

Review

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# Electrochemical conversion of CO<sub>2</sub> via C–X bond formation: recent progress and perspective

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**How to cite this article:** Jia S, Dong M, Zhu Q, Kang X, Wu H, Han B. Electrochemical conversion of CO<sub>2</sub> 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 (CO<sub>2</sub>). Currently, the electrochemical production of high-value-added chemicals and fuels from CO<sub>2</sub> has aroused great interest from scientists. However, to make full use of CO<sub>2</sub> 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 CO<sub>2</sub> with different substrates. In general, CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> and different substrate molecules. Finally, (i) strategies for the



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design and activity optimization of catalyst materials and (ii) the future development of forming five types of bonds from CO<sub>2</sub> and small molecules are discussed, along with an outlook on their future research prospects.

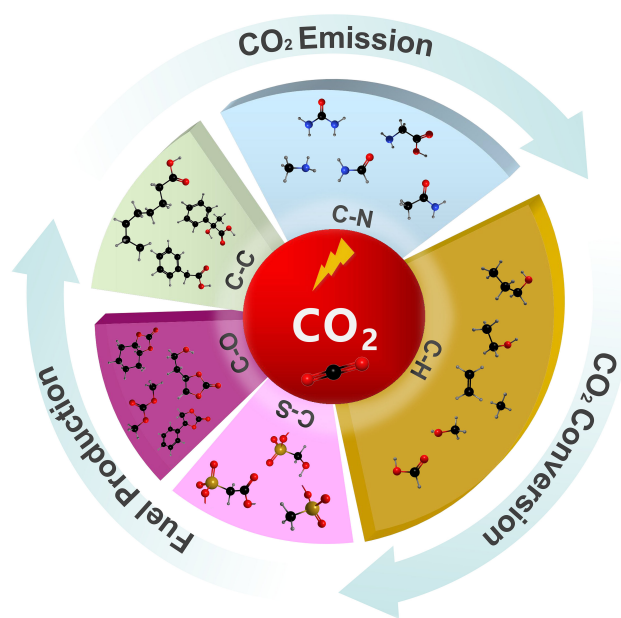
**Keywords:** Carbon dioxide, electrosynthesis, C–X bonds, new covalent bonds, high-value-added chemicals

## INTRODUCTION

Excessive emissions of carbon dioxide (CO<sub>2</sub>) 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 CO<sub>2</sub> emissions. Aside from crafting strategies for mitigation and removal, CO<sub>2</sub> 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, CO<sub>2</sub> fixation, and carbon recycling to utilize carbon resources efficiently and minimize net CO<sub>2</sub> emission”<sup>[1]</sup>. The design of many environmental catalytic systems and process technologies is guided by the general principles of this concept. To facilitate CO<sub>2</sub> capture and conversion, to date, various strategies have been developed to use CO<sub>2</sub> 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<sup>[2-5]</sup>, which is the key to future new energy storage and conversion technologies<sup>[6-10]</sup>. 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<sup>[11-12]</sup>.

Electrosynthesis, as an efficient and environmentally friendly synthesis method, employs electrons as redox reagents<sup>[13-14]</sup>. In CO<sub>2</sub> fixation, coupling CO<sub>2</sub> with small molecule compounds or organic compounds by electrochemical methods has recently been promoted as an environmentally friendly and sustainable synthesis technique<sup>[15-19]</sup>. In general, CO<sub>2</sub> 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 CO<sub>2</sub> molecule must first be adsorbed and activated on the catalyst surface because CO<sub>2</sub> is a stable molecule and breaking or hydrogenating one of the oxygen atoms of CO<sub>2</sub> is needed for its utilization in electrochemical C–X bond formation reactions. The activated CO<sub>2</sub> 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 CO<sub>2</sub> conversion, the C–H bond is constructed from the hydrogenation of CO<sub>2</sub> to produce CO, CH<sub>4</sub>, HCOOH, and C<sub>2+</sub> 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<sup>[20-21]</sup>.

This paper reviewed the recent advances in the electrosynthesis of C–X bonds (C–H, C–C, C–N, C–O, C–S) using CO<sub>2</sub> and substrate molecules, including the electrochemical C–H bond formation for hydrocarbon/carbohydrate, electrochemical C–C bond formation for carboxylation of CO<sub>2</sub>, 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.

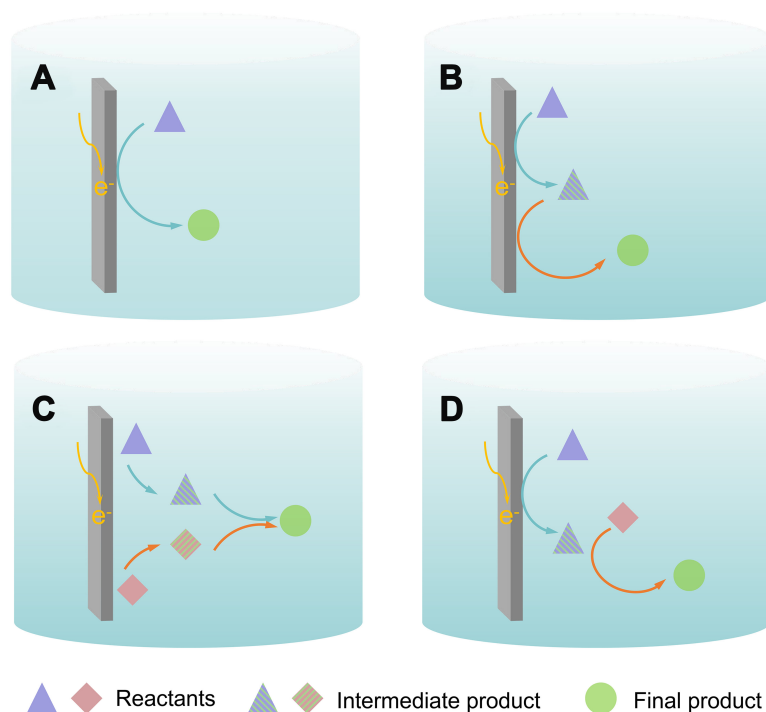
formation for organic nitrates synthesis, electrochemical C-O bond formation for cyclic carbonates and dimethyl carbonate (DMC) and electrochemical C-S bond formation for sulfonates<sup>[22-23]</sup>. Recent developments, prospects, and challenges in electrochemical CO<sub>2</sub> utilization, and the fundamentals of electrocatalytic reactions on the initial activation of CO<sub>2</sub> and product selectivity will also be described. Finally, improvement strategies for the shortcomings of electrocatalytic CO<sub>2</sub> coupled organic reactions and outlooks on their future research prospects are proposed<sup>[24]</sup>.

## FUNDAMENTALS OF ELECTROCATALYTIC REACTIONS

The electrochemical CO<sub>2</sub>-catalyzed reaction is capable of using various substrate molecules to prepare advanced products in addition to the direct conversion of CO<sub>2</sub> and water into carbon-containing chemicals<sup>[25-28]</sup>. Typically, [Figure 2A](#) and [B](#) can represent the construction of C-H bonds between water and CO<sub>2</sub>, 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 CO<sub>2</sub> 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<sup>[29]</sup>. 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 C<sub>3</sub>



**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.

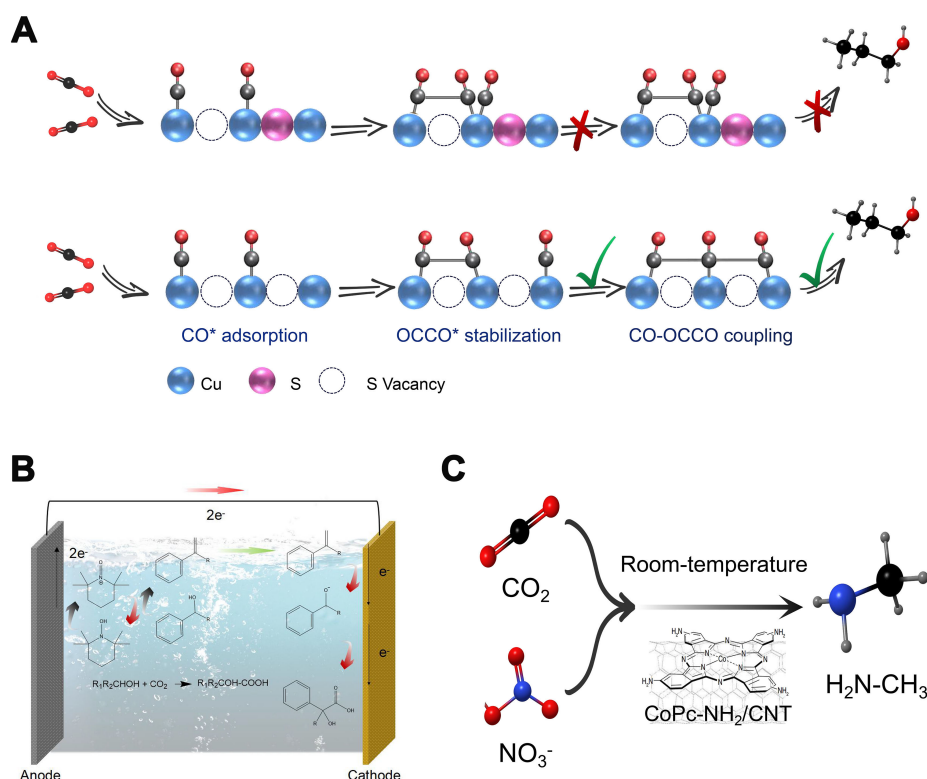
compounds [Figure 3A]<sup>[30]</sup>. In another study of the CO<sub>2</sub> electrocarboxylation reaction, ketones are first reduced by two-electron transfer at the cathode, and then further converted to carboxylates by coupling with CO<sub>2</sub> [Figure 3B]<sup>[31]</sup>. It is also a typical pathway for a tandem reaction.

