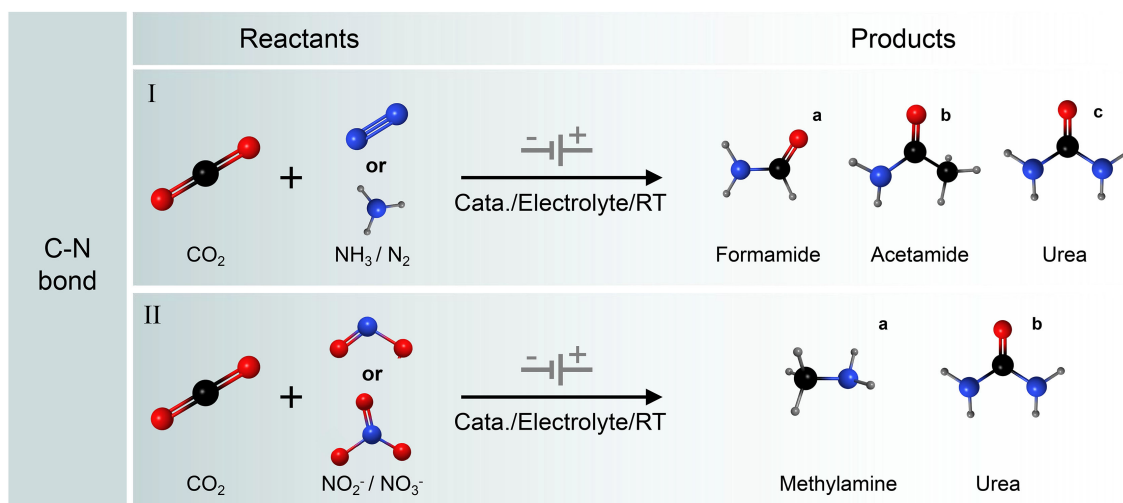


Figure 8. Electrocatalytic C–N coupling reactions. (I) Simultaneous reduction of CO₂ and NH₃/N₂ to formamide/acetamide/urea; (II) Simultaneous reduction of CO₂ and NO₃⁻/NO₂⁻ to methylamine/urea.

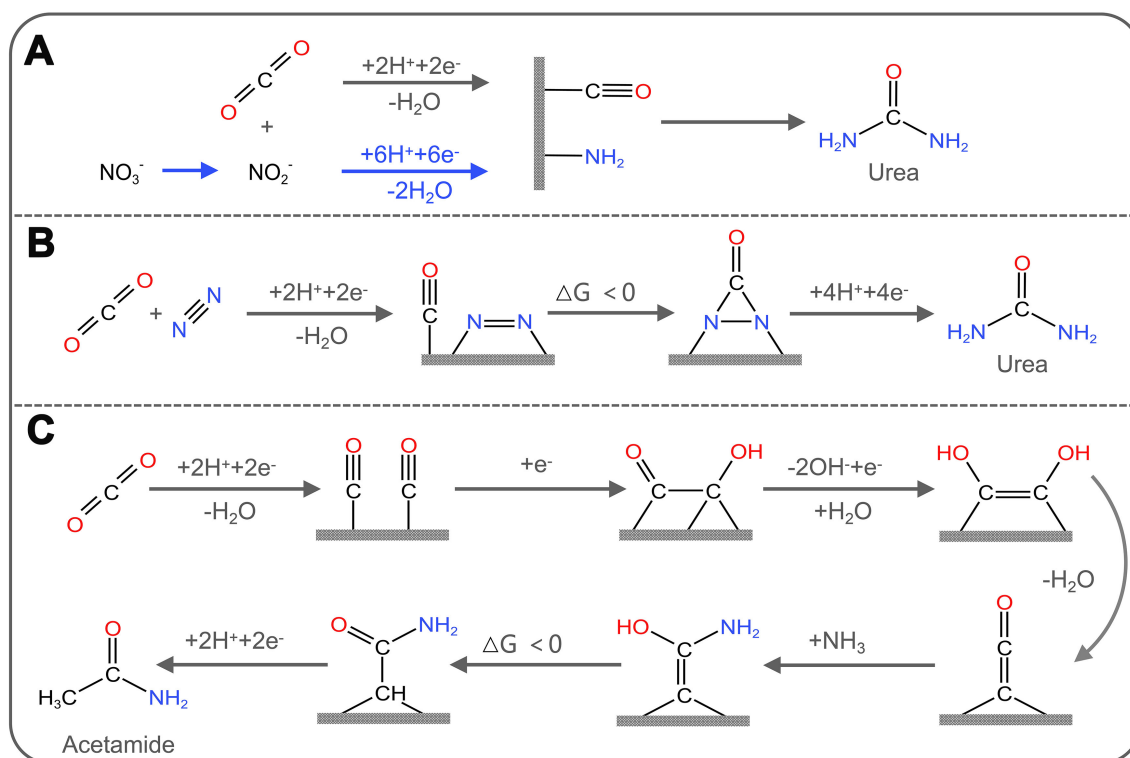


Figure 9. (A) Electrochemical synthetic pathway for urea from CO_2 and $\text{NO}_3^-/\text{NO}_2^-$; (B) Electrochemical synthetic pathway for urea from CO_2 and N_2 ; (C) Electrochemical synthetic pathway for urea from CO_2 and NH_3 .

Recently, remarkable progress has been made in C–N coupling reactions by electrocatalytic method using CO_2 and NO_x^- as feedstocks. NO_x^- have relatively low dissociation energies and high aqueous solubility compared to non-polar N_2 , which makes them more suitable for the electrosynthesis of compounds containing nitrogen (e.g., urea, amides, amino acids, *etc.*) via C–N coupling reactions. Jouny *et al.* reported that the ketene intermediate ($^*\text{C}=\text{C}=\text{O}$) produced by the coupling of two CO molecules adsorbed on the cathode acts as an electrophilic carbon center and is attacked by a nucleophilic amine to form the end product acetamide through successive protonation [Figure 9C]^[111]. Lv *et al.* achieved electrochemical coupling of NO_3^- with CO_2 over $\text{In}(\text{OH})_3$. The selectivity and yield of urea were 53.4% and $533.1 \mu\text{g}\cdot\text{h}^{-1}\cdot\text{mg}^{-1}$, respectively^[125]. In another study, Xu *et al.* achieved a yield urea of $436.9 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ with a FE up to 66.4%, and an ultra-long cyclic stability of 1,000 h by modulating the C- and N- reduction kinetics through Cu doping and $\text{Pd}_4\text{Cu}_1/\text{FeNi}(\text{OH})_2$ interface^[126]. In terms of amide product synthesis, Guo *et al.* reported a sustainable electrosynthesis method to synthesize formamide using CO_2 -derived HCOO^- and NO_2^- ^[127]. The FE of formamide on low-coordinated copper nanocubes (ER-Cu) could reach 29.7%. Furthermore, using CO_2 -derived CH_3OH and N_2 -derived NH_3 as feedstocks for direct synthesis of formamide by electrooxidation is also an effective strategy. The FE of formamide was up to 41.2% on commercial boron-doped diamond (BDD) catalysts^[128]. In terms of amino acid preparation, Fang *et al.* first discovered that the synthesis of C_{3+} amino acids from CO_2 and NH_3 can be electrocatalytically catalyzed by employing chiral Cu thin films (CCFs) as the electrodes, in which the FE of serine reached 1.2%^[129].

These studies suggest that typically, the amalgamation of electrophilic intermediates-containing carbon with nucleophilic intermediates-containing nitrogen generated through the co-reduction of CO_2 and nitrogen

oxides is a pivotal process in the establishment of C–N bonds. Consequently, the strategic development of electrocatalysts featuring dual active sites is crucial for enhancing the selectivity of the C–N coupling reaction.

As shown in Table 3, we summarized some representative examples of CO₂ electrolytic conversion and reactions with nitrogen-containing small molecules by constructing C–N bonds.

C–O bond formation

Redox-neutral CO₂ conversion is an important process for producing various carbonates [Figure 10]^[131-135]. Among the synthesizable carbonates, DMC has a wide range of applications, often as a solvent for lithium batteries, reagents for biodiesel production, fuel additives, and intermediates for polycarbonate synthesis. The market size for DMC is expected to grow to \$1.207 billion by 2025^[136-138]. Thermochemical methods have been developed to synthesize DMC from CO₂, but their inefficiencies and complex separation processes make them less likely to be industrialized. Therefore, the development of green and efficient synthesis methods remains an important challenge. To address this, Lee *et al.* explored a redox-neutral reaction approach to the formation of DMC from CO₂^[139]. A scheme for the redox-neutral electrochemical synthesis of DMC from CO₂ and CH₃OH is shown in Figure 11A. With the cathode and anode acting together in an undivided cell, solution-based non-homogeneous redox cycles are coupled to achieve electrical neutrality. Thus, electrons are transferred between the two electrodes by a CO₂RR reaction at the cathode and two redox cycles at the anode: CO₂/CO, Pd(0)/Pd(II), and Br⁻/Br₂. Experimental results show a maximum FE of 60% for DMC production at room temperature. The mechanism study shows that CO₂ and CH₃OH may be reduced to produce CO and MeO⁻ at the cathode. The Br₂ generated by anodizing Br⁻ oxidizes the Pd(0) complex to the Pd(II)Br₂ complex, which can react with CO to produce the Pd(II)(CO)Br adduct. Finally, DMC was formed by the reaction of Pd(II)(CO)Br adduct with MeO⁻ with generating Pd(0) complexes.

Recently, Li *et al.* developed a novel Ni single-atom catalyst (SAC) featuring a dual-channel superstructure. This SAC exhibits a distinctive site coordination configuration, characterized by bonding with one axial oxygen atom and four planar nitrogen atoms^[140]. The unique active sites are beneficial for the activation and conversion of CO₂ to CO with a high FE of 99%. Furthermore, the preparation of CO₂ to DMC with a purity of up to 80% was achieved through the petticoated Ni SAC. Studies on the mechanism have demonstrated that the axial oxygen coordination arrangement of the catalyst expedites the convergent paired electrosynthesis by diminishing the energy barriers associated with the formation of the *COOH intermediate and the dissociation of H₂O and CH₃OH.

The coupling of CO₂ with epoxides with the formation of cyclic carbonates is a highly attractive 100% atom economic reaction. It represents a greener and safer alternative to the conventional synthesis of cyclic carbonates from diols and toxic phosgene. The electrochemical synthesis of cyclic carbonates from diols and CO₂ in a reusable ionic liquid (IL)-based electrolyte without additional catalyst was reported by Wang *et al.* The reaction of CO₂⁻ with 1,2-butanediol is supposed to produce intermediates [Figure 10]. Then, the intermediate is converted into a linear carbonate during the esterification process, which immediately becomes a cyclic carbonate^[141]. Xiao *et al.* concurrently pioneered a one-step synthesis of enantiomerically pure cyclic carbonates through the electrolysis of chiral epoxides and CO₂ in an undivided cell. They utilized tetraethyl ammonium iodide (TEAI) in acetonitrile (MeCN) as the supporting electrolyte and solvent, maintaining a constant current [Figure 11B]^[142,143]. In another work, Pérez-Gallent *et al.* studied the reaction process of propylene oxide and CO₂ to synthesize propylene carbonate on copper electrodes in detail^[144]. The results indicated that the key to this reaction was the reduction of CO₂ to CO₂⁻ and the C–O bond was generated by CO₂⁻ attacking the epoxide.

