Recent Advances and Challenges in Electrocatalytic Carboxylation of CO_2

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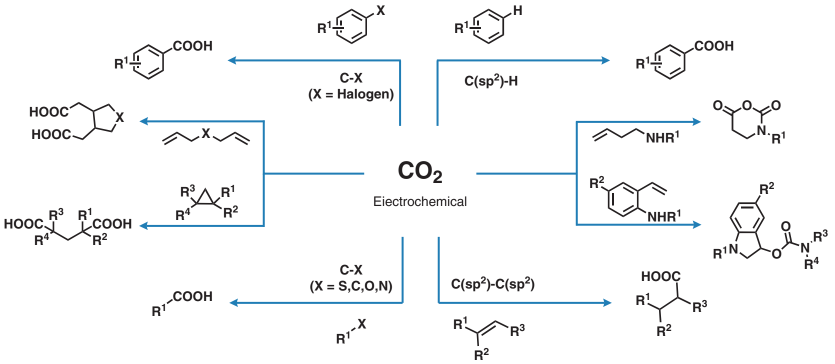

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Abstract The electrochemical fixation of carbon dioxide onto organic matter has emerged as a promising approach in recent years. By combining the unique features of electrochemistry with the goal of carbon dioxide fixation, researchers aim to develop new strategies that can contribute to a more sustainable and environmentally friendly synthesis of organic compounds. One advantage of electrochemical methods is their ability to provide both electrons and energy for chemical transformations. This allows for the direct conversion of carbon dioxide into valuable organic products, without the need for transition metal catalysts or harsh reaction conditions. As a result, electrochemical carbon dioxide fixation offers the potential for milder and more efficient processes compared to traditional methods. Scientists have made noteworthy progress in exploring different strategies for the fixation of carbon dioxide under electrochemical conditions. These strategies involve the activation of various types of chemical bonds, including C(sp^2)–C(sp^2), C(sp^2)–H, C–X (X = halogen), and C(sp^3)–X (X = S, C, O, N). This review aims to provide an overview of the current state of research on electrochemical carbon dioxide fixation into organic matter. It will discuss the different strategies employed, the key findings, and the challenges that remain to be addressed. By highlighting the recent advancements in this field, this review hopes to inspire further exploration and innovation in the area of electrochemical synthesis for carbon dioxide fixation.

Key words electrochemical, carbon dioxide, carboxylation, esterification, chemical selectivity

1 Introduction

Carbon dioxide is considered an excellent source of C1 in comparison to carbon monoxide and formaldehyde due to its nontoxicity, renewability, and copious presence in the environment.[1] Despite its intrinsic chemical inertness, carbon dioxide holds enormous potential as a feedstock for the synthesis of organic compounds, a process of considerable relevance for mitigating the impact of the global greenhouse effect. To fix carbon dioxide, various strategies, including transition-metal-catalyzed and photocatalytic approaches, have been developed.[2] However, most of these methods require the use of stoichiometric precious metal catalysts or extreme reaction conditions. In contrast, electrochemical carboxylation method offers a more sustainable alternative, circumventing some of these limitations and facilitating the conversion of carbon dioxide into organic molecules under comparatively mild conditions.

Electrochemistry offers unique advantage over other catalytic methods, such as transition metal catalytic and photocatalytic reactions, due to the source of electrons and energy supply. The use of electrons to replace foreign redox reagents is a fundamental advantage of electrochemistry, making it possible to better control the energy supply by adjusting the current and voltage. This advantage has led to the exploration of electrochemical means for achieving carbon dioxide carboxylation, with the goal of avoiding external electron sources and controlling energy supply to achieve directional bond breaking and improve carboxylation selectivity. Despite starting later than transition metal catalysis and photocatalysis, electrochemical carboxylation has become an increasingly desirable strategy and has gained widespread attention. Various techniques have been developed over time, however, the process of electroreduction often involves the sacrifice of metal anodes to provide electrons for the entire system, which conflicts with envi-

Biographical Sketches

Jie Wang was born in 1999 in Chizhou of Anhui Province, China. He received his B.S. degree from West of Anhui University in 2021. He is currently a postgraduate student under the supervision of Prof. Renjie Song at Nanchang Hangkong University. The focus of his research lies in the field of organic chemistry methodology.