The other is the coupling reaction mode. The electrocatalytic CO<sub>2</sub> conversion reactions can potentially derive new chemistries by simultaneous activation of small molecules other than CO<sub>2</sub> 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<sup>[32-34]</sup>. Wu *et al.* recently proposed a possible coupling reaction pathway for the electrocatalytic synthesis of methylamine<sup>[35]</sup>. This pathway integrates the electrochemical reduction of CO<sub>2</sub> (CO<sub>2</sub>RR) and nitrate (NO<sub>3</sub>-RR) [Figure 3C]. First, CO<sub>2</sub>RR and NO<sub>3</sub>-RR can occur independently to form formaldehyde (HCHO) and hydroxylamine (NH<sub>2</sub>OH) intermediates, respectively. Then, formaldoxime is produced by nucleophilic NH<sub>2</sub>OH 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<sub>2</sub>OH and HCHO intermediates from NO<sub>3</sub>-RR and CO<sub>2</sub>RR, respectively.

## INTEGRATED ELECTROCATALYTIC REACTIONS

### C–H bond formation

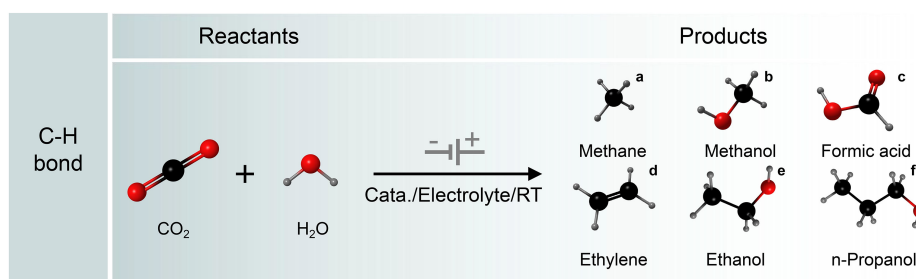
The generation of C–H bonds occurs during the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) with multiple proton-electron transfer steps that yield carbon-based products. A typical CO<sub>2</sub> electrolysis usually involves a multi-electron/proton transfer process: (i) CO<sub>2</sub> adsorption 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<sub>x</sub>-DSV, showing the dimerization of CO–CO followed by CO–OCCO coupling; (B) Electrosynthesis of  $\alpha$ -hydroxy acids through the electrocatalytic coupling of alcohols and CO<sub>2</sub>; (C) Cascade electrocatalysis of methylamine from CO<sub>2</sub> and NO<sub>3</sub><sup>-</sup>. CuS<sub>x</sub>-DSV: CuS<sub>x</sub> double sulfur vacancy.

electrolyte. Therefore, both electrocatalysts and electrolyte are pivotal for designing efficient electrochemical devices<sup>[36–38]</sup>. Generally, various electrocatalysts have been utilized in CO<sub>2</sub> 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 CO<sub>2</sub> reduction coupling by facilitating the transfer of electrons and protons<sup>[39]</sup>. 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<sup>[40–46]</sup>, and a wide range of products have been generated<sup>[47–49]</sup>.

As shown in Figure 4, electrochemical CO<sub>2</sub>RR involves the transfer of multiple protons and electrons, which involves diverse pathways. CO<sub>2</sub> can undergo reduction to yield a variety of products comprising both single- and multiple-carbon compounds, including carbon monoxide (CO), methane (CH<sub>4</sub>), methanol (CH<sub>3</sub>OH), formate (HCOO<sup>-</sup>), ethylene (C<sub>2</sub>H<sub>4</sub>), ethanol (C<sub>2</sub>H<sub>5</sub>OH), and propanol (C<sub>3</sub>H<sub>7</sub>OH), among others. There are three types of bonding steps in the CO<sub>2</sub>RR route: oxygen hydrogenation, carbon hydrogenation, and carbon-carbon coupling<sup>[50–53]</sup>. Hydrocarbonation often occurs during the evolution of intermediates and the formation of products<sup>[54–56]</sup>. By calculating the relevant intermediates, the resulting hydrogen (H<sub>2</sub>), HCOO<sup>-</sup>, and hydrocarbon moieties can be distinguished<sup>[57]</sup>. 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 CO<sub>2</sub> is typically more negative than the hydrogen evolution potential. At extremely



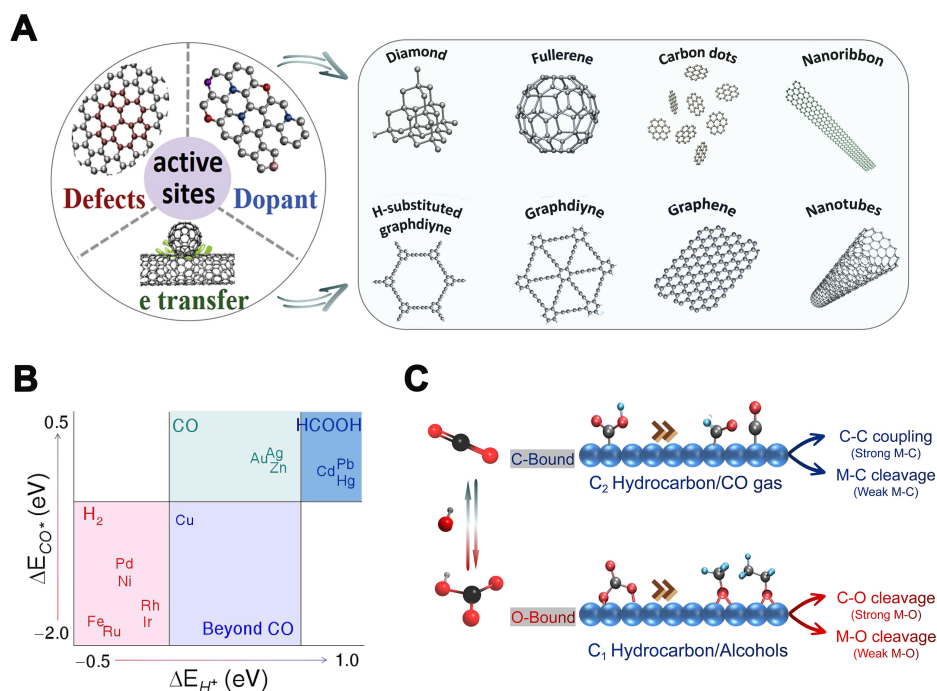
**Figure 4.** C–H bond formation by electrocatalytic reaction of CO<sub>2</sub> and H<sub>2</sub>O.

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 CO<sub>2</sub> 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 CO<sub>2</sub>RR.

Numerous reports have demonstrated the excellent catalytic properties and potential of carbon-based materials for CO<sub>2</sub>RR [Figure 5A]<sup>[58]</sup>. 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 CO<sub>2</sub>RR. 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 CO<sub>2</sub>RR process, the carbon atoms adjacent to pyridinic N can act as Lewis base sites to adsorb CO<sub>2</sub>, which makes the reduced carbon atoms the active sites for CO<sub>2</sub>RR<sup>[59]</sup>. However, Guo *et al.* showed that the acidic CO<sub>2</sub> molecules can only adsorb on the pyridinic N sites, and the Lewis base sites for CO<sub>2</sub>RR are generated by pyridinic N rather than graphitic N. Therefore, pyridinic N is considered as the active site for CO<sub>2</sub>RR<sup>[60]</sup>.