Table 3. Selected examples of electrolytic conversion of CO₂ and (NO, NO₂⁻, NO₃⁻, NH₃, and N₂)

Substrate	Product	Electrode	Electrolyte	Current density or potential (vs. RHE)	FE
CO ₂ , NO	Urea	Zn NBs ^[122]	0.2 M KHCO ₃	- 0.92 V	11.3%
CO ₂ , NO ₂ ⁻	Urea	ZnO-V ^[117]	0.2 M NaHCO ₃ and 0.1 M NaNO ₂	- 0.79 V	23.3%
CO ₂ , NO ₃ ⁻	Urea	In(OH) ₃ -S ^[125]	0.1 M KNO ₃	- 0.6 V	53.4%
CO ₂ , NO ₃ ⁻	Urea	Pd ₄ Cu ₁ /FeNi(OH) ₂ ^[130]	0.1 M KHCO ₃ , 0.1 M KNO ₃	- 0.5 V	66.4%
CO ₂ , N ₂	Urea	Bi-BiVO ₄ ^[110]	KHCO ₃	- 0.40 V	12.6%
CO ₂ , N ₂	Urea	BiFeO ₃ /BiVO ₄ ^[124]	0.1 M KHCO ₃	- 0.4 V	17.2%
CO ₂ , N ₂	Urea	InOOH-100 ^[115]	0.1 M KHCO ₃	- 0.40 V	21.0%
CO ₂ , N ₂	Urea	V _N -Cu ₃ N-300 ^[123]	0.1 M KHCO ₃	- 0.4 V	28.7%
CO ₂ , N ₂	Urea	MOF Co-PMDA-2-mbIM ^[114]	0.1 M KHCO ₃	- 0.50 V	49.0%
CO ₂ , N ₂	Urea	Ga ₇₉ Cu ₁₁ Mo ₁₀ @C ^[113]	0.1 M KHCO ₃	- 0.40 V	60.6%
CO ₂ , NO ₃ ⁻	CH ₃ NH ₂	CoPc-NH ₂ /CNT ^[31]	0.1 M KNO ₃	- 0.92 V	13.0%
CO ₂ , NH ₃	Acetamide	Cu NPs ^[112]	1 M KOH	- 0.58 V	10.0%
CO, NH ₃	Acetamide	Cu NPs ^[111]	1 M KOH	300 mA·cm ⁻²	40.0%
CH ₃ OH, NH ₃	Formamide	BDD ^[128]	0.5 M NaHCO ₃	120 mA·cm ⁻²	41.2 %

RHE: Reversible hydrogen electrode; FE: Faradaic efficiency; NBs: nanobelts; CNT: carbon nanotube; NPs: nanoparticles; BDD: boron-doped diamond.

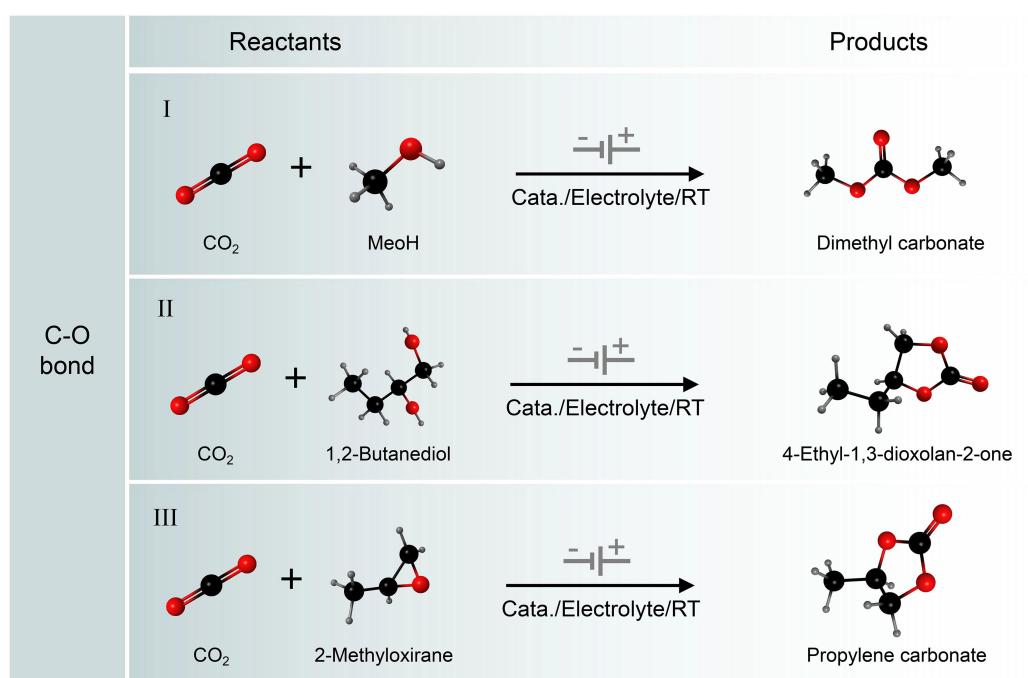


Figure 10. Electrocatalytic C–O coupling reactions. (I) Electrochemical conversion of CO₂ to dimethyl carbonate without altering the redox state; (II) Electrosynthesis of Cyclic Carbonates from CO₂ and Diols; (III) Electrosynthesis of cyclic carbonates from CO₂ and epoxides.

As shown in Table 4, we summarized some representative reactions of coupling CO₂ and organic small molecule substrates by constructing C–O bonds.

C–S bond formation

The construction of C–S bonds from CO₂ and S-containing species is important to the synthesis of

Table 4. Selected examples of electrolytic conversion of CO₂ and (methanol, diols, epoxides, and propylene oxide)

Substrate	Product	Electrode	Catalyst	Electrolyte	Solvent	Current or voltage	Yield
CO ₂ , methanol	DMC	Au plate ^[139]	Pd/C NaBr	0.1 M NaBr	Methanol	12 mA·cm ⁻²	60%
CO ₂ , methanol	DMC	Ni Sas/OMMNC ^[140]	Pd/C KBr	0.1 M KBr	Methanol	12 mA·cm ⁻²	80%
CO ₂ , diols	Cyclic carbonate	(-)Ni-Mg(+) ^[141]	/	C ₄ MIMBF ₄	C ₄ MIMBF ₄	-1.7 V	12%
CO ₂ , epoxides	Cyclic carbonate	(-)SS-Mg(+) ^[142]	/	TEAI	MeCN	2.88 mA	54%
CO ₂ , propylene oxide	Cyclic carbonate	Cu/CS-Il ^[143]	/	TEAI	MeCN	4.14 mA	95%

DMC: Dimethyl carbonate; TEAI: tetraethyl ammonium iodide; MeCN: acetonitrile.

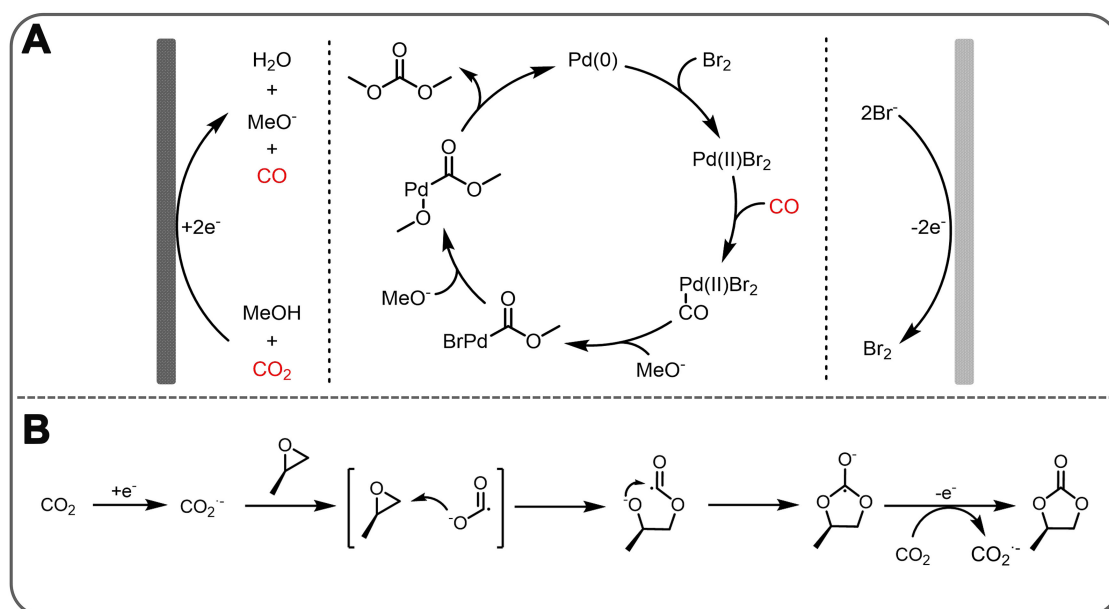


Figure 11. (A) Redox-neutral electrochemical system for dimethyl carbonate synthesis from CO₂ and schematic of the proposed reaction mechanism for DMC synthesis; (B) Electrochemical synthetic pathway for propylene carbonate from CO₂ and propylene oxide. DMC: Dimethyl carbonate.

sulfonates, which is widely used in pharmaceuticals, agriculture, and biology industries. Inspired by the electrochemical C–N bond formation from CO₂ and small-molecule N-sources, the C–S coupling may be in principle according to a similar reaction pathway, because S and N have similar properties from diagonal relationships [Figure 12]. Recently, Li *et al.* first constructed C–S bonds from CO₂ and SO₃²⁻ as the C and S resources on Cu-based catalysts^[145]. The electrosynthesis was carried out in a modified gas diffusion half-cell configuration, where CO₂ was supplied through the gas phase and 1 mol/L KOH with 200 mmol/L SO₃²⁻ was used as the electrolyte. After postreaction electrolysis at -0.68 V [vs. the reversible hydrogen electrode (RHE)] for 1 h, hydroxymethanesulfonate (HMS), sulfoacetate (SA), and methanesulfonate (MS) products were generated with a FE of up to 6.8%. The three products generated from CO₂ and SO₃²⁻ suggested three possible reaction pathways.