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Chang-Hai Lu was born in 1993 in Jiangxi. He received a Ph.D. degree from Jinan University, Guangzhou, China, in 2021. The same year, he carried out postdoctoral research at the Institute of Photonics Technology, Jinan University, Guangzhou, China. In 2023, he joined Nanchang Hangkong University in China. His research focuses on the fabrication and functionalization of nonmetallic plasmonic nanostructures and their applications in CO_2 reduction and organic conversion.

Ren-Jie Song was born in 1983 in Hunan, China. He received his Ph.D. in 2006 from the College of Chemistry and Chemical Engineering at Hunan Normal University (P. R. of China). In 2011, he moved to Hunan University with Professor Jin-Heng Li as a postdoctoral fellow. In 2013, he became a research assistant in the College of Chemistry and Chemical Engineering at Hunan University and then moved to Nanchang Hangkong University in 2016. In 2019, he became a professor at Nanchang Hangkong University. His current research interests include the development of new synthetic methodologies and heterocycle synthesis.

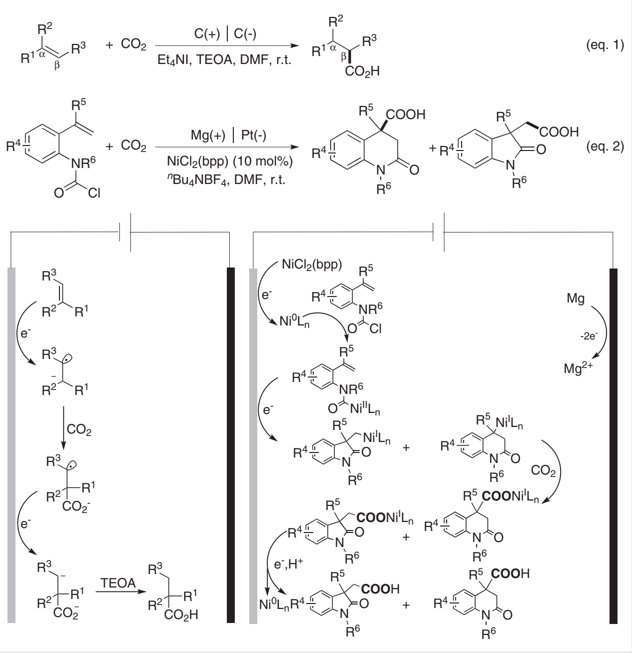
ronmental protection concepts as most sacrificial anodes are metals that lose electrons easily. Therefore, contemporary research is directed towards the development of novel electrochemical systems that forgo the use of sacrificial anodes while attaining high chemoselectivity and regioselectivity in electrochemical carboxylation. Herein, this review presents the latest research progress on electrochemical carbon dioxide fixation by carboxylation since 2021.

2 Electrocatalytic Monocarboxylation of CO_2

2.1 Monocarboxylation of C(sp^2)–C(sp^2)

The carboxylation of unsaturated olefins with carbon dioxide has long been a captivating field of study. Transition metal catalysis and photocatalysis have been extensively used as effective methodologies for this transformation. In contrast, the electrochemical approaches for this process have faced considerable limitations thus far, including restricted substrate scope and poor regioselectivity.[3] These challenges present substantial obstacles, which currently impede the broader application and advancement of electrochemical carboxylation in this research.

For example, in 2021, the Buckley group reported a breakthrough method for the carboxylation of unsaturated olefins using electrochemical means with excellent regioselectivity.[4] This report not only broadens the range of application substrates from limited aryl olefins to alkyl olefins, but also introduces an electrocatalytic strategy that obviates the need for sacrificial electrodes (Scheme 1, eq. 1). The yield and regioselectivity for the carboxylation of the β-position is remarkable in this electrocatalytic strategy, which utilizes triethanolamine (TEOA) as a proton source and enables the products to be directly separated and crystallized without the need for column chromatography. Moreover, the Zhang group unveiled a novel electrochemical cyclic carboxylation reaction strategy for carbon dioxide in 2023.[5] This reaction is carried out in an unseparated electroreactor under constant pressure and current conditions, facilitating the electrochemically cyclization and carboxylation of alkenyl-tethered carbamoyl chlorides and carbon dioxide by nickel catalysis (Scheme 1, eq. 2). Prior to this report, electrochemical CO_2 cyclization reactions predominantly focused on converting carbon dioxide into an ester group. Although this reaction can exclude aryl olefin based substrates, the challenge of regioselectivity has been a persistent issue in the domain of electrochemical CO_2 utilization.