Metal-based catalysts are often the most common electrocatalysts in the CO<sub>2</sub>RR. 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<sub>B</sub>\*, and \*CO<sup>[61]</sup>. 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<sup>[62-64]</sup>; (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<sub>B</sub>\*; (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 CO<sub>2</sub>RR on them; (C) The impact of surface-bound carbon and oxygen reaction intermediates on the selectivity of CO<sub>2</sub>RR products. CO<sub>2</sub>RR: CO<sub>2</sub> reduction reaction.

Katayama *et al.* further clarified the surface reaction properties of metal catalysts [Figure 5C]<sup>[62]</sup>. 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, C<sub>2</sub> products, *etc.* of intermediate species adsorbed on the carbon end, while intermediate species adsorbed on the oxygen end eventually form C<sub>1</sub>, 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<sup>[65]</sup>. 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 CO<sub>2</sub> 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, CO<sub>2</sub> electrolysis occurs at the gas-liquid-solid three-phase interface.

In order to enhance the CO<sub>2</sub>RR 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 CO<sub>2</sub> to the active catalyst surface, resulting in CO<sub>2</sub> electrolysis to ethylene at the current density of 1 A·cm<sup>-2</sup><sup>[66]</sup>. The electrolysis was conducted in 7 M KOH electrolyte, leading to an ethylene partial current density of 1.3 A·cm<sup>-2</sup> 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 CO<sub>2</sub>RR<sup>[67]</sup>. The results show that the ionomer has ionic conductivity, which can activate CO<sub>2</sub> 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<sup>-2</sup> 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 CO<sub>2</sub>RR to CO<sup>[68]</sup>. Utilizing a PiperION membrane in a membrane electrode assembly (MEA) resulted in a current density of more than 1 A·cm<sup>-2</sup> for CO production. These works provide theoretical guidance for the industrial application of CO<sub>2</sub> 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 CO<sub>2</sub> 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<sup>[15-17,92]</sup>. Among the many products of CO<sub>2</sub> 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<sup>[93,94]</sup>. Therefore, the synthesis of carboxylic acids and their derivatives by electrocarboxylation of CO<sub>2</sub> is of great importance [Figure 6]. In recent years, the method of CO<sub>2</sub> 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<sup>[14,95-98]</sup>.

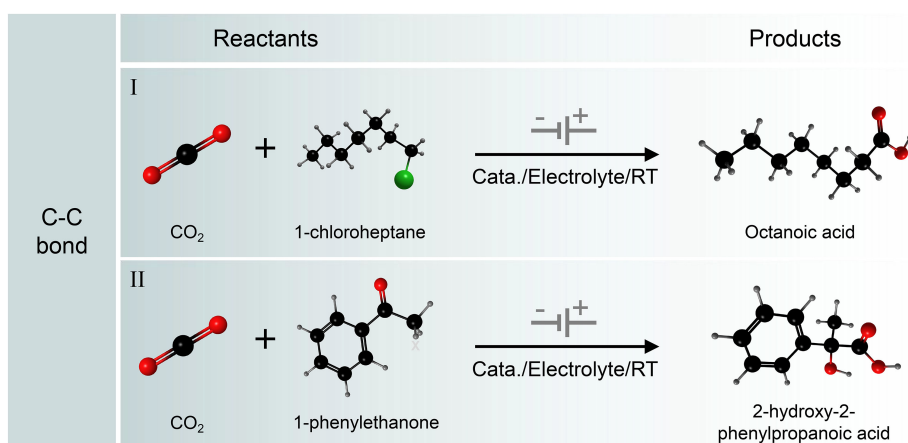
In recent years, there has been a growing focus on research into electrocarboxylation, a process that utilizes CO<sub>2</sub> as a feedstock. Under mild conditions, the carbon negative ions generated by the electroreduction of organic substrates can trap CO<sub>2</sub> in the system, which, in turn, generates organic carboxylic compounds with multifunctional groups and higher added value<sup>[99-104]</sup>. For example, CO<sub>2</sub> can react with olefins or alkynes to generate organic carboxylic acids through electroreductive addition reactions<sup>[99,100]</sup>. 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<sup>[101,102]</sup>. On silver electrodes, organic halides can undergo electrocarboxylation reactions with CO<sub>2</sub> to generate carboxylic acid compounds<sup>[103]</sup>. In addition, aromatic imine compounds can also react with CO<sub>2</sub> 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<sup>[104]</sup>.

Generally, in a CO<sub>2</sub> 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 CO<sub>2</sub> generally proceeds via the following two possible pathways [Figure 7B]. The first pathway is the direct electroreduction of CO<sub>2</sub> to form a CO<sub>2</sub> 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 CO<sub>2</sub> to obtain valuable dicarboxylic acids. Control experiments and theoretical studies indicate that CO<sub>2</sub> 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 CO<sub>2</sub> to give the desired product<sup>[16]</sup>. The other pathway is the electroreduction of the substrate to form a carbon ion or radical anion, followed by a carboxylation

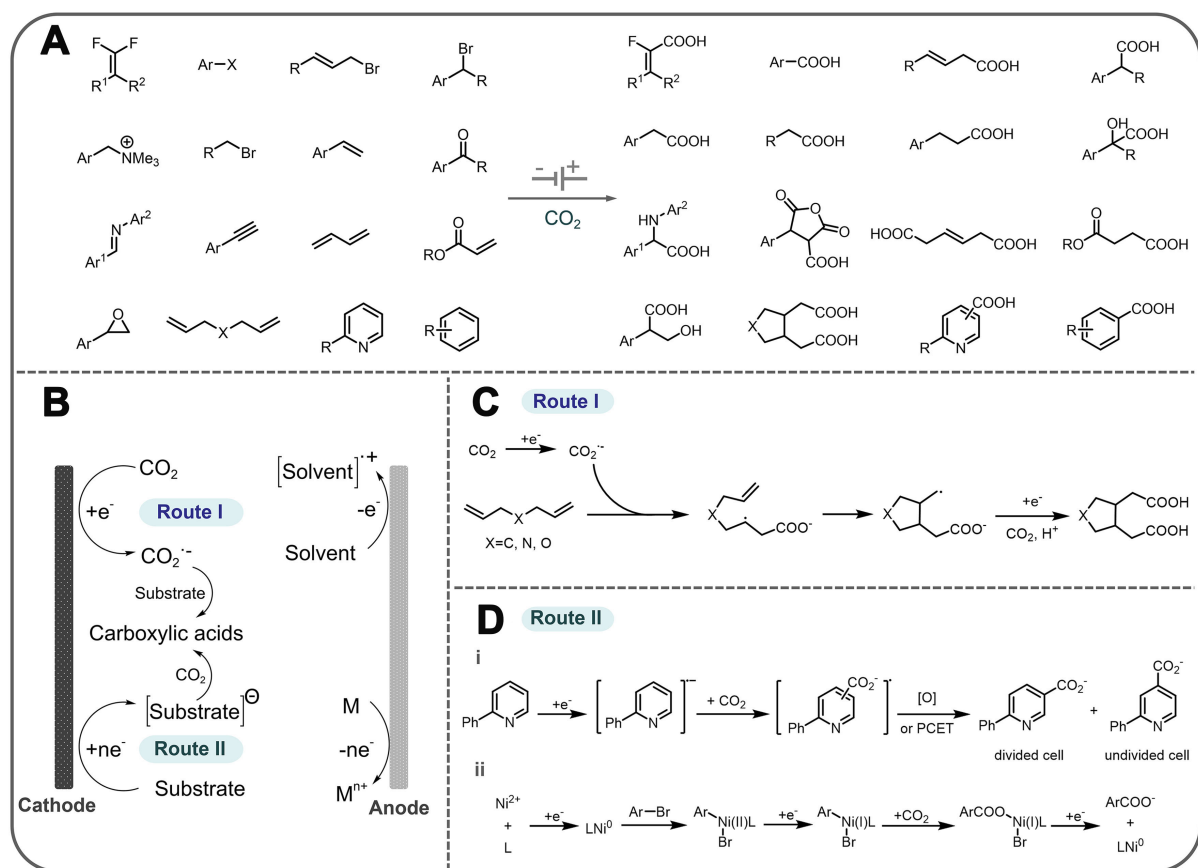
**Table 1. C<sub>1</sub>-C<sub>3</sub> compound (CH<sub>4</sub>, formate, CO, C<sub>2</sub>H<sub>4</sub>, EtOH, acetic acid, and *n*-propanol, etc.) production from CO<sub>2</sub>RR**

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

CO<sub>2</sub>RR: CO<sub>2</sub> 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 CO<sub>2</sub> fixation to unsaturated organic compounds.