The relevant *in-situ* characterization experiments indicate that the C–S bond is formed by the attack of the SO₃²⁻ ion in the solution on the *CHOH intermediate generated on the catalyst surface [Figure 13]. The

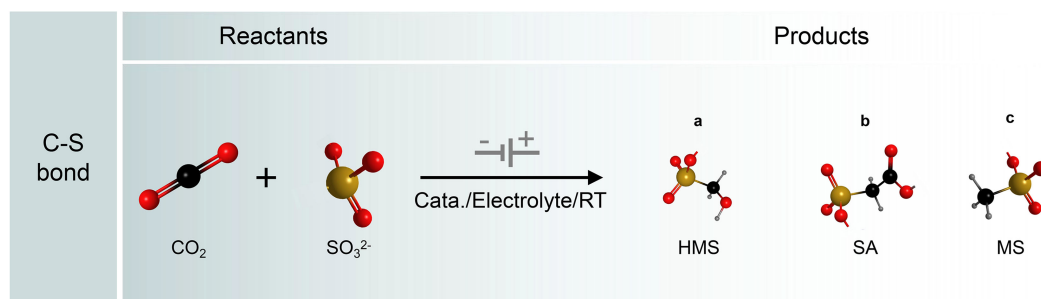


Figure 12. Electrocatalytic C–S coupling reactions and C–S products.

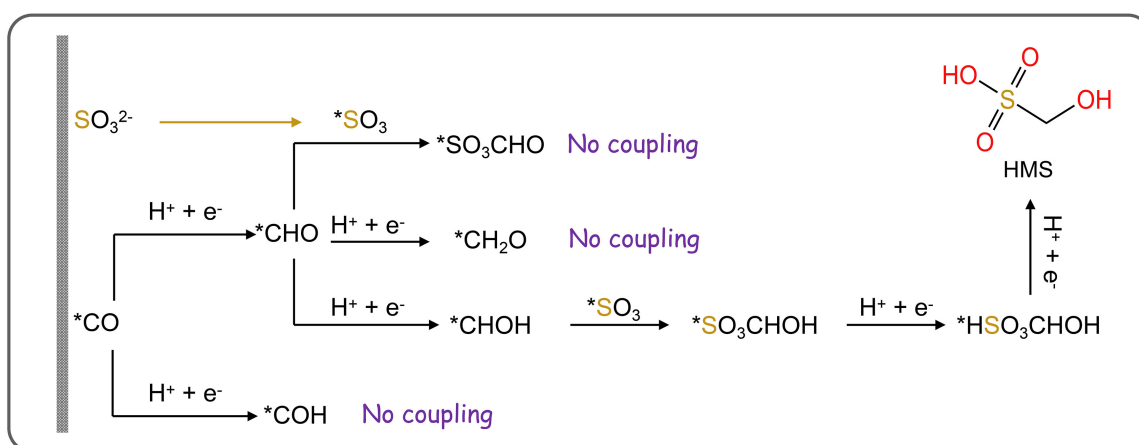


Figure 13. Reaction pathway from *CO to HMS. HMS: Hydroxymethanesulfonate.

authors speculate that the partially hydrogenated *CO (e.g., *CHO or CH_2O) in the pathway of CO_2 reduction to CH_4 may be the main species coupled to SO_3^{2-} to form HMS. SA and MS were preliminarily formed with SO_3^{2-} nucleophilically attacking on C_2 intermediates generated in the pathways of CO_2 reduction to CH_4 or acetic acid. Theoretical calculations reveal that among the intermediates (*COH , *CHO , and *CHOH) involved in C–S bond formation, coupling *CHOH with SO_3^{2-} exhibited the lowest energy barrier (0.74 eV) over Cu (100), compared to *COH and SO_3^{2-} coupling (1.37 eV). This indicates that *CHOH and SO_3^{2-} coupling is the key step. Enhancing C–S coupling efficiency in future studies requires designing catalytically active sites to reduce energy barriers for *CHOH and SO_3^{2-} coupling. Wu *et al.* underscored this study and remarked that it presents significant potential for synthesizing other high-value organics containing C–S bonds by adjusting CO_2 reduction pathways or employing alternative catalysts and sulfur sources to minimize redundancy^[146].

EFFECT OF THE ELECTROLYTE FOR ELECTROCATALYTIC REACTION

The type of electrolyte can also significantly influence electrocatalytic performance. The primary reason is that different concentrations of anions and cations in the electrolyte can lead to variations in buffering capacity^[147-149], pH value^[150,151], and proton donors^[152]. These factors often interact with each other, making it difficult to discuss the impact of any particular factor in detail. The following is a brief introduction to the effects of pH, cations, and anions in the electrolyte on the electrocatalytic CO_2 reactions, using the CO_2 reduction as a representative example.

As shown in Figure 14A, changes in proton donors (e.g., from H_3O^+ to H_2O) or oxidants (e.g., from OH^- to H_2O) with pH can have an order-of-magnitude effect on the rate of electrochemical CO_2 reduction steps. Electrochemical interfaces are, in general, highly charged, and these charges give rise to large interfacial electric fields at the electrode-electrolyte interface. These fields drive the transfer of electrons between the adsorbates involved in the reaction. The pH of the electrolyte also affects electrocatalytic activity through a solution-phase reaction with OH^- without any involvement of the electrode^[153]. When CO_2 dissolves in an aqueous solution, different carbonaceous species such as CO_2 , H_2CO_3 , HCO_3^- , and CO_3^{2-} are formed, thus leading to debate about the true active species in the reaction process [Figure 14B]^[149,152]. Studies have shown that under alkaline conditions, over 50% of the energy is used to recover CO_2 to CO_3^{2-} . In contrast, acidic conditions inhibit the conversion of CO_2 to CO_3^{2-} and facilitate material separation. However, under strong acidic conditions, protons are more likely to capture electrons, thus favoring hydrogen evolution over CO_2 reduction^[154]. To date, the aqueous solutions used in most studies are weakly acidic or alkaline electrolytes containing cations and buffering/non-buffering anions [Figure 14C]^[149,155,156]. In these electrolytes, larger cations such as K^+ and Cs^+ could adsorb on the electrode and reduce hydrogen evolution by repelling H^+ ions, whereas smaller cations such as Li^+ do not. In addition, larger cations are hydrolyzed in the vicinity of the cathode, thereby lowering the pH and increasing the local CO_2 concentration, increasing the product selectivity and reducing the formation of H_2 ^[155]. In addition to cations, anions also have a significant effect on the outcome of the electrocatalytic CO_2 reaction. Non-buffering halides such as Cl^- and Br^- enhance the product selectivity by affecting surface charges and inhibiting proton adsorption, whereas F^- negatively affects the product selectivity due to its weak adsorption capacity and high pH value. The use of anions with low buffering capacity inhibits the formation of H_2 and thus improves the reaction efficiency^[156].

DEVELOPMENT OF THE REACTOR IN THE ELECTROCATALYTIC REACTION

An in-depth study of the structural characteristics of different CO_2 electrolyzers and facilitating their engineering are all key to large-scale applications^[157]. Currently, the electrocatalytic performance is typically evaluated in H-cell electrolyzers, which employ an ion exchange membrane to separate anode and cathode compartments [Figure 15A]^[158-160]. However, the large distance between electrodes, membranes, and dilute electrolytes results in a high cell voltage and limited current density. To address these limitations, flow-cell [Figure 15B] and MEA-cell [Figure 15C] electrolyzers have been developed^[145,161-164]. Both can be operated continuously and utilize GDEs to improve CO_2 reaction efficiency. Flow-cell electrolyzers include a liquid electrolyte layer, while MEA-cell electrolyzers use a solid electrolyte membrane, resulting in lower ohmic resistance and improving energy efficiency^[165,166]. MEA-cell electrolyzers enable CO_2 electrolysis with pure water, similar to alkaline polymer electrolyte water electrolysis, but lack the ability to accurately measure potentials, posing a challenge to fundamental catalysis research^[67]. Although exciting progress has been made in GDE-type electrolyzers to prepare liquid products, such as formate and acetate, these liquid products are typically generated in and mixed with the electrolyte, requiring additional separation and concentration processes to recover a pure liquid product solution. To address this challenge, researchers designed a solid-state electrolyte (SSE)-type electrolyzer [Figure 15D], which is divided into three chambers, i.e., cathode, SSE, and anode chambers. It is used for direct production of pure liquid product solutions^[167,168]. Currently, electrolyzers used for C-H reactions formed from CO_2 and H_2O have been well applied in these devices. However, research on CO_2 -involved organic reactions (C-C, C-N, C-O bond formation) predominantly revolves around simple single-cell electrolyzers or H-type electrolyzers. In order to further improve the reaction efficiency, it is necessary to select suitable reactors according to different reaction systems.

According to the understanding of the above four types of electrolyzers and the review of related progress, we further summarize the advantages and disadvantages of each type [Figure 16], with the aim of accelerating the industrial application of CO_2 electrocatalytic conversion technology.

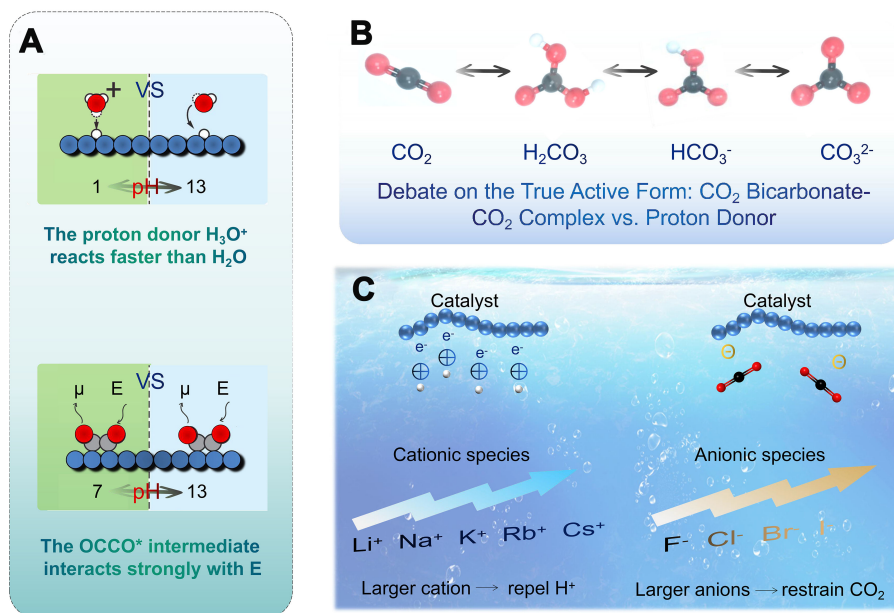


Figure 14. (A) The rate of electrocatalytic reactions can change with electrolyte pH primarily. Relative current densities are shown as bold numbers (Large electric fields E at high pH stabilize reactive intermediates with large dipole moments μ); (B) The discussion of $\text{CO}_2/\text{H}_2\text{CO}_3, \text{H}_2\text{CO}_3/\text{HCO}_3^-$, and $\text{HCO}_3^-/\text{CO}_3^{2-}$ equilibria in aqueous solutions; (C) The cation and anion effects relating to the CO_2 electroreduction.