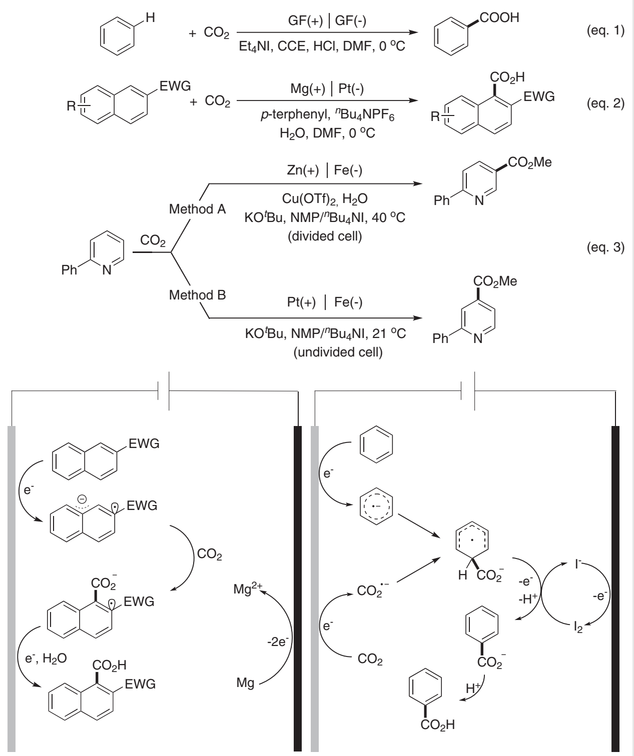


Scheme 1 Monocarboxylation reactions of C(sp^2)–C(sp^2) bonds and mechanisms

2.2 Monocarboxylation of C(sp^2)–H

The activation of C–H bonds on arenes to synthesize high-value aryl carboxylic acids has been a focal point of research. Strategies such as photocatalysis and transition metal catalysis have been explored to achieve this transformation.[6,7] High-value aryl carboxylic acids hold immense research significance in numerous chemical fields, leading to the continuous exploration of novel approaches for their synthesis. Recently, the field has advanced further with successful carboxylation of C(sp^2)–H bonds between carbon dioxide and aryl groups via electrochemical means.

In 2022, the Qiu group published a breakthrough report of a metal-free electrochemical catalysis method for carbon dioxide carboxylation with high regioselectivity.[8] Their method enabled directional carboxylation of C–H bonds on unactivated aromatic hydrocarbons without external catalysts, metals, and bases, making it suitable for challenging aromatic hydrocarbons including electron-deficient naphthalenes and simple phenyl derivatives (Scheme 2, eq. 1). This significant achievement laid the foundation for subsequent developments in electrochemical inactivated aromatic carboxylation reactions. Building on this advance, the Mita group in 2023 presented a new approach for the selective monocarboxylation of 2-substituted naphthalenes (Scheme 2, eq. 2),[9] inspired by Wearring's pioneering work on the carboxylation of naphthalene with carbon dioxide in 1959.[10] The Mita group achieved selective modification of electron-deficient naphthalene derivatives, utilizing a redox medium and water as additives to perform monocarboxylation at the naphthalene C1-position. The study indicated that the redox medium and water used inhibited further reduced carboxylation during the reaction, ensuring high selectivity and yields. However, attempts to apply this method to electron-rich naphthalene derivatives yielded unsatisfactory results, underscoring the limitations in substrate scope. Despite these challenges, the research enhanced our comprehension of the factors affecting selectivity in electrochemical carbon dioxide carboxylation.



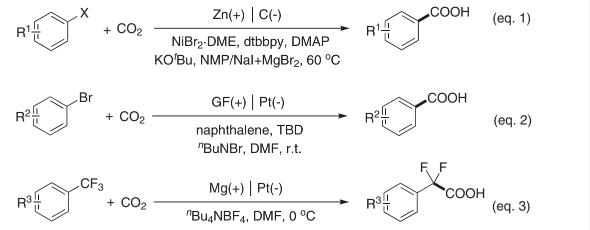
Scheme 2 Monocarboxylation reactions of C(sp^2)–H bonds and mechanisms

In the same year, the Lin group also made an important contribution by reporting the electrochemically induced carboxylation of *N*-heteroaromatic hydrocarbons at different sites employing varied electrochemical reactors (Scheme 2, eq. 3).[11] This study showed that split electrochemical reactors (divided cell) in the reaction system favored C5 carboxylation, whereas unsplit electrochemical reactors (undivided cell) promoted C4 carboxylation. When this strategy was extended to other substrates by Wang, Xiao, and Chen, the type of electrochemical reactor selected significantly influenced the reaction site preference for most substrates.[12] The authors further explained that intrinsic electronic properties of intermediates in the reaction determined regioselectivity, as supported by experiments and energy level calculations. Their proposal of this strategy opened up a new direction for adjusting regioselectivity in electrochemical carboxylation, providing a rare technological breakthrough in this field where most methods only involve unsplit electrochemical reactors.