**Figure 7.** (A) List of electrochemical CO<sub>2</sub> carboxylation reactions involving different types of substrates; (B) A comprehensive method for electrochemically catalyzed carboxylation reactions utilizing CO<sub>2</sub> as a substrate to produce carboxylic acids; (C) The process of electrochemically-driven dicarboxylation of unactivated skipped dienes with CO<sub>2</sub>; (D) Mechanism of electrochemical carboxylation of (i) N-heteroarenes and (ii) aryl halide.

reaction with CO<sub>2</sub> [Figure 7D]. In this pathway, N-heteroarenes and organic halides are also an ideal class of carboxyl substrates in the presence of an electric current or a metal catalyst. Using CO<sub>2</sub> as a carboxyl source, Sun *et al.* have achieved site-selective C-H bond carboxylation of pyridine and the related N-heteroarenes by switching different electrochemical cells<sup>[98]</sup>. In a divided electrochemical cell, C<sub>5</sub>-carboxylation occurs, whereas in an undivided electrochemical cell, C<sub>4</sub>-carboxylation occurs [Figure 7D (i)]. This method has good substrate applicability and functional group tolerance, providing a new approach for the preparation of important nitrogen-containing heterocyclic carboxylic acid compounds. In addition, Sun *et al.* report a versatile and practical electro-reductive Ni-catalytic system for the electrocatalytic carboxylation of unactivated aryl chlorides and alkyl bromides with CO<sub>2</sub> [Figure 7D (ii)]<sup>[96]</sup>. A variety of unactivated aryl bromides, iodides and sulfonates also perform this reaction without difficulty. Remarkably, they have also achieved a catalytic electrochemical carboxylation of aryl (pseudo)halides with CO<sub>2</sub>, avoiding the use of sacrificial electrodes. Mechanistic investigations suggest that the reaction might proceed via oxidative addition of aryl halides to Ni(0) complex, the reduction of aryl-Ni(II) adduct to the Ni(I) species, and subsequent carboxylation with CO<sub>2</sub>.

Despite many advances made in the construction of C-C bonds, there are still many problems that need to be further studied and solved in CO<sub>2</sub> carboxylation reactions. On the one hand, there are side reactions such as electrochemical hydrogenation and electrochemical dimerization in the process of electrocarboxylation,

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 CO<sub>2</sub> 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

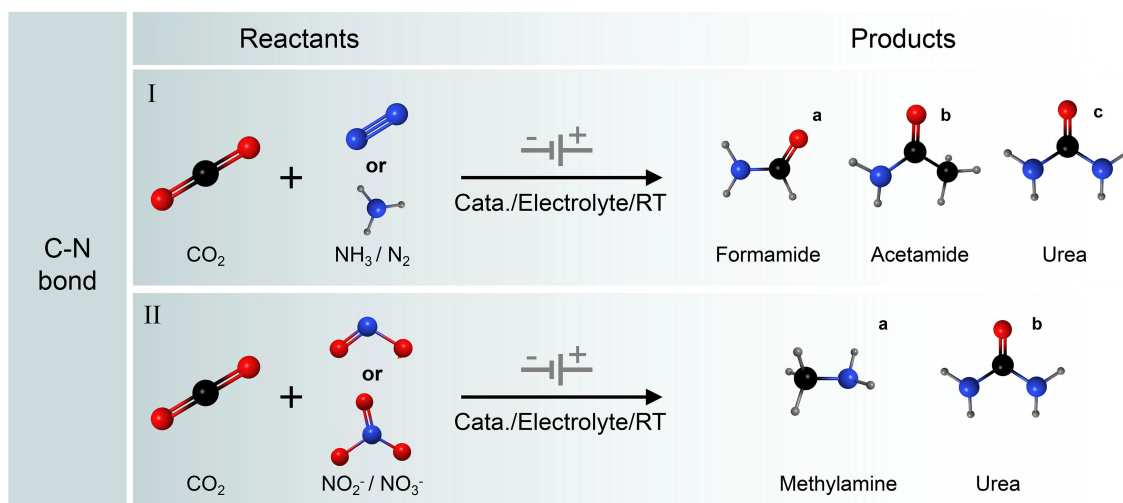
Compounds containing nitrogen have been applied extensively in chemical synthesis, medicinal chemistry, agriculture, and aerospace industries. Therefore, the development of efficient electrocatalytic C–N coupling strategies is of great significance for the production of organic nitrogen compounds. The combination of electrochemical CO<sub>2</sub> with N<sub>2</sub> reduction reaction (NRR), which utilizes the earth's abundant small molecules N molecules (N<sub>2</sub>, NO, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, *etc.*), is a viable approach to obtain valuable organic nitrogen compounds<sup>[109–111]</sup>. 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 CO<sub>2</sub> 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 CO<sub>2</sub> and N-containing small molecules, as well as HER. Driving both electrochemical reduction reactions (CO<sub>2</sub>RR/NRR) in the same electrochemical system to selectively produce the C–N coupling products is more difficult ] [[Figure 8](#)]<sup>[112–115]</sup>. However, this approach offers significant advantages over currently reported industrial synthetic routes<sup>[116–118]</sup>.

To address the problem of C–N bond co-activation, Chen *et al.* pioneered a new method to prepare urea by electrochemically coupling CO<sub>2</sub> and N<sub>2</sub> in water. The electrocatalyst used in this method consists of PdCu alloy nanoparticles attached to TiO<sub>2</sub> nanosheets with oxygen-rich vacancies. The yield of urea was 3.36 mmol·g<sup>-1</sup>·h<sup>-1</sup> at a Faradaic efficiency (FE) of 8.92% in a flow cell. The experimental results indicated that N<sub>2</sub> is activated by binding to the catalyst surface and by the reduction of CO<sub>2</sub> 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](#)]<sup>[119]</sup>. In another example, it is reported that in NO<sub>2</sub><sup>-</sup>-integrated electrocatalytic CO<sub>2</sub> reduction, only those electrocatalysts that promote CO<sub>2</sub><sup>-</sup>-CO and NO<sub>2</sub><sup>-</sup>-NH<sub>3</sub> reduction can produce urea<sup>[120,121]</sup>. The \*CO and \*NH<sub>2</sub> intermediates are obtained from the co-reduction of NO<sub>3</sub><sup>-</sup>/NO<sub>2</sub><sup>-</sup> and CO<sub>2</sub>. 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., \*CONH<sub>2</sub>) is constructed by coupling \*CO and \*NH<sub>2</sub>; the second C–N bond in urea is formed by the combination of \*CONH<sub>2</sub> and \*NH<sub>2</sub> [[Figure 9B](#)]<sup>[122,123]</sup>. Yuan *et al.* also demonstrated that the use of non-precious-metal Bi–BiVO<sub>4</sub> and BiFeO<sub>3</sub>/BiVO<sub>4</sub> heterojunctions could efficiently electro-synthesize urea from CO<sub>2</sub> and N<sub>2</sub><sup>[124]</sup>. 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 N<sub>2</sub> and CO<sub>2</sub> molecules within specific electrophilic and nucleophilic regions of the catalyst, thereby enhancing urea selectivity.