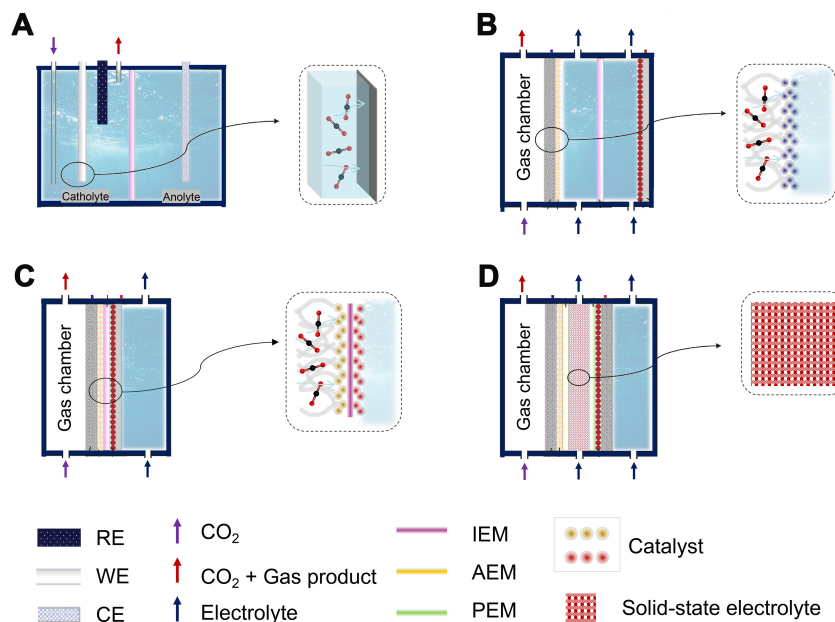


Figure 15. Different types of electrolyzers. (A) H-type electrolyzer; (B) GDE-type electrolyzer; (C) MEA-type electrolyzer; (D) Solid-state electrolyte type electrolyzer. GDE: Gas diffusion electrode; MEA: membrane electrode assembly; RE: reference electrode; WE: work electrode; CE: counter electrode; IEM: ion-exchange membranes; AEM: anion-exchange membrane; PEM: proton-exchange membrane.

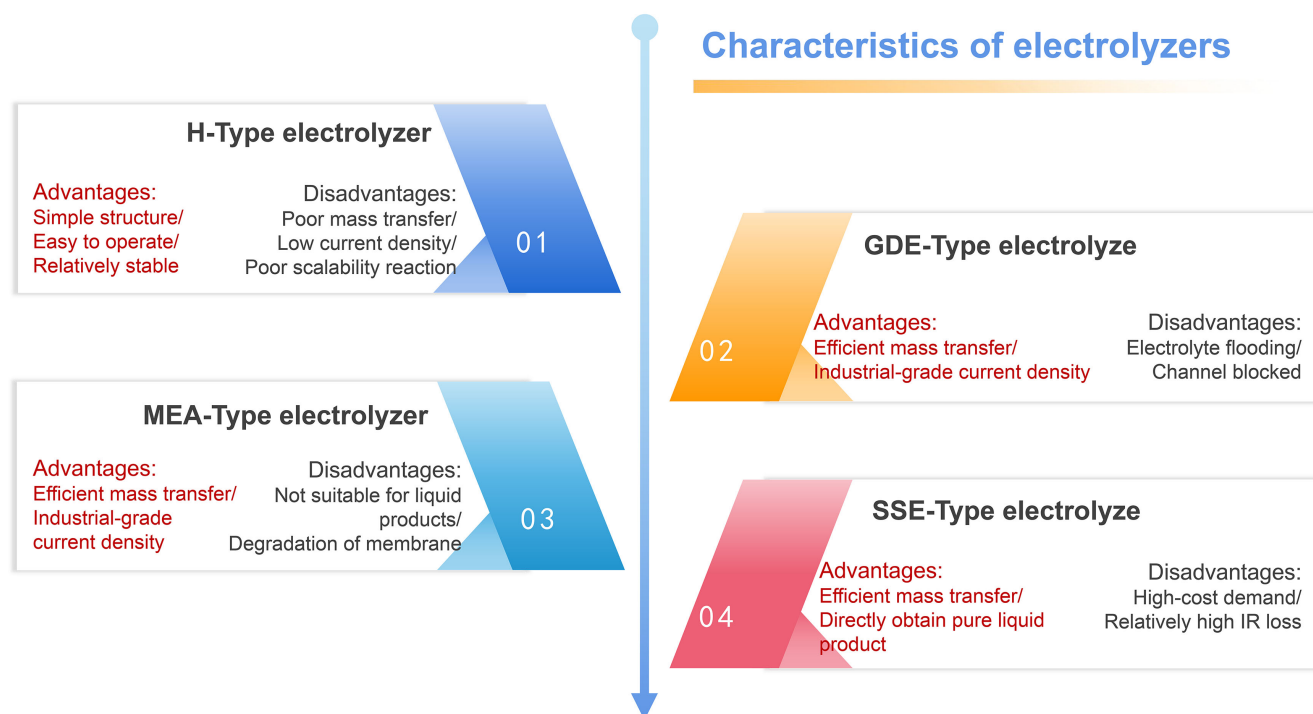


Figure 16. The advantages and disadvantages of electrolyzers.

CONCLUSIONS AND OUTLOOKS

In conclusion, the electrochemical conversion of CO₂ into value-added chemicals is a promising way to address the severely increasing CO₂ concentration in the atmosphere. New covalent bonds can be formed between CO₂ and substrate molecules, including C-H, C-C, C-N, C-O and C-S bonds, thereby broadening reaction pathways and producing diversified products. In this review, we summarize the recent advances in the electrocatalysis-enabled CO₂ cycle including the electrochemical C-X bond formation for high-value-added chemicals. We also discussed the fundamentals of electrocatalytic reactions on the initial activation of CO₂ and focused on the research progress of electrochemical C-X (C-H, C-C, C-N, C-O, C-S) coupling reactions, proposing improvement strategies for the shortcomings of electrocatalytic CO₂ coupled organic reactions and outlooks of their future research prospects. The following will give some views on (i) the strategies for the catalyst materials design and activity optimization and (ii) the future development of CO₂ and small molecules to form five kinds of bonds.

(I) The strategies for the catalyst materials design and activity optimization

In order to optimize the design and activity of catalyst materials for the electrochemical conversion of CO₂ into value-added chemicals, several advanced strategies can be employed. For example, nanostructural modification of catalysts can increase surface area and control morphology to improve catalytic activity and selectivity. Utilizing metallic and bimetallic catalysts as well as non-metallic options and heteroatom doping can modulate electronic properties and improve CO₂ activation. Electronic structure engineering through defect and strain engineering can create active sites and improve performance. The use of composite and hybrid catalysts can improve electron transfer and stability. Specifically, the integration of multiple types of active sites into a single system is a simple and versatile strategy that allows for the independent optimization of intermediate adsorption and catalytic activity for each component reaction. By leveraging the synergistic effects between various active sites at the atomic scale, the coordination environment of

atoms can be optimally adjusted. This approach provides active centers with varying charge distribution densities for the adsorption, activation, and conversion of different reactive molecules, and is becoming an important direction for the development of high-performance catalysts.

The following are some key factors in catalyst materials design:

(1) Active site design

Transition metal ligands: selecting appropriate transition metal ligands such as platinum, palladium, copper, *etc.*, and their coordination environments can adjust the electrophilicity and coordination ability of active sites. Ancillary ligands: introducing different ancillary ligands can modulate the catalyst's electronic structure and charge distribution, affecting the rate and selectivity of electron transfer.

(2) Surface modification

Synthesis methods: choosing suitable synthesis methods to control the crystal surface structure and surface chemical states of the catalyst can influence electron transfer capabilities and the specificity of chemical reactions. Surface engineering: enhancing catalyst surface site density and accessibility can improve reaction rates and selectivity.

(3) Control of electron transfer and energy barriers

Electron transfer pathways: designing catalysts to facilitate or hinder electron transfer can control the generation and dissociation of intermediates in reactions. Energy barrier tuning: adjusting the activation energy of reactions by modulating local electron densities on catalyst surfaces can enhance reaction rates and selectivity.

(4) Catalyst stability and regeneration

Enhancing stability: choosing stable catalyst materials and designing reaction conditions to minimize catalyst deactivation and corrosion. Regeneration strategies: developing effective catalyst regeneration methods to prolong catalyst lifetimes and reduce costs.

In addition, optimization of the electrolyte and design of an efficient catalyst-electrolyte interface can enhance reaction rates and reduce the energy barrier. Adjusting reaction conditions, including temperature, pressure, and applied potential, can optimize selectivity and efficiency. Improving stability and durability through corrosion-resistant materials and stable support structures ensures longer operational lifespans. Advanced characterization techniques and computational modeling provide deep insights into reaction mechanisms and guide the development of more effective catalysts. By implementing these strategies, researchers can significantly advance the field of electrocatalytic CO₂ conversion to address environmental and economic challenges.

(II) The future development of CO₂ and small molecules

(1) C-H bonds: currently, a variety of well-designed catalysts have been successfully used to convert CO₂ into various C₁ and C₂ products, and the reaction efficiency has also been greatly improved, but for C₃ and above products, the catalytic efficiency of the catalyst remains relatively low. The production of C₂ products often requires coupling between C₁ active species. If multiple C₁ active species are required for coupling, the formation of C₃, C₄, and other products must be a huge challenge because it involves the complex transfer of multiple electrons and protons. If C₁ and C₂ products can be further activated on the catalyst, coupled themselves, or further combined with CO₂, the primitive steps of the reaction will be greatly simplified, to achieve the synthesis of high-carbon products. For example, ethylene from the electrochemical conversion

of CO₂ can be activated by adsorption on a catalyst; then, there is the possibility of coupling between two or more molecules to obtain butane or high-carbon alkanes. The activated ethylene may also combine with one or two molecules of CO₂ to produce propionic or succinic acid. Of course, the special structure of the catalyst and microenvironment of the system is very demanding, but for the synthesis of high-carbon products, this is an effective strategy.