2.3 Monocarboxylation of C–X (X = I, Br, Cl, F)

Selective carboxylation remains a signification challenge due to the low reactivity of carbon dioxide and unactivated halogenated compounds. While research efforts have been extensive, the electrochemical activation of C–halogen bonds for carboxylation is not a widely employed technique at present.[13]

In 2021, the Manthiram group proposed a novel approach for electrochemical carboxylation,[14] which introduced anhydrous $MgBr_2$ into the reaction system to ensure a sufficient concentration of Mg^{2+} and inhibit the nucleophilicity of carboxylates. This method achieved highly selective carboxylation of halogenated substances, including polyaliphatic, phenyl, and aromatic halogenated compounds, without reliance on sacrificial anodes. Although the yields are moderate, this strategy offers a substantial reference value for the future development of the electrocarboxylation of halogenated compounds. Concurrently, the Yu group made a significant contribution by designed an electrochemical nickel-catalyzed carboxylation reaction for unactivated halogenated substrates with carbon dioxide (Scheme 3, eq. 1).[15] This method overcomes the limitations of substrate selection by enabling the carboxylation of electron-deficient heteroaromatic hydrocarbons and activated aryl halides containing electron-withdrawing groups. Also, it circumvented the need for sacrificial anodes by employing a completely different mechanism from previous reductive electrocarboxylation reactions. In 2022, Xue, Qiu, and co-workers proposed a reaction pathway for the carboxylation of organic halogenated substrates without using sacrificial anode (Scheme 3, eq. 2).[16] The strategy assist in the transfer of electrons and addressed the problem of high reduction potential of organohalogens by added a catalytic amount of naphthalene to the reaction system.[14,17] This approach, which avoids the use of sacrificial electrodes and transition metal catalysts, represents a promising sustainable alternative for the electrocarboxylation of organic halogenated substrates.

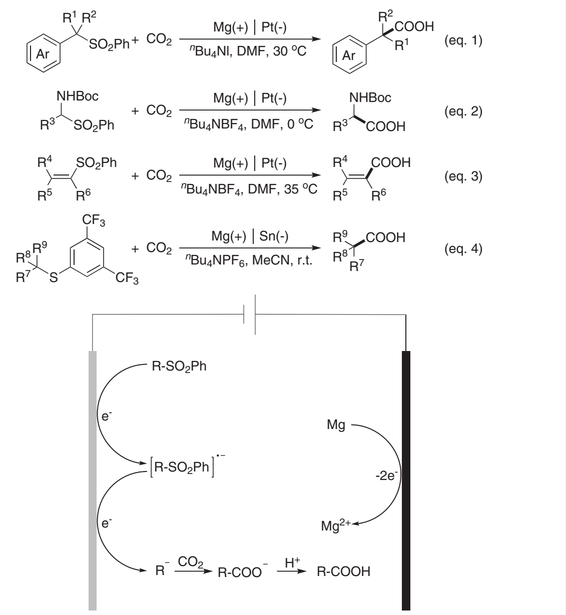


Scheme 3 Monocarboxylation reactions of C–X (X = I, Br, Cl, F) bonds

The use of electrochemical as a means for C–F carboxylations has been a target for many research groups. In 2023, the Meanwell group made a breakthrough in this field.[18] Starting from trifluoromethyl-substituted arenes, electrolysis using an undivided cell with Mg anode and Pt cathode, with $^{n}Bu_4NBF_4$ as electrolyte in DMF at 0 °C gave α,α-difluoro carboxylic acids (Scheme 3, eq. 3). The traditional gaseous carbon dioxide was replaced by ground dry ice, which increases the concentration of carbon dioxide in the system, and can avoid the requirements of previous water-free and inert conditions. This method provides new ideas for subsequent research and increases the electrochemical methods for the study of dehalogenative carboxylation.