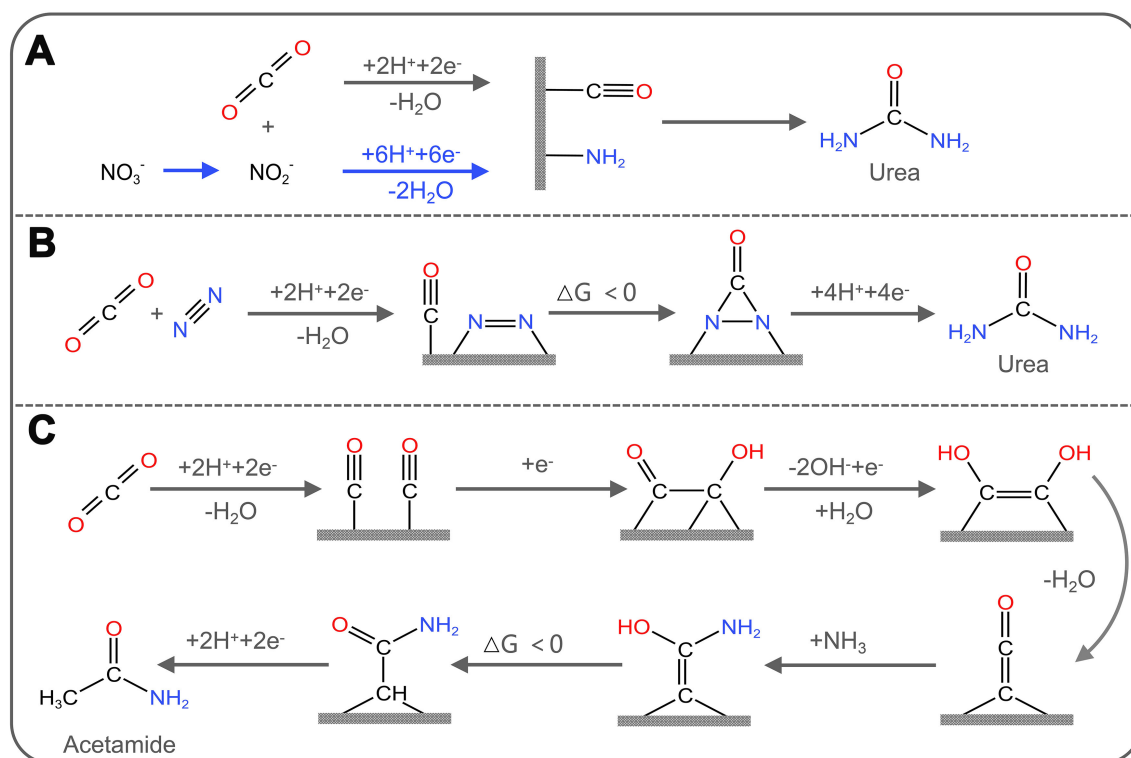
**Table 2. Selected examples of electrolytic conversion of CO<sub>2</sub> and substrate by constructing C–C bonds**

Substrate	Electrode	Catalyst	Electrolyte	Solvent	Current or voltage	Yield
	(-)Pt-Ni(+) <sup>[105]</sup>	/	TBAI	DMF	8 mA	75%
	(-)Ni-Mg(+) <sup>[106]</sup>	Co(OAc) <sub>2</sub> PPh <sub>3</sub>	TBAPF <sub>6</sub>	DMF	10 mA	59%
	(-)Ag NPs-Mg(+) <sup>[103]</sup>	/	TEAI	MeCN	5 mA	98%
	(-)C-Pt(+) <sup>[107]</sup>	/	TBAPF <sub>4</sub>	DMF	4.5 V	70%
	(-)C-Zn(+) <sup>[96]</sup>	NiBr <sub>2</sub> DME dmbpy	LiClO <sub>4</sub>	NMP	8 mA	70%
	(-)C-C(+) <sup>[92]</sup>	/	TEAI	DMF	10 V	70%
	(-)SS-Mg(+) <sup>[101]</sup>	/	TEAI	MeCN	1.2 mA	41%
	(-)Ni-Al(+) <sup>[104]</sup>	/	TBAB	DMF	10 mA	68%
	(-)Ni-Al(+) <sup>[108]</sup>	/	TBAB	DMF	10 mA	70%
	(-)Ni-Al(+) <sup>[100]</sup>	/	TBAB	DMF	10 mA	84%
	(-)C-C(+) <sup>[93]</sup>	/	TEAI	DMF	10 V	76%
	(-)Pt-Mg(+) <sup>[17]</sup>	/	TBAI	DMF	10 mA	94%
	(-)Ni-Al(+) <sup>[16]</sup>	/	TBAI	NMP	12.5 mA	78%
	(-)Fe-Zn(+) <sup>[98]</sup>	Cu(OTf) <sub>2</sub>	TEAI	NMP	5 mA	72% (C5)
	(-)Fe-Pt(+) <sup>[98]</sup>	/	TEAI	NMP	6 mA	85% (C4)
	(-)GF-GF(+) <sup>[15]</sup>	/	TEAI	DMF	20 mA	87%
	(-)Nb-Zn(+) <sup>[95]</sup>	/	TBAPF <sub>4</sub>	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 CO<sub>2</sub> and NH<sub>3</sub>/N<sub>2</sub> to formamide/acetamide/urea; (II) Simultaneous reduction of CO<sub>2</sub> and NO<sub>2</sub><sup>-</sup>/NO<sub>3</sub><sup>-</sup> to methylamine/urea.



**Figure 9.** (A) Electrochemical synthetic pathway for urea from  $\text{CO}_2$  and  $\text{NO}_3^-/\text{NO}_2^-$ ; (B) Electrochemical synthetic pathway for urea from  $\text{CO}_2$  and  $\text{N}_2$ ; (C) Electrochemical synthetic pathway for urea from  $\text{CO}_2$  and  $\text{NH}_3$ .

Recently, remarkable progress has been made in C–N coupling reactions by electrocatalytic method using  $\text{CO}_2$  and  $\text{NO}_x^-$  as feedstocks.  $\text{NO}_x^-$  have relatively low dissociation energies and high aqueous solubility compared to non-polar  $\text{N}_2$ , 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]<sup>[111]</sup>. Lv *et al.* achieved electrochemical coupling of  $\text{NO}_3^-$  with  $\text{CO}_2$  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<sup>[125]</sup>. 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<sup>[126]</sup>. In terms of amide product synthesis, Guo *et al.* reported a sustainable electrosynthesis method to synthesize formamide using  $\text{CO}_2$ -derived  $\text{HCOO}^-$  and  $\text{NO}_2^-$ <sup>[127]</sup>. The FE of formamide on low-coordinated copper nanocubes (ER-Cu) could reach 29.7%. Furthermore, using  $\text{CO}_2$ -derived  $\text{CH}_3\text{OH}$  and  $\text{N}_2$ -derived  $\text{NH}_3$  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<sup>[128]</sup>. In terms of amino acid preparation, Fang *et al.* first discovered that the synthesis of  $\text{C}_{3+}$  amino acids from  $\text{CO}_2$  and  $\text{NH}_3$  can be electrocatalytically catalyzed by employing chiral Cu thin films (CCFs) as the electrodes, in which the FE of serine reached 1.2%<sup>[129]</sup>.

These studies suggest that typically, the amalgamation of electrophilic intermediates-containing carbon with nucleophilic intermediates-containing nitrogen generated through the co-reduction of  $\text{CO}_2$  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 CO<sub>2</sub> electrolytic conversion and reactions with nitrogen-containing small molecules by constructing C–N bonds.

### C–O bond formation

Redox-neutral CO<sub>2</sub> conversion is an important process for producing various carbonates [Figure 10]<sup>[131-135]</sup>. 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<sup>[136-138]</sup>. Thermochemical methods have been developed to synthesize DMC from CO<sub>2</sub>, 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 CO<sub>2</sub><sup>[139]</sup>. A scheme for the redox-neutral electrochemical synthesis of DMC from CO<sub>2</sub> and CH<sub>3</sub>OH 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 CO<sub>2</sub>RR reaction at the cathode and two redox cycles at the anode: CO<sub>2</sub>/CO, Pd(0)/Pd(II), and Br<sup>-</sup>/Br<sub>2</sub>. Experimental results show a maximum FE of 60% for DMC production at room temperature. The mechanism study shows that CO<sub>2</sub> and CH<sub>3</sub>OH may be reduced to produce CO and MeO<sup>-</sup> at the cathode. The Br<sub>2</sub> generated by anodizing Br<sup>-</sup> oxidizes the Pd(0) complex to the Pd(II)Br<sub>2</sub> 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<sup>-</sup> with generating Pd(0) complexes.