(2) C–C bonds: the electrochemical carboxylation of CO₂ with organic compounds is the main strategy to construct the C–C bond. Most of these organic compounds contain unsaturated bonds or highly polar covalent bonds, which help them to be activated at the cathode or easily bind to CO₂ anion radicals. Such reactions usually employ ordinary graphite electrodes or bare metal sheet electrodes as cathodes, and the high selectivity of the product is obtained by optimizing the electrolyte solution. The larger the conjugated structure of the substrate or the stronger the polarity of the covalent bond, the higher the reactivity is. However, less research has been done on the carboxylation of substrates with non-conjugated structures and weakly polar covalent bonds. These electrochemically inert substrates are difficult to activate on the surface of ordinary electrodes and do not readily combine with the radical anion of CO₂. Although some teams have recently realized the carboxylation of sp² C–H bonds, the current efficiency is extremely low. For the carboxylation reaction of electrochemically inert substrates, it may be necessary to get rid of simple bare electrodes and rely on new electrocatalysts to activate the inert substrate and reduce its activation potential to achieve efficient binding with CO₂. Based on current research progress, the application of electrocatalysts in electrochemical carboxylation reactions is still widely unexplored. However, it will be a powerful tool to explore the carboxylation of electrochemical inert substrates in the future and help to achieve highly selective carboxylation of common sp³ C–H bonds.

(3) C–N bonds: the reaction between CO₂ and inorganic nitrogen sources to form urea by constructing C–N bonds is being widely explored. However, amides, another class of products that form new C–N bonds, have been less studied. The transition of C–N bond products from urea to amide by designing catalysts may become the focus of future research. The formation of the C–N bond does not have to be limited to the combination of CO₂ and inorganic nitrogen sources, but CO₂ can also be combined with organic nitrogen sources to achieve the functional group of organic compounds. Furthermore, enhancing the efficiency, cost-effectiveness, and environmental sustainability of catalytic systems for large-scale electrosynthesis of organic nitrogen compounds via C–N coupling reactions under mild conditions requires further investigation.

(4) C–O bonds: the reaction of alcohols or epoxides with CO₂ to form carbonates by constructing C–O bonds has been extensively studied. By adjusting the electrode and electrolyte, the target product can be obtained with high selectivity. Cyclic carbonates are in high demand as monomers for polymers. The strategy of obtaining cyclic carbonates directly from CO₂ is extremely attractive, but there are few related studies. In principle, CO₂ can be converted into ethylene oxide by pairwise reaction of anode and cathode. By further combining ethylene oxide with CO₂, cyclic carbonates can be obtained. In the future, this will be an attractive green synthetic strategy.

(5) C–S bonds: at present, the electrolyte system of this reaction was alkaline, which will cause low CO₂ utilization efficiency. Acid electrolyte system can be explored to improve the utilization efficiency of CO₂. On the other hand, it is necessary to design efficient catalysts and electrolyzers to improve the FEs of C–S products and understand the mechanism of the reaction. Finally, the types of S sources can be explored, which may result in more diverse products.

Meanwhile, to advance the field, great achievements have been made in understanding the reaction pathways of electrocatalytic CO₂ conversion using advanced *in situ* and operational techniques and theoretical calculations. To further explain the catalytic mechanism, analyzing the reaction pathways, surface charges, and free energies on the catalyst surface by constructing emerging operational computational models can be beneficial for us to better understand the energy and thermodynamics of non-uniform electrocatalytic reactions, such as the potential dependence of the activation energy, the interactions between intermediate coverings, and the adsorption-adsorption interactions.

More importantly, the following factors should be considered for future large-scale application of electrocatalytic production: (i) the decreasing price of renewable electrical energy; (ii) developing low-cost and long-term stable catalysts; (iii) avoiding use of harmful organic solvent and additives; (iv) preparing efficient electrolyzers and durable membranes; and (v) solving the problem of product separation and purification. In this regard, direct-current electrolyzer units have shown great advantages in realizing industrial-scale currents and hold promise for large-scale production of valuable fuels and high-value-added chemicals.

DECLARATIONS

Authors' contributions

Manuscript preparation: Jia S, Dong M

Manuscript correction: Zhu Q, Kang X, Wu H, Han B

All authors contributed to the general discussion.

Availability of data and materials

Not applicable.

Financial support and sponsorship

The work was supported by the National Key Research and Development Program of China (2023YFA1507440, 2020YFA0710201), the National Natural Science Foundation of China (22279146, 21890761, 22121002), the China Postdoctoral Science Foundation (2023M731096), and the Fundamental Research Funds for the Central Universities.

Conflicts of interest

Zhu Q and Kang X are Junior Editorial Board members of the journal *Chemical Synthesis*, while the other authors have declared that they have no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Copyright

© The Author(s) 2024.

REFERENCES

1. He M, Sun Y, Han B. Green carbon science: scientific basis for integrating carbon resource processing, utilization, and recycling. *Angew Chem Int Ed Engl* 2013;52:9620-33. DOI PubMed
2. Wang Y, Wang C, Li M, Yu Y, Zhang B. Nitrate electroreduction: mechanism insight, *in situ* characterization, performance evaluation, and challenges. *Chem Soc Rev* 2021;50:6720-33. DOI

3. Huang Y, Wang Y, Wu Y, Yu Y, Zhang B. Electrocatalytic construction of the C-N bond from the derivatives of CO₂ and N₂. *Sci China Chem* 2022;65:204-6. [DOI](#)
4. Pang Y, Li J, Wang Z, et al. Efficient electrocatalytic conversion of carbon monoxide to propanol using fragmented copper. *Nat Catal* 2019;2:251-8. [DOI](#)
5. Ran CK, Xiao HZ, Liao LL, Ju T, Zhang W, Yu DG. Progress and challenges in dicarboxylation with CO₂. *NSO* 2023;2:20220024. [DOI](#)
6. Zhou Z, Pei Z, Wei L, Zhao S, Jian X, Chen Y. Electrocatalytic hydrogen evolution under neutral pH conditions: current understandings, recent advances, and future prospects. *Energy Environ Sci* 2020;13:3185-206. [DOI](#)
7. Guo N, Xue H, Bao A, et al. Achieving superior electrocatalytic performance by surface copper vacancy defects during electrochemical etching process. *Angew Chem Int Ed Engl* 2020;59:13778-84. [DOI](#)
8. Zhou Y, Che F, Liu M, et al. Dopant-induced electron localization drives CO₂ reduction to C₂ hydrocarbons. *Nat Chem* 2018;10:974-80. [DOI](#) [PubMed](#)
9. Yang D, Zhu Q, Han B. Electroreduction of CO₂ in ionic liquid-based electrolytes. *Innovation* 2020;1:100016. [DOI](#) [PubMed](#) [PMC](#)
10. Wang Q, Wang Y, Liu M, Chu G, Qiu Y. Recent advances in photochemical/electrochemical carboxylation of olefins with CO₂. *Chin J Chem* 2024;42:2249-66. [DOI](#)
11. Jin H, Yu H, Li H, et al. MXene analogue: a 2D nitridene solid solution for high-rate hydrogen production. *Angew Chem Int Ed Engl* 2022;61:e202203850. [DOI](#) [PubMed](#) [PMC](#)
12. Chang S, Bu J, Li J, et al. Highly efficient electrocatalytic deuteration of acetylene to deuterated ethylene using deuterium oxide. *Chin Chem Lett* 2023;34:107765. [DOI](#)
13. Zeng W, Qiu Y. Electrochemical conversion of organic compounds and inorganic small molecules. *Sci China Chem* 2024;67:3223-46. [DOI](#)
14. Liu X, Zhang K, Tao L, Lu X, Zhang W. Recent advances in electrochemical carboxylation reactions using carbon dioxide. *Green Chem Eng* 2022;3:125-37. [DOI](#)
15. Zhao Z, Liu Y, Wang S, et al. Site-selective electrochemical C-H carboxylation of arenes with CO₂. *Angew Chem Int Ed Engl* 2023;62:e202214710. [DOI](#) [PubMed](#)
16. Zhang W, Liao LL, Li L, et al. Electroreductive dicarboxylation of unactivated skipped dienes with CO₂. *Angew Chem Int Ed Engl* 2023;62:e202301892. [DOI](#) [PubMed](#)
17. Wang Y, Tang S, Yang G, Wang S, Ma D, Qiu Y. Electrocatalytic carboxylation of aryl epoxides with CO₂ for the facile and selective synthesis of β-hydroxy acids. *Angew Chem Int Ed Engl* 2022;61:e202207746. [DOI](#) [PubMed](#)
18. Zhou H, Ren Y, Li Z, et al. Electrocatalytic upcycling of polyethylene terephthalate to commodity chemicals and H₂ fuel. *Nat Commun* 2021;12:4679. [DOI](#) [PubMed](#) [PMC](#)
19. Wang T, Tao L, Zhu X, et al. Combined anodic and cathodic hydrogen production from aldehyde oxidation and hydrogen evolution reaction. *Nat Catal* 2022;5:66-73. [DOI](#)
20. Zhang B, Jiang Y, Gao M, Ma T, Sun W, Pan H. Recent progress on hybrid electrocatalysts for efficient electrochemical CO₂ reduction. *Nano Energy* 2021;80:105504. [DOI](#)
21. Singh K, Sohal HS, Singh B. Synthesis of α-hydroxycarboxylic acids from various aldehydes and ketones by direct electrocarboxylation: a facile, efficient and atom economy protocol. *Asian J Chem* 2021;33:839-45. [DOI](#)
22. Krzywda PM, Paradelo Rodríguez A, Benes NE, Mei BT, Mul G. Carbon-nitrogen bond formation on Cu electrodes during CO₂ reduction in NO₃⁻ solution. *Appl Catal B Environ* 2022;316:121512. [DOI](#)
23. Li JY, Song QW, Zhang K, Liu P. Catalytic conversion of carbon dioxide through C-N bond formation. *Molecules* 2019;24:182. [DOI](#) [PubMed](#) [PMC](#)
24. Li R, Xiang K, Liu Z, Peng Z, Zou Y, Wang S. Recent advances in upgrading of low-cost oxidants to value-added products by electrocatalytic reduction reaction. *Adv Funct Mater* 2022;32:2208212. [DOI](#)
25. You B, Sun Y. Innovative strategies for electrocatalytic water splitting. *Acc Chem Res* 2018;51:1571-80. [DOI](#) [PubMed](#)
26. Seh ZW, Kibsgaard J, Dickens CF, Chorkendorff I, Nørskov JK, Jaramillo TF. Combining theory and experiment in electrocatalysis: insights into materials design. *Science* 2017;355:eaad4998. [DOI](#) [PubMed](#)
27. Zhang H, Chang X, Chen JG, et al. Computational and experimental demonstrations of one-pot tandem catalysis for electrochemical carbon dioxide reduction to methane. *Nat Commun* 2019;10:3340. [DOI](#) [PubMed](#) [PMC](#)
28. Wang X, de Araújo JF, Ju W, et al. Mechanistic reaction pathways of enhanced ethylene yields during electroreduction of CO₂-CO co-feeds on Cu and Cu-tandem electrocatalysts. *Nat Nanotechnol* 2019;14:1063-70. [DOI](#) [PubMed](#)
29. Tang C, Zheng Y, Jaroniec M, Qiao SZ. Electrocatalytic refinery for sustainable production of fuels and chemicals. *Angew Chem Int Ed Engl* 2021;60:19572-90. [DOI](#) [PubMed](#)
30. Peng C, Luo G, Zhang J, et al. Double sulfur vacancies by lithium tuning enhance CO₂ electroreduction to n-propanol. *Nat Commun* 2021;12:1580. [DOI](#) [PubMed](#) [PMC](#)
31. Muechez L, De Vos DE, Kim M. Sacrificial anode-free electrosynthesis of α-hydroxy acids via electrocatalytic coupling of carbon dioxide to aromatic alcohols. *ACS Sustainable Chem Eng* 2019;7:15860-4. [DOI](#)
32. Li Z, Qu Y, Wang J, et al. Highly selective conversion of carbon dioxide to aromatics over tandem catalysts. *Joule* 2019;3:570-83. [DOI](#)
33. Lum Y, Ager JW. Sequential catalysis controls selectivity in electrochemical CO₂ reduction on Cu. *Energy Environ Sci* 2018;11:2935-44. [DOI](#)

34. Leow WR, Lum Y, Ozden A, et al. Chloride-mediated selective electrosynthesis of ethylene and propylene oxides at high current density. *Science* 2020;368:1228-33. DOI PubMed
35. Wu Y, Jiang Z, Lin Z, Liang Y, Wang H. Direct electrosynthesis of methylamine from carbon dioxide and nitrate. *Nat Sustain* 2021;4:725-30. DOI
36. Deng T, Jia S, Han S, et al. Electrochemical CO₂ reduction to C₂₊ products over Cu/Zn intermetallic catalysts synthesized by electrodeposition. *Front Energy* 2024;18:80-8. DOI
37. De Luna P, Quintero-Bermudez R, Dinh CT, et al. Catalyst electro-redeposition controls morphology and oxidation state for selective carbon dioxide reduction. *Nat Catal* 2018;1:103-10. DOI
38. Zhu Q, Ma J, Kang X, et al. Efficient reduction of CO₂ into formic acid on a lead or tin electrode using an ionic liquid catholyte mixture. *Angew Chem Int Ed Engl* 2016;55:9012-6. DOI PubMed
39. Zhang S, Fan Q, Xia R, Meyer TJ. CO₂ reduction: from homogeneous to heterogeneous electrocatalysis. *Acc Chem Res* 2020;53:255-64. DOI
40. Kim D, Xie C, Becknell N, et al. Electrochemical activation of CO₂ through atomic ordering transformations of AuCu nanoparticles. *J Am Chem Soc* 2017;139:8329-36. DOI PubMed
41. Gao S, Lin Y, Jiao X, et al. Partially oxidized atomic cobalt layers for carbon dioxide electroreduction to liquid fuel. *Nature* 2016;529:68-71. DOI PubMed
42. Gao D, Zhou H, Wang J, et al. Size-dependent electrocatalytic reduction of CO₂ over Pd nanoparticles. *J Am Chem Soc* 2015;137:4288-91. DOI
43. Lu Q, Rosen J, Zhou Y, et al. A selective and efficient electrocatalyst for carbon dioxide reduction. *Nat Commun* 2014;5:3242. DOI PubMed
44. Medina-Ramos J, DiMeglio JL, Rosenthal J. Efficient reduction of CO₂ to CO with high current density using in situ or ex situ prepared Bi-based materials. *J Am Chem Soc* 2014;136:8361-7. DOI PubMed PMC
45. Ma W, Xie S, Liu T, et al. Electrocatalytic reduction of CO₂ to ethylene and ethanol through hydrogen-assisted C-C coupling over fluorine-modified copper. *Nat Catal* 2020;3:478-87. DOI
46. Zhang S, Kang P, Meyer TJ. Nanostructured tin catalysts for selective electrochemical reduction of carbon dioxide to formate. *J Am Chem Soc* 2014;136:1734-7. DOI
47. Wu Y, Jiang Z, Lu X, Liang Y, Wang H. Domino electroreduction of CO₂ to methanol on a molecular catalyst. *Nature* 2019;575:639-42. DOI
48. Jia S, Zhu Q, Wu H, et al. Preparation of trimetallic electrocatalysts by one-step co-electrodeposition and efficient CO₂ reduction to ethylene. *Chem Sci* 2022;13:7509-15. DOI PubMed PMC
49. Song Y, Chen W, Zhao C, Li S, Wei W, Sun Y. Metal-free nitrogen-doped mesoporous carbon for electroreduction of CO₂ to ethanol. *Angew Chem Int Ed Engl* 2017;56:10840-4. DOI PubMed
50. Jia S, Zhu Q, Chu M, et al. Hierarchical metal-polymer hybrids for enhanced CO₂ electroreduction. *Angew Chem Int Ed Engl* 2021;60:10977-82. DOI PubMed
51. Nam DH, De Luna P, Rosas-Hernández A, et al. Molecular enhancement of heterogeneous CO₂ reduction. *Nat Mater* 2020;19:266-76. DOI
52. Li F, Thevenon A, Rosas-Hernández A, et al. Molecular tuning of CO₂-to-ethylene conversion. *Nature* 2020;577:509-13. DOI PubMed
53. Ren S, Joulié D, Salvatore D, et al. Molecular electrocatalysts can mediate fast, selective CO₂ reduction in a flow cell. *Science* 2019;365:367-9. DOI PubMed
54. Nørskov JK, Bligaard T, Logadottir A, et al. Trends in the exchange current for hydrogen evolution. *J Electrochem Soc* 2005;152:J23. DOI
55. Shi R, Wang Z, Zhao Y, et al. Room-temperature electrochemical acetylene reduction to ethylene with high conversion and selectivity. *Nat Catal* 2021;4:565-74. DOI
56. Zhang Z, Wen G, Luo D, et al. "Two ships in a bottle" design for Zn-Ag-O catalyst enabling selective and long-lasting CO₂ electroreduction. *J Am Chem Soc* 2021;143:6855-64. DOI PubMed
57. Ren W, Tan X, Yang W, et al. Isolated diatomic Ni-Fe metal-nitrogen sites for synergistic electroreduction of CO₂. *Angew Chem Int Ed Engl* 2019;58:6972-6. DOI PubMed
58. Hu C, Gao Y, Zhao L, Dai L. Carbon-based metal-free electrocatalysts: recent progress and forward looking. *Chem Catal* 2022;2:2150-6. DOI
59. Kondo T, Casolo S, Suzuki T, et al. Atomic-scale characterization of nitrogen-doped graphite: effects of dopant nitrogen on the local electronic structure of the surrounding carbon atoms. *Phys Rev B* 2012;86:035436. DOI
60. Guo D, Shibuya R, Akiba C, Saji S, Kondo T, Nakamura J. Active sites of nitrogen-doped carbon materials for oxygen reduction reaction clarified using model catalysts. *Science* 2016;351:361-5. DOI PubMed
61. Bagger A, Ju W, Varela AS, Strasser P, Rossmeisl J. Electrochemical CO₂ reduction: a classification problem. *Chemphyschem* 2017;18:3266-73. DOI PubMed
62. Katayama Y, Nattino F, Giordano L, et al. An *in situ* surface-enhanced infrared absorption spectroscopy study of electrochemical CO₂ reduction: selectivity dependence on surface C-bound and O-bound reaction intermediates. *J Phys Chem C* 2019;123:5951-63. DOI