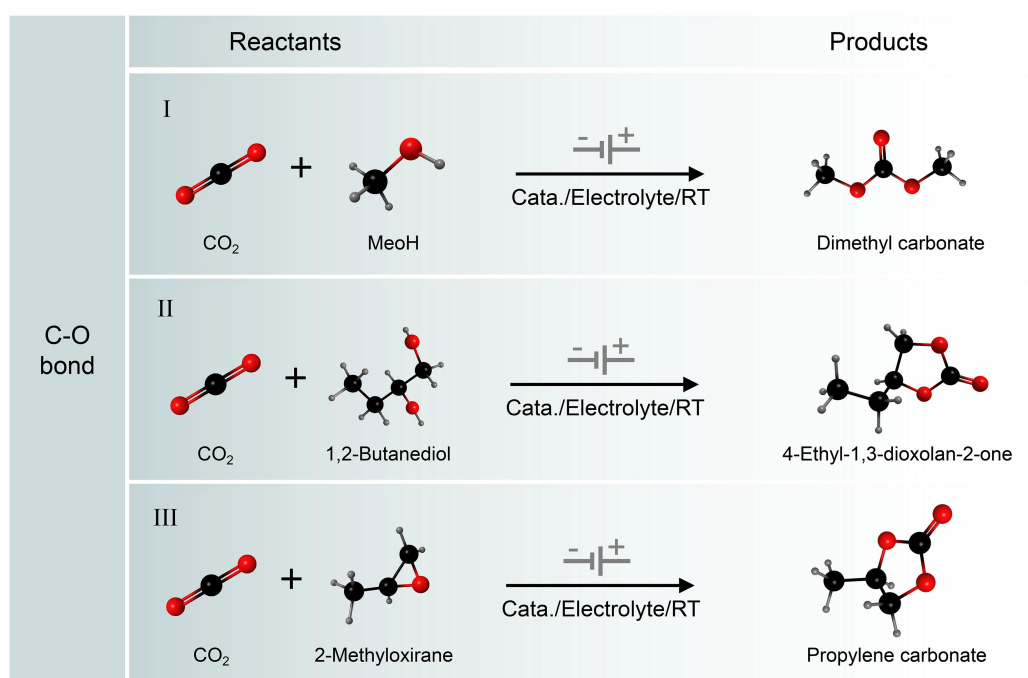
Recently, Li *et al.* developed a novel Ni single-atom catalyst (SAC) featuring a dual-channel superstructure. This SAC exhibits a distinctive site coordination configuration, characterized by bonding with one axial oxygen atom and four planar nitrogen atoms<sup>[140]</sup>. The unique active sites are beneficial for the activation and conversion of CO<sub>2</sub> to CO with a high FE of 99%. Furthermore, the preparation of CO<sub>2</sub> 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 H<sub>2</sub>O and CH<sub>3</sub>OH.

The coupling of CO<sub>2</sub> 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 CO<sub>2</sub> in a reusable ionic liquid (IL)-based electrolyte without additional catalyst was reported by Wang *et al.* The reaction of CO<sub>2</sub><sup>-</sup> 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<sup>[141]</sup>. Xiao *et al.* concurrently pioneered a one-step synthesis of enantiomerically pure cyclic carbonates through the electrolysis of chiral epoxides and CO<sub>2</sub> 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]<sup>[142,143]</sup>. In another work, Pérez-Gallent *et al.* studied the reaction process of propylene oxide and CO<sub>2</sub> to synthesize propylene carbonate on copper electrodes in detail<sup>[144]</sup>. The results indicated that the key to this reaction was the reduction of CO<sub>2</sub> to CO<sub>2</sub><sup>-</sup> and the C–O bond was generated by CO<sub>2</sub><sup>-</sup> attacking the epoxide.

**Table 3. Selected examples of electrolytic conversion of CO<sub>2</sub> and (NO, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>3</sub>, and N<sub>2</sub>)**

Substrate	Product	Electrode	Electrolyte	Current density or potential (vs. RHE)	FE
CO <sub>2</sub> , NO	Urea	Zn NBs <sup>[122]</sup>	0.2 M KHCO <sub>3</sub>	- 0.92 V	11.3%
CO <sub>2</sub> , NO <sub>2</sub> <sup>-</sup>	Urea	ZnO-V <sup>[117]</sup>	0.2 M NaHCO <sub>3</sub> and 0.1 M NaNO <sub>2</sub>	- 0.79 V	23.3%
CO <sub>2</sub> , NO <sub>3</sub> <sup>-</sup>	Urea	In(OH) <sub>3</sub> -S <sup>[125]</sup>	0.1 M KNO <sub>3</sub>	- 0.6 V	53.4%
CO <sub>2</sub> , NO <sub>3</sub> <sup>-</sup>	Urea	Pd <sub>4</sub> Cu <sub>1</sub> /FeNi(OH) <sub>2</sub> <sup>[130]</sup>	0.1 M KHCO <sub>3</sub> , 0.1 M KNO <sub>3</sub>	- 0.5 V	66.4%
CO <sub>2</sub> , N <sub>2</sub>	Urea	Bi-BiVO <sub>4</sub> <sup>[110]</sup>	KHCO <sub>3</sub>	- 0.40 V	12.6%
CO <sub>2</sub> , N <sub>2</sub>	Urea	BiFeO <sub>3</sub> /BiVO <sub>4</sub> <sup>[124]</sup>	0.1 M KHCO <sub>3</sub>	- 0.4 V	17.2%
CO <sub>2</sub> , N <sub>2</sub>	Urea	InOOH-100 <sup>[115]</sup>	0.1 M KHCO <sub>3</sub>	- 0.40 V	21.0%
CO <sub>2</sub> , N <sub>2</sub>	Urea	V <sub>N</sub> -Cu <sub>3</sub> N-300 <sup>[123]</sup>	0.1 M KHCO <sub>3</sub>	- 0.4 V	28.7%
CO <sub>2</sub> , N <sub>2</sub>	Urea	MOF Co-PMDA-2-mbIM <sup>[114]</sup>	0.1 M KHCO <sub>3</sub>	- 0.50 V	49.0%
CO <sub>2</sub> , N <sub>2</sub>	Urea	Ga <sub>79</sub> Cu <sub>11</sub> Mo <sub>10</sub> @C <sup>[113]</sup>	0.1 M KHCO <sub>3</sub>	- 0.40 V	60.6%
CO <sub>2</sub> , NO <sub>3</sub> <sup>-</sup>	CH <sub>3</sub> NH <sub>2</sub>	CoPc-NH <sub>2</sub> /CNT <sup>[31]</sup>	0.1 M KNO <sub>3</sub>	- 0.92 V	13.0%
CO <sub>2</sub> , NH <sub>3</sub>	Acetamide	Cu NPs <sup>[112]</sup>	1 M KOH	- 0.58 V	10.0%
CO, NH <sub>3</sub>	Acetamide	Cu NPs <sup>[111]</sup>	1 M KOH	300 mA·cm <sup>-2</sup>	40.0%
CH <sub>3</sub> OH, NH <sub>3</sub>	Formamide	BDD <sup>[128]</sup>	0.5 M NaHCO <sub>3</sub>	120 mA·cm <sup>-2</sup>	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 CO<sub>2</sub> to dimethyl carbonate without altering the redox state; (II) Electrosynthesis of Cyclic Carbonates from CO<sub>2</sub> and Diols; (III) Electrosynthesis of cyclic carbonates from CO<sub>2</sub> and epoxides.

As shown in Table 4, we summarized some representative reactions of coupling CO<sub>2</sub> and organic small molecule substrates by constructing C–O bonds.

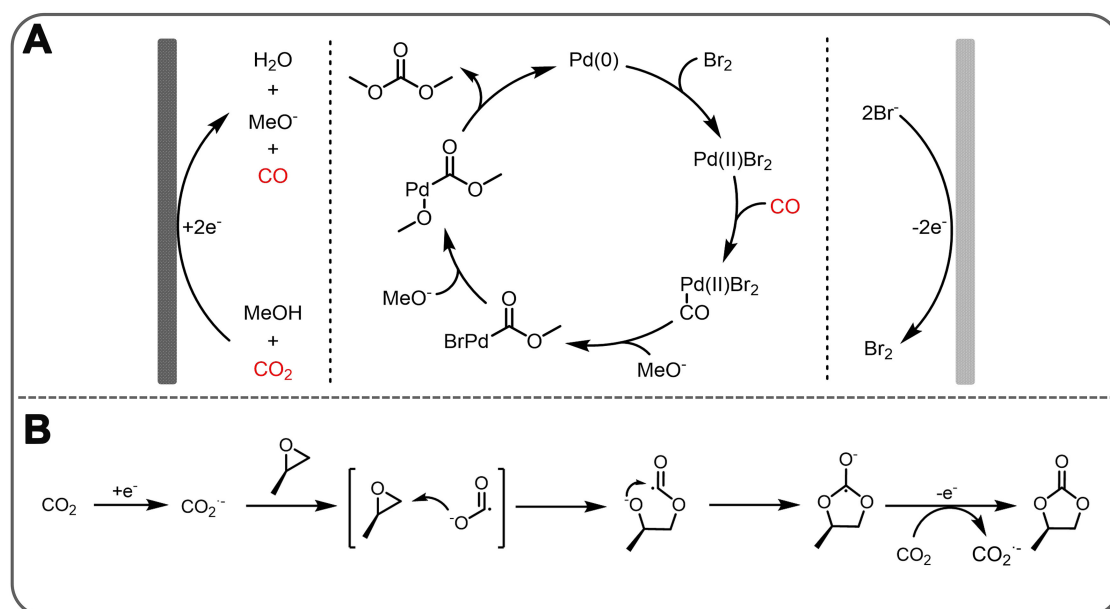
### C–S bond formation

The construction of C–S bonds from CO<sub>2</sub> and S-containing species is important to the synthesis of