63. Lin R, Ma X, Cheong WC, et al. PdAg bimetallic electrocatalyst for highly selective reduction of CO₂ with low COOH* formation energy and facile CO desorption. *Nano Res* 2019;12:2866-71. DOI
64. Deng T, Jia S, Chen C, et al. Polymer modification strategy to modulate reaction microenvironment for enhanced CO₂ electroreduction to ethylene. *Angew Chem Int Ed Engl* 2024;63:e202313796. DOI PubMed
65. Chen X, Jia S, Chen C, et al. Highly stable layered coordination polymer electrocatalyst toward efficient CO₂-to-CH₄ conversion. *Adv Mater* 2024;36:e2310273. DOI PubMed
66. de Arquer FPG, Dinh CT, Ozden A, et al. CO₂ electrolysis to multicarbon products at activities greater than 1 A cm⁻². *Science* 2020;367:661-6. DOI PubMed
67. Li W, Yin Z, Gao Z, et al. Bifunctional ionomers for efficient co-electrolysis of CO₂ and pure water towards ethylene production at industrial-scale current densities. *Nat Energy* 2022;7:835-43. DOI
68. Endrődi B, Kecsenovity E, Samu A, et al. High carbonate ion conductance of a robust PiperION membrane allows industrial current density and conversion in a zero-gap carbon dioxide electrolyzer cell. *Energy Environ Sci* 2020;13:4098-105. DOI
69. Zhang Y, Zhang XY, Sun WY. In situ carbon-encapsulated copper-doped cerium oxide derived from MOFs for boosting CO₂-to-CH₄ electro-conversion. *ACS Catal* 2023;13:1545-53. DOI
70. Jiang Y, Mao K, Li J, et al. Pushing the performance limit of Cu/CeO₂ catalyst in CO₂ electroreduction: a cluster model study for loading single atoms. *ACS Nano* 2023;17:2620-8. DOI
71. Li H, Cao S, Sun H, et al. CuNCN derived Cu-based/CxNy catalysts for highly selective CO₂ electroreduction to hydrocarbons. *Appl Catal B Environ* 2023;320:121948. DOI
72. Zou H, Zhao G, Dai H, et al. Electronic perturbation of copper single-atom CO₂ reduction catalysts in a molecular way. *Angew Chem Int Ed Engl* 2023;62:e202217220. DOI PubMed
73. Shi G, Xie Y, Du L, et al. Constructing Cu-C bonds in a graphdiyne-regulated cu single-atom electrocatalyst for CO₂ reduction to CH₄. *Angew Chem Int Ed Engl* 2022;61:e202203569. DOI PubMed
74. Wang Z, Zhou Y, Xia C, Guo W, You B, Xia BY. Efficient electroconversion of carbon dioxide to formate by a reconstructed amino-functionalized indium-organic framework electrocatalyst. *Angew Chem Int Ed Engl* 2021;60:19107-12. DOI PubMed
75. Cui K, Zhang Z, Wang C, Lyu P, Tang X, Xu Y. Modulating the D-π-A interactions in metal-covalent organic frameworks for efficient electroreduction of CO₂ into formate. *Angew Chem Int Ed Engl* 2024;63:e202407298. DOI PubMed
76. Zhu ZH, Zhao BH, Hou SL, et al. A facile strategy for constructing a carbon-particle-modified metal-organic framework for enhancing the efficiency of CO₂ electroreduction into formate. *Angew Chem Int Ed Engl* 2021;60:23394-402. DOI PubMed
77. Luo W, Xie W, Mutschler R, et al. Selective and stable electroreduction of CO₂ to CO at the copper/indium interface. *ACS Catal* 2018;8:6571-81. DOI
78. Rasul S, Anjum DH, Jedidi A, Minenkov Y, Cavallo L, Takanabe K. A highly selective copper-indium bimetallic electrocatalyst for the electrochemical reduction of aqueous CO₂ to CO. *Angew Chem Int Ed Engl* 2015;54:2146-50. DOI PubMed
79. Yan C, Li H, Ye Y, et al. Coordinatively unsaturated nickel-nitrogen sites towards selective and high-rate CO₂ electroreduction. *Energy Environ Sci* 2018;11:1204-10. DOI
80. Jia S, Zhu Q, Han S, et al. Ultra-fast synthesis of three-dimensional porous Cu/Zn heterostructures for enhanced carbon dioxide electroreduction. *Chem Sci* 2023;14:11474-80. DOI PubMed PMC
81. Liu C, Zhang XD, Huang JM, Guan MX, Xu M, Gu ZY. In situ reconstruction of Cu-N coordinated MOFs to generate dispersive Cu/Cu₂O nanoclusters for selective electroreduction of CO₂ to C₂H₄. *ACS Catal* 2022;12:15230-40. DOI
82. Zhang XD, Liu T, Liu C, et al. Asymmetric low-frequency pulsed strategy enables ultralong CO₂ reduction stability and controllable product selectivity. *J Am Chem Soc* 2023;145:2195-206. DOI PubMed
83. He Q, Li H, Hu Z, Lei L, Wang D, Li TT. Highly selective CO₂ electroreduction to C₂H₄ using a dual-sites Cu(II) porphyrin framework coupled with Cu₂O nanoparticles via a synergistic-tandem strategy. *Angew Chem Int Ed Engl* 2024;63:e202407090. DOI PubMed
84. Zhang Y, Li P, Zhao C, et al. Multicarbon generation factory: CuO/Ni single atoms tandem catalyst for boosting the productivity of CO₂ electrocatalysis. *Sci Bull* 2022;67:1679-87. DOI PubMed
85. Xu H, Rebollar D, He H, et al. Highly selective electrocatalytic CO₂ reduction to ethanol by metallic clusters dynamically formed from atomically dispersed copper. *Nat Energy* 2020;5:623-32. DOI
86. Gu Z, Shen H, Chen Z, et al. Efficient electrocatalytic CO₂ reduction to C₂₊ alcohols at defect-site-rich Cu surface. *Joule* 2021;5:429-40. DOI
87. Guo C, Guo Y, Shi Y, et al. Electrocatalytic reduction of CO₂ to ethanol at close to theoretical potential via engineering abundant electron-donating Cu^{δ+} species. *Angew Chem Int Ed Engl* 2022;61:e202205909. DOI PubMed
88. Qiu XF, Huang JR, Yu C, et al. A stable and conductive covalent organic framework with isolated active sites for highly selective electroreduction of carbon dioxide to acetate. *Angew Chem Int Ed Engl* 2022;61:e202206470. DOI PubMed
89. Liu Y, Chen S, Quan X, Yu H. Efficient electrochemical reduction of carbon dioxide to acetate on nitrogen-doped nanodiamond. *J Am Chem Soc* 2015;137:11631-6. DOI
90. Sun X, Zhu Q, Kang X, et al. Design of a Cu(i)/C-doped boron nitride electrocatalyst for efficient conversion of CO₂ into acetic acid. *Green Chem* 2017;19:2086-91. DOI
91. Zhang R, Zhang J, Wang S, et al. Synthesis of n-Propanol from CO₂ electroreduction on bicontinuous Cu₂O/Cu nanodomains. *Angew Chem Int Ed Engl* 2024;63:e202405733. DOI PubMed

92. Alkayal A, Tabas V, Montanaro S, Wright IA, Malkov AV, Buckley BR. Harnessing applied potential: selective β -hydrocarboxylation of substituted olefins. *J Am Chem Soc* 2020;142:1780-5. DOI PubMed
93. Sheta AM, Alkayal A, Mashaly MA, et al. Selective electrocatalytic hydrocarboxylation of α,β -unsaturated esters with carbon dioxide**. *Angew Chem Int Ed Engl* 2021;60:21832-7. DOI PubMed PMC
94. Sheta AM, Mashaly MA, Said SB, Elmorsy SS, Malkov AV, Buckley BR. Selective α,δ -hydrocarboxylation of conjugated dienes utilizing CO₂ and electrosynthesis. *Chem Sci* 2020;11:9109-14. DOI PubMed PMC
95. Liao LL, Wang ZH, Cao KG, et al. Electrochemical ring-opening dicarboxylation of strained carbon-carbon single bonds with CO₂: facile synthesis of diacids and derivatization into polyesters. *J Am Chem Soc* 2022;144:2062-8. DOI
96. Sun GQ, Zhang W, Liao LL, et al. Nickel-catalyzed electrochemical carboxylation of unactivated aryl and alkyl halides with CO₂. *Nat Commun* 2021;12:7086. DOI PubMed PMC
97. Wang Y, Zhao Z, Pan D, et al. Metal-free electrochemical carboxylation of organic halides in the presence of catalytic amounts of an organomediator. *Angew Chem Int Ed Engl* 2022;61:e202210201. DOI PubMed
98. Sun GQ, Yu P, Zhang W, et al. Electrochemical reactor dictates site selectivity in N-heteroarene carboxylations. *Nature* 2023;615:67-72. DOI PubMed PMC
99. Yuan G, Jiang H, Lin C, Liao S. Efficient electrochemical synthesis of 2-arylsuccinic acids from CO₂ and aryl-substituted alkenes with nickel as the cathode. *Electrochimica Acta* 2008;53:2170-6. DOI
100. Li C, Yuan G, Ji X, Wang X, Ye J, Jiang H. Highly regioselective electrochemical synthesis of dioic acids from dienes and carbon dioxide. *Electrochim Acta* 2011;56:1529-34. DOI
101. Chen BL, Tu ZY, Zhu HW, Sun WW, Wang H, Lu JX. CO₂ as a C₁-organic building block: Enantioselective electrocarboxylation of aromatic ketones with CO₂-catalyzed by cinchona alkaloids under mild conditions. *Electrochimica Acta* 2014;116:475-83. DOI
102. Feng Q, Huang K, Liu S, Yu J, Liu F. Electrocatalytic carboxylation of aromatic ketones with carbon dioxide in ionic liquid 1-butyl-3-methylimidazoliumtetrafluoroborate to α -hydroxy-carboxylic acid methyl ester. *Electrochim Acta* 2011;56:5137-41. DOI
103. Yang H, Wu L, Wang H, Lu J. Cathode made of compacted silver nanoparticles for electrocatalytic carboxylation of 1-phenethyl bromide with CO₂. *Chin J Catal* 2016;37:994-8. DOI
104. Li C, Song X, Tao L, et al. Electrogenerated-bases promoted electrochemical synthesis of N-bromoamino acids from imines and carbon dioxide. *Tetrahedron* 2014;70:1855-60. DOI
105. Xie SL, Gao XT, Wu HH, Zhou F, Zhou J. Direct electrochemical defluorinative carboxylation of gem-difluoroalkenes with carbon dioxide. *Org Lett* 2020;22:8424-9. DOI PubMed
106. Ang NWJ, Oliveira JCA, Ackermann L. Electroreductive cobalt-catalyzed carboxylation: cross-electrophile electrocoupling with atmospheric CO₂. *Angew Chem Int Ed Engl* 2020;59:12842-7. DOI PubMed PMC
107. Yang D, Zhu M, Schiffer ZJ, et al. Direct electrochemical carboxylation of benzylic C–N bonds with carbon dioxide. *ACS Catal* 2019;9:4699-705. DOI
108. Li C, Yuan G, Jiang H. Electrocarboxylation of alkynes with carbon dioxide in the presence of metal salt catalysts. *Chin J Chem* 2010;28:1685-9. DOI
109. Kong Y, Wei W, Xu L, Chen C. Electrochemical synthesis of organonitrogen compounds from N-integrated CO₂ reduction reaction. *Acta Phys Chim Sin* 2024;40:2307049. DOI
110. Yuan M, Chen J, Bai Y, et al. Unveiling electrochemical urea synthesis by co-activation of CO₂ and N₂ with mott-schottky heterostructure catalysts. *Angew Chem Int Ed Engl* 2021;60:10910-8. DOI PubMed
111. Jouny M, Lv JJ, Cheng T, et al. Formation of carbon-nitrogen bonds in carbon monoxide electrolysis. *Nat Chem* 2019;11:846-51. DOI PubMed
112. Li J, Kornienko N. Electrochemically driven C–N bond formation from CO₂ and ammonia at the triple-phase boundary. *Chem Sci* 2022;13:3957-64. DOI PubMed PMC
113. Yu Y, Lv Z, Liu Z, et al. Activation of Ga liquid catalyst with continuously exposed active sites for electrocatalytic C–N coupling. *Angew Chem Int Ed Engl* 2024;63:e202402236. DOI PubMed
114. Yuan M, Chen J, Zhang H, et al. Host-guest molecular interaction promoted urea electrosynthesis over a precisely designed conductive metal-organic framework. *Energy Environ Sci* 2022;15:2084-95. DOI
115. Yuan M, Zhang H, Xu Y, et al. Artificial frustrated Lewis pairs facilitating the electrochemical N₂ and CO₂ conversion to urea. *Chem Catal* 2022;2:309-20. DOI
116. Liu S, Yin S, Wang Z, et al. AuCu nanofibers for electrosynthesis of urea from carbon dioxide and nitrite. *Cell Rep Phys Sci* 2022;3:100869. DOI
117. Meng N, Huang Y, Liu Y, Yu Y, Zhang B. Electrosynthesis of urea from nitrite and CO₂ over oxygen vacancy-rich ZnO porous nanosheets. *Cell Rep Phys Sci* 2021;2:100378. DOI
118. Saravanakumar D, Song J, Lee S, Hur NH, Shin W. Electrocatalytic conversion of carbon dioxide and nitrate ions to urea by a titania-nafion composite electrode. *ChemSusChem* 2017;10:3999-4003. DOI PubMed
119. Chen C, Zhu X, Wen X, et al. Coupling N₂ and CO₂ in H₂O to synthesize urea under ambient conditions. *Nat Chem* 2020;12:717-24. DOI PubMed
120. Shibata M, Yoshida K, Furuya N. Electrochemical synthesis of urea on reduction of carbon dioxide with nitrate and nitrite ions using Cu-loaded gas-diffusion electrode. *J Electroanal Chem* 1995;387:143-5. DOI
121. Shibata M, Furuya N. Electrochemical synthesis of urea at gas-diffusion electrodes: Part VI. Simultaneous reduction of carbon dioxide and nitrite ions with various metallophthalocyanine catalysts. *J Electroanal Chem* 2001;507:177-84. DOI