**Table 4. Selected examples of electrolytic conversion of CO<sub>2</sub> and (methanol, diols, epoxides, and propylene oxide)**

Substrate	Product	Electrode	Catalyst	Electrolyte	Solvent	Current or voltage	Yield
CO <sub>2</sub> , methanol	DMC	Au plate <sup>[139]</sup>	Pd/C NaBr	0.1 M NaBr	Methanol	12 mA·cm <sup>-2</sup>	60%
CO <sub>2</sub> , methanol	DMC	Ni Sas/OMMNC <sup>[140]</sup>	Pd/C KBr	0.1 M KBr	Methanol	12 mA·cm <sup>-2</sup>	80%
CO <sub>2</sub> , diols	Cyclic carbonate	(-)Ni-Mg(+) <sup>[141]</sup>	/	C <sub>4</sub> MIMBF <sub>4</sub>	C <sub>4</sub> MIMBF <sub>4</sub>	-1.7 V	12%
CO <sub>2</sub> , epoxides	Cyclic carbonate	(-)SS-Mg(+) <sup>[142]</sup>	/	TEAI	MeCN	2.88 mA	54%
CO <sub>2</sub> , propylene oxide	Cyclic carbonate	Cu/CS-Il <sup>[143]</sup>	/	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 CO<sub>2</sub> and schematic of the proposed reaction mechanism for DMC synthesis; (B) Electrochemical synthetic pathway for propylene carbonate from CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> and SO<sub>3</sub><sup>2-</sup> as the C and S resources on Cu-based catalysts<sup>[145]</sup>. The electrosynthesis was carried out in a modified gas diffusion half-cell configuration, where CO<sub>2</sub> was supplied through the gas phase and 1 mol/L KOH with 200 mmol/L SO<sub>3</sub><sup>2-</sup> 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 CO<sub>2</sub> and SO<sub>3</sub><sup>2-</sup> suggested three possible reaction pathways.

The relevant *in-situ* characterization experiments indicate that the C–S bond is formed by the attack of the SO<sub>3</sub><sup>2-</sup> ion in the solution on the \*CHOH intermediate generated on the catalyst surface [Figure 13]. The

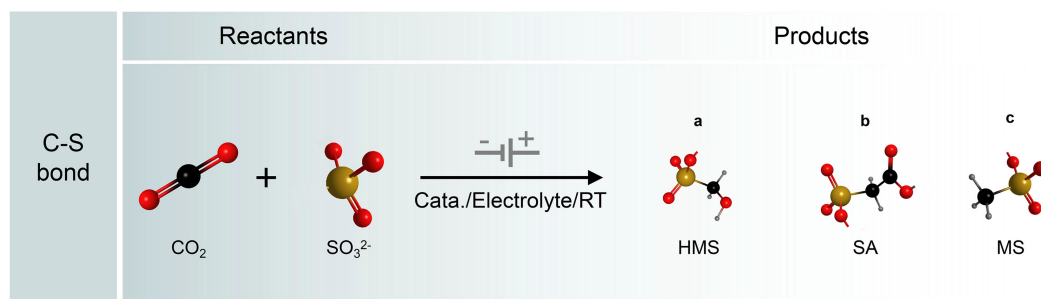


Figure 12. Electrocatalytic C–S coupling reactions and C–S products.

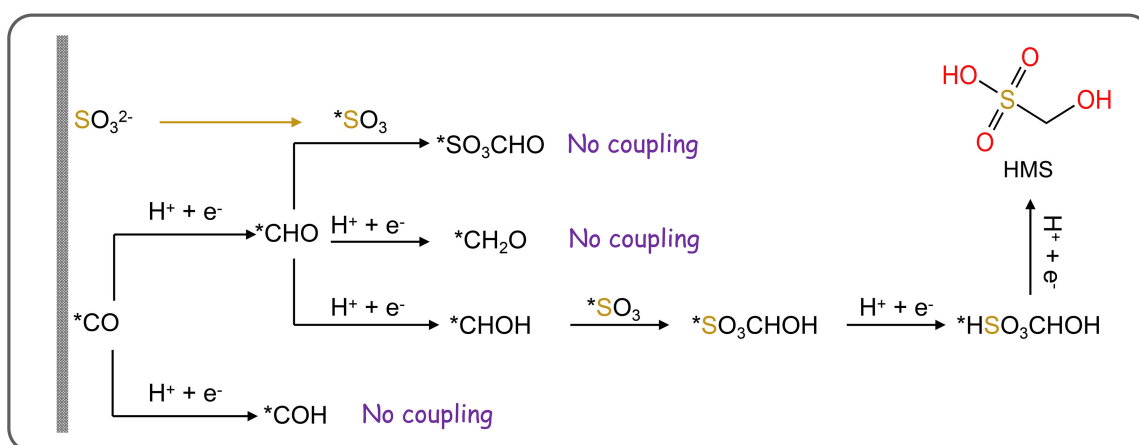


Figure 13. Reaction pathway from  $^*CO$  to HMS. HMS: Hydroxymethanesulfonate.

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<sup>[146]</sup>.

## EFFECT OF THE ELECTROLYTE FOR ELECTROCATALYTIC REACTION

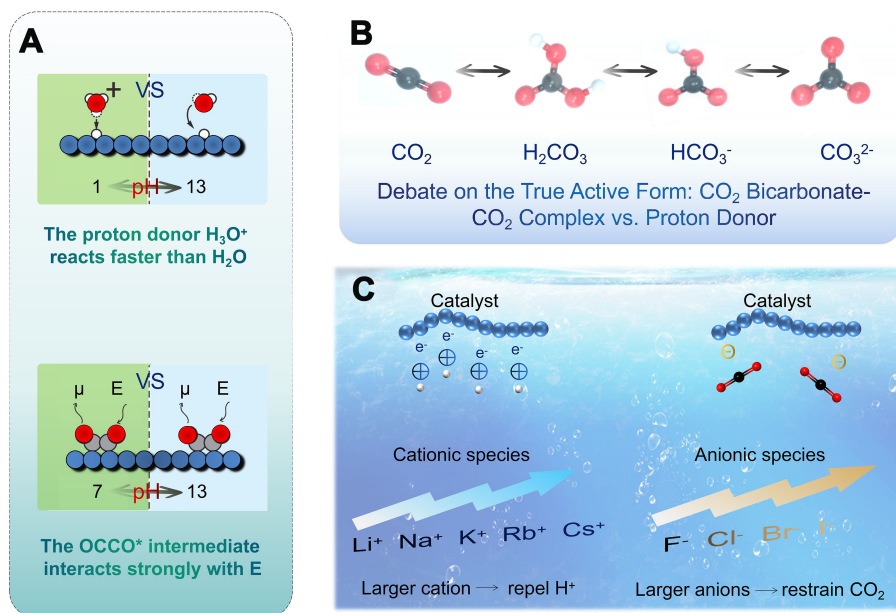
The type of electrolyte can also significantly influence electrocatalytic performance. The primary reason is that different concentrations of anions and cations in the electrolyte can lead to variations in buffering capacity<sup>[147-149]</sup>, pH value<sup>[150,151]</sup>, and proton donors<sup>[152]</sup>. 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  $\text{H}_3\text{O}^+$  to  $\text{H}_2\text{O}$ ) or oxidants (e.g., from  $\text{OH}^-$  to  $\text{H}_2\text{O}$ ) with pH can have an order-of-magnitude effect on the rate of electrochemical  $\text{CO}_2$  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  $\text{OH}^-$  without any involvement of the electrode<sup>[153]</sup>. When  $\text{CO}_2$  dissolves in an aqueous solution, different carbonaceous species such as  $\text{CO}_2$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$  are formed, thus leading to debate about the true active species in the reaction process [Figure 14B]<sup>[149,152]</sup>. Studies have shown that under alkaline conditions, over 50% of the energy is used to recover  $\text{CO}_2$  to  $\text{CO}_3^{2-}$ . In contrast, acidic conditions inhibit the conversion of  $\text{CO}_2$  to  $\text{CO}_3^{2-}$  and facilitate material separation. However, under strong acidic conditions, protons are more likely to capture electrons, thus favoring hydrogen evolution over  $\text{CO}_2$  reduction<sup>[154]</sup>. To date, the aqueous solutions used in most studies are weakly acidic or alkaline electrolytes containing cations and buffering/non-buffering anions [Figure 14C]<sup>[149,155,156]</sup>. In these electrolytes, larger cations such as  $\text{K}^+$  and  $\text{Cs}^+$  could adsorb on the electrode and reduce hydrogen evolution by repelling  $\text{H}^+$  ions, whereas smaller cations such as  $\text{Li}^+$  do not. In addition, larger cations are hydrolyzed in the vicinity of the cathode, thereby lowering the pH and increasing the local  $\text{CO}_2$  concentration, increasing the product selectivity and reducing the formation of  $\text{H}_2$ <sup>[155]</sup>. In addition to cations, anions also have a significant effect on the outcome of the electrocatalytic  $\text{CO}_2$  reaction. Non-buffering halides such as  $\text{Cl}^-$  and  $\text{Br}^-$  enhance the product selectivity by affecting surface charges and inhibiting proton adsorption, whereas  $\text{F}^-$  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  $\text{H}_2$  and thus improves the reaction efficiency<sup>[156]</sup>.

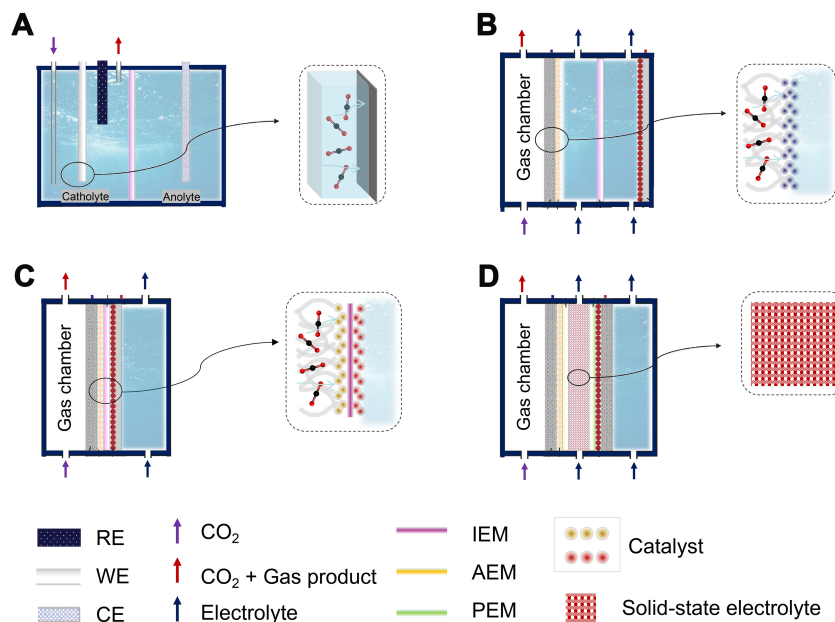
## DEVELOPMENT OF THE REACTOR IN THE ELECTROCATALYTIC REACTION

An in-depth study of the structural characteristics of different  $\text{CO}_2$  electrolyzers and facilitating their engineering are all key to large-scale applications<sup>[157]</sup>. 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]<sup>[158-160]</sup>. 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<sup>[145,161-164]</sup>. Both can be operated continuously and utilize GDEs to improve  $\text{CO}_2$  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<sup>[165,166]</sup>. MEA-cell electrolyzers enable  $\text{CO}_2$  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<sup>[67]</sup>. 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<sup>[167,168]</sup>. Currently, electrolyzers used for C-H reactions formed from  $\text{CO}_2$  and  $\text{H}_2\text{O}$  have been well applied in these devices. However, research on  $\text{CO}_2$ -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  $\text{CO}_2$  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  $\mu$ ); (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  $\text{CO}_2$  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.

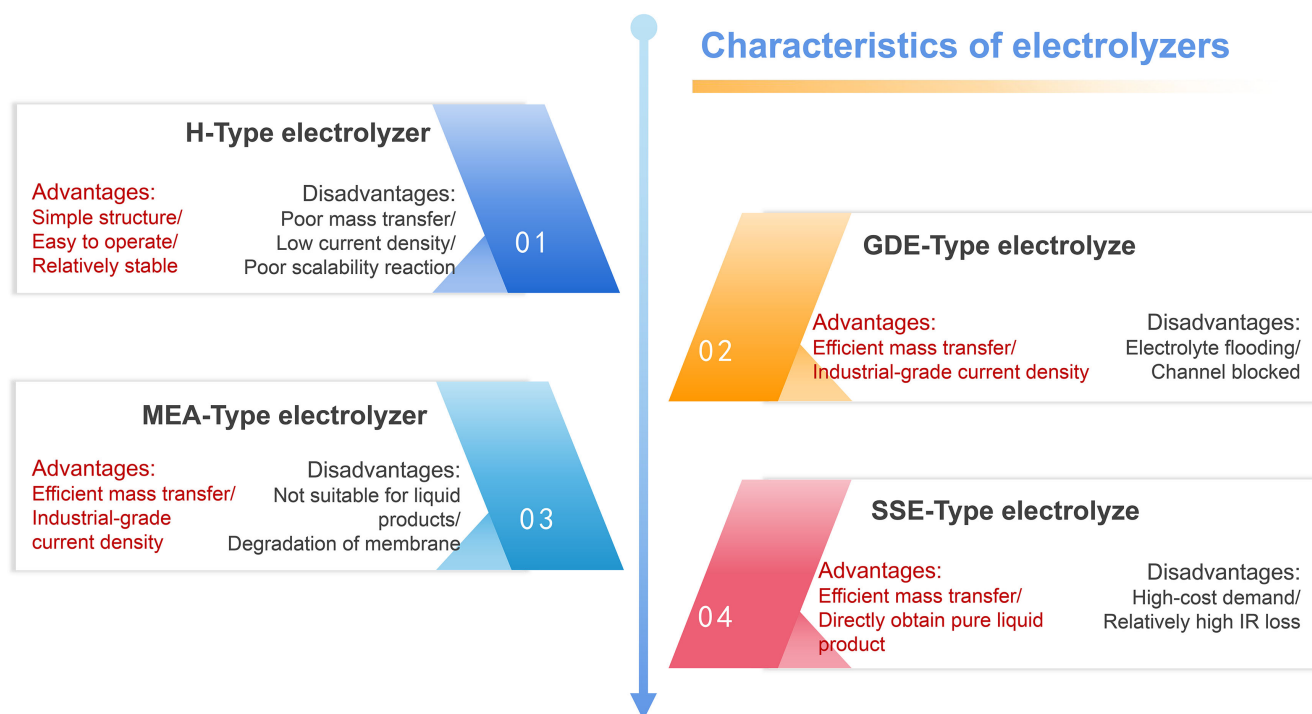


Figure 16. The advantages and disadvantages of electrolyzers.

## CONCLUSIONS AND OUTLOOKS

In conclusion, the electrochemical conversion of CO<sub>2</sub> into value-added chemicals is a promising way to address the severely increasing CO<sub>2</sub> concentration in the atmosphere. New covalent bonds can be formed between CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> conversion to address environmental and economic challenges.

## (II) The future development of CO<sub>2</sub> and small molecules

(1) C-H bonds: currently, a variety of well-designed catalysts have been successfully used to convert CO<sub>2</sub> into various C<sub>1</sub> and C<sub>2</sub> products, and the reaction efficiency has also been greatly improved, but for C<sub>3</sub> and above products, the catalytic efficiency of the catalyst remains relatively low. The production of C<sub>2</sub> products often requires coupling between C<sub>1</sub> active species. If multiple C<sub>1</sub> active species are required for coupling, the formation of C<sub>3</sub>, C<sub>4</sub>, and other products must be a huge challenge because it involves the complex transfer of multiple electrons and protons. If C<sub>1</sub> and C<sub>2</sub> products can be further activated on the catalyst, coupled themselves, or further combined with CO<sub>2</sub>, 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>. Although some teams have recently realized the carboxylation of sp<sup>2</sup> 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 CO<sub>2</sub>. 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 sp<sup>3</sup> C–H bonds.

(3) C–N bonds: the reaction between CO<sub>2</sub> 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 CO<sub>2</sub> and inorganic nitrogen sources, but CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> is extremely attractive, but there are few related studies. In principle, CO<sub>2</sub> can be converted into ethylene oxide by pairwise reaction of anode and cathode. By further combining ethylene oxide with CO<sub>2</sub>, 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 CO<sub>2</sub> utilization efficiency. Acid electrolyte system can be explored to improve the utilization efficiency of CO<sub>2</sub>. 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 CO<sub>2</sub> 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

All authors declared that there are no conflicts of interest.

### Ethical approval and consent to participate

Not applicable.

### Consent for publication

Not applicable.

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