122. Huang Y, Yang R, Wang C, et al. Direct electrosynthesis of urea from carbon dioxide and nitric oxide. *ACS Energy Lett* 2022;7:284-91. DOI
123. Lv Z, Zhou S, Zhao L, et al. Coactivation of multiphase reactants for the electrosynthesis of urea. *Adv Energy Mater* 2023;13:2300946. DOI
124. Yuan M, Chen J, Bai Y, et al. Electrochemical C-N coupling with perovskite hybrids toward efficient urea synthesis. *Chem Sci* 2021;12:6048-58. DOI PubMed PMC
125. Lv C, Zhong L, Liu H, et al. Selective electrocatalytic synthesis of urea with nitrate and carbon dioxide. *Nat Sustain* 2021;4:868-76. DOI
126. Xu M, Wu F, Zhang Y, et al. Kinetically matched C-N coupling toward efficient urea electrosynthesis enabled on copper single-atom alloy. *Nat Commun* 2023;14:6994. DOI PubMed PMC
127. Guo C, Zhou W, Lan X, et al. Electrochemical upgrading of formic acid to formamide via coupling nitrite co-reduction. *J Am Chem Soc* 2022;144:16006-11. DOI
128. Shao J, Meng N, Wang Y, et al. Scalable electrosynthesis of formamide through C-N coupling at the industrially relevant current density of 120 mA cm⁻². *Angew Chem Int Ed Engl* 2022;61:e202213009. DOI PubMed
129. Fang Y, Liu X, Liu Z, et al. Synthesis of amino acids by electrocatalytic reduction of CO₂ on chiral Cu surfaces. *Chem* 2023;9:460-71. DOI
130. Han L, Wu Y, Fang K, et al. The splanchnic mesenchyme is the tissue of origin for pancreatic fibroblasts during homeostasis and tumorigenesis. *Nat Commun* 2023;14:1. DOI PubMed PMC
131. Weng LC, Bell AT, Weber AZ. Towards membrane-electrode assembly systems for CO₂ reduction: a modeling study. *Energy Environ Sci* 2019;12:1950-68. DOI
132. Garg S, Li M, Weber AZ, et al. Advances and challenges in electrochemical CO₂ reduction processes: an engineering and design perspective looking beyond new catalyst materials. *J Mater Chem A* 2020;8:1511-44. DOI
133. Mo Y, Lu Z, Rughoobur G, et al. Microfluidic electrochemistry for single-electron transfer redox-neutral reactions. *Science* 2020;368:1352-7. DOI PubMed
134. Vara BA, Struble TJ, Wang W, Dobish MC, Johnston JN. Enantioselective small molecule synthesis by carbon dioxide fixation using a dual Brønsted acid/base organocatalyst. *J Am Chem Soc* 2015;137:7302-5. DOI PubMed PMC
135. Yousefi R, Struble TJ, Payne JL, Vishe M, Schley ND, Johnston JN. Catalytic, enantioselective synthesis of cyclic carbamates from dialkyl amines by CO₂-capture: discovery, development, and mechanism. *J Am Chem Soc* 2019;141:618-25. DOI PubMed PMC
136. Bansode A, Urakawa A. Continuous DMC synthesis from CO₂ and methanol over a CeO₂ catalyst in a fixed bed reactor in the presence of a dehydrating agent. *ACS Catal* 2014;4:3877-80. DOI
137. Selva M, Perosa A, Rodríguez-padrón D, Luque R. Applications of dimethyl carbonate for the chemical upgrading of biosourced platform chemicals. *ACS Sustainable Chem Eng* 2019;7:6471-9. DOI
138. Zhang M, Alferov K, Xiao M, Han D, Wang S, Meng Y. Continuous dimethyl carbonate synthesis from CO₂ and methanol using Cu-Ni@VSiO as catalyst synthesized by a novel sulfuration method. *Catalysts* 2018;8:142. DOI
139. Lee KM, Jang JH, Balamurugan M, Kim JE, Jo YI, Nam KT. Redox-neutral electrochemical conversion of CO₂ to dimethyl carbonate. *Nat Energy* 2021;6:733-41. DOI
140. Li X, Han S, Wu W, et al. Convergent paired electrosynthesis of dimethyl carbonate from carbon dioxide enabled by designing the superstructure of axial oxygen coordinated nickel single-atom catalysts. *Energy Environ Sci* 2023;16:502-12. DOI
141. Wang H, Wu L, Lan Y, Zhao J, Lu J. Electrosynthesis of cyclic carbonates from CO₂ and diols in ionic liquids under mild conditions. *Int J Electrochem Sci* 2011;6:4218-27. DOI
142. Xiao Y, Chen B, Yang H, Wang H, Lu J. Electrosynthesis of enantiomerically pure cyclic carbonates from CO₂ and chiral epoxides. *Electrochem Commun* 2014;43:71-4. DOI
143. Zhang J, Shan S, Shi Y, Hou Y, Wang H, Lu J. Highly efficient electrocatalysis for the fixation of CO₂ into cyclic carbonates with carbon sphere-loaded copper nanoparticles cathode material. *J Electroanal Chem* 2021;882:114962. DOI
144. Pérez-Gallent E, Figueiredo MC, Koper MTM. Mechanistic study of the electrosynthesis of propylene carbonate from propylene oxide and CO₂ on copper electrodes. *ChemElectroChem* 2019;6:2917-23. DOI
145. Li J, Al-mahayni H, Chartrand D, Seifitokaldani A, Kornienko N. Electrochemical formation of C-S bonds from CO₂ and small-molecule sulfur species. *Nat Synth* 2023;2:757-65. DOI
146. Wu Y, Zhao J, Zhang B. Electrochemical C-S bond construction from CO₂ and an inorganic sulfur source. *Sci Bull* 2023;68:1466-8. DOI PubMed
147. Pan B, Wang Y, Li Y. Understanding and leveraging the effect of cations in the electrical double layer for electrochemical CO₂ reduction. *Chem Catal* 2022;2:1267-76. DOI
148. Qin X, Hansen HA, Honkala K, Melander MM. Cation-induced changes in the inner- and outer-sphere mechanisms of electrocatalytic CO₂ reduction. *Nat Commun* 2023;14:7607. DOI PubMed PMC
149. Jin S, Hao Z, Zhang K, Yan Z, Chen J. Advances and challenges for the electrochemical reduction of CO₂ to CO: from fundamentals to industrialization. *Angew Chem Int Ed Engl* 2021;60:20627-48. DOI PubMed
150. Yang Y, Shi Y, Yu H, Zeng J, Li K, Li F. Mitigating carbonate formation in CO₂ electrolysis. *Next Energy* 2023;1:100030. DOI
151. Govindarajan N, Xu A, Chan K. How pH affects electrochemical processes. *Science* 2022;375:379-80. DOI PubMed
152. Zhong H, Fujii K, Nakano Y, Jin F. Effect of CO₂ bubbling into aqueous solutions used for electrochemical reduction of CO₂ for

- energy conversion and storage. *J Phys Chem C* 2015;119:55-61. DOI
153. Overa S, Crandall BS, Shrimant B, et al. Enhancing acetate selectivity by coupling anodic oxidation to carbon monoxide electroreduction. *Nat Catal* 2022;5:738-45. DOI
 154. Huang JE, Li F, Ozden A, et al. CO₂ electrolysis to multicarbon products in strong acid. *Science* 2021;372:1074-8. DOI PubMed
 155. Nguyen DLT, Jee MS, Won DH, Oh H, Min BK, Hwang YJ. Effect of halides on nanoporous Zn-based catalysts for highly efficient electroreduction of CO₂ to CO. *Catal Commun* 2018;114:109-13. DOI
 156. Resasco J, Lum Y, Clark E, Zeledon JZ, Bell AT. Effects of anion identity and concentration on electrochemical reduction of CO₂. *ChemElectroChem* 2018;5:1064-72. DOI
 157. Yuan L, Zeng S, Zhang X, Ji X, Zhang S. Advances and challenges of electrolyzers for large-scale CO₂ electroreduction. *Mater Rep Energy* 2023;3:100177. DOI
 158. Jia S, Zhu Q, Wu H, et al. Efficient electrocatalytic reduction of carbon dioxide to ethylene on copper-antimony bimetallic alloy catalyst. *Chin J Catal* 2020;41:1091-8. DOI
 159. Feng J, Gao H, Zheng L, et al. A Mn-N₃ single-atom catalyst embedded in graphitic carbon nitride for efficient CO₂ electroreduction. *Nat Commun* 2020;11:4341. DOI PubMed PMC
 160. Zhao Q, Zhang C, Hu R, et al. Selective etching quaternary MAX phase toward single atom copper immobilized MXene (Ti₃C₂Cl_x) for efficient CO₂ electroreduction to methanol. *ACS Nano* 2021;15:4927-36. DOI
 161. Chen Z, Zhang X, Liu W, et al. Amination strategy to boost the CO₂ electroreduction current density of M-N/C single-atom catalysts to the industrial application level. *Energy Environ Sci* 2021;14:2349-56. DOI
 162. Hoang TTH, Verma S, Ma S, et al. Nanoporous copper-silver alloys by additive-controlled electrodeposition for the selective electroreduction of CO₂ to ethylene and ethanol. *J Am Chem Soc* 2018;140:5791-7. DOI
 163. Ren W, Tan X, Jia C, et al. Electronic regulation of nickel single atoms by confined nickel nanoparticles for energy-efficient CO₂ electroreduction. *Angew Chem Int Ed Engl* 2022;61:e202203335. DOI
 164. Gabardo CM, O'Brien CP, Edwards JP, et al. Continuous carbon dioxide electroreduction to concentrated multi-carbon products using a membrane electrode assembly. *Joule* 2019;3:2777-91. DOI
 165. Endrődi B, Samu A, Kecsenovity E, Halmágyi T, Sebők D, Janáky C. Operando cathode activation with alkali metal cations for high current density operation of water-fed zero-gap carbon dioxide electrolyzers. *Nat Energy* 2021;6:439-48. DOI PubMed PMC
 166. Wu Y, Chen C, Yan X, et al. Enhancing CO₂ electroreduction to CH₄ over Cu nanoparticles supported on N-doped carbon. *Chem Sci* 2022;13:8388-94. DOI PubMed PMC
 167. Xia C, Zhu P, Jiang Q, et al. Continuous production of pure liquid fuel solutions via electrocatalytic CO₂ reduction using solid-electrolyte devices. *Nat Energy* 2019;4:776-85. DOI
 168. Zhu P, Xia C, Liu CY, et al. Direct and continuous generation of pure acetic acid solutions via electrocatalytic carbon monoxide reduction. *Proc Natl Acad Sci U S A* 2021;118:e2010868118. DOI PubMed PMC