2.4 Monocarboxylation of C(sp^3)–X (X = S, C, O, N)

In 2021, the Ye group developed a highly efficient pathway for the electrochemical desulfurization carboxylation (Scheme 4, eq. 1).[19] This reaction uses an active metal as the sacrificial anode to provide electrons, these electrons activate the C–S single bond to produce a benzyl anion that nucleophilically attacks carbon dioxide to form carboxylates. Notably, the scope of this reaction extended beyond primary sulfones, with secondary and tertiary sulfones also demonstrating notable reactivity. Simultaneously, the Senboku group reported an electrocarboxylation synthesis of *N*-Boc-α-amino acids (Scheme 4, eq. 2),[20] while sharing similarities with Ye's process in terms of their reaction conditions and mechanisms, except for the variation in temperature settings.



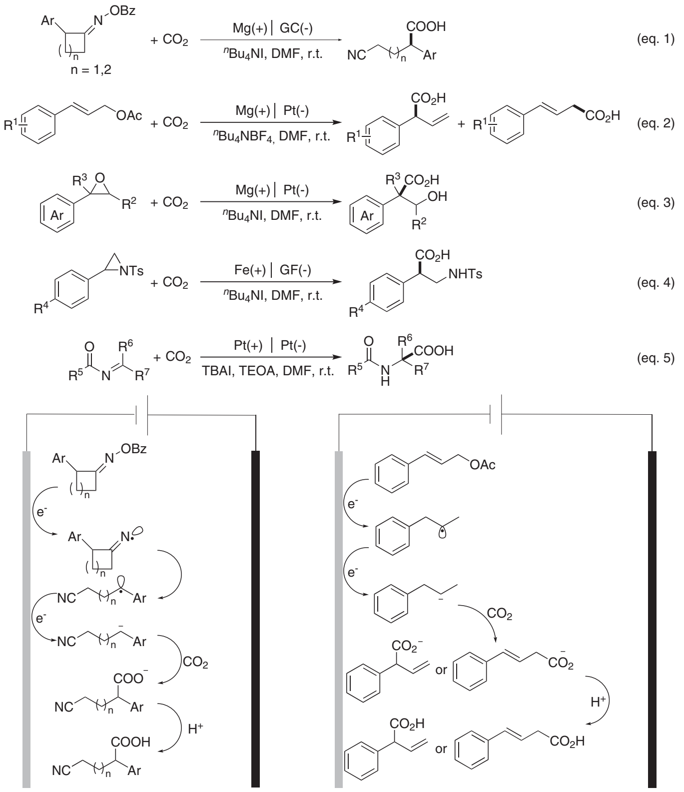
Scheme 4 Monocarboxylation reactions of C–S bonds and mechanism

In 2022, the Chen group conducted a highly selective electrocarboxylation reaction of α,β-unsaturated sulfones (Scheme 4, eq. 3).[21] This reaction was distinguished by its exceptional regioselectivity and its strategic avoidance of a sacrificial anode. Additionally, it is notable for its ability to preserve the integrity of the original unsaturated structures within the alkene and alkyne substrates. In 2023, Ahlquist, Lundberg, and co-workers reported an electrochemical carbon dioxide carboxylation reaction of sulfides, as part of their research on the electrochemical desulfurization conversion of thioethers (Scheme 4, eq. 4).[22] It should be noted that this reaction only entails a change in solvent and cathode electrode from the previous reaction.

In 2022, the Zhang group reported an electrochemical ring-opening carboxylation of cycloketone oxime esters (Scheme 5, eq. 1),[23] employing magnesium metal as the sacrificial anode and a glassy carbon electrode as the cathode. The mechanism of this reaction follows a typical electrocarboxylation pathway, where the cyclic ketoxime ester substrate undergoes a ring-opening reaction at the cathode, generating cyanoalkyl radicals and cyanoalkyl anions that subsequently attack carbon dioxide to form carboxylate salts. Although this reaction does not represent a significant breakthrough in mechanism, it offers new possibilities for carboxylation reactions.

Previous studies have primarily focused on carboxylation reactions involving C–X, C–H, and unsaturated olefins with carbon dioxide due to the low reactivity and high bond dissociation energy of C–C single bonds. Pioneering work by Yu demonstrated C–C single bond carboxylation through photochemical strategies.[24] Moreover, the electrochemical approach of the Zhang group offer a more sustainable alternative that avoids the use of expensive iridium catalysts and toxic reducing agents (Scheme 5, eq. 1).[25] In 2022, the Ackermann group also reported an electrocarboxylation method between allyl esters and carbon dioxide at atmospheric pressure (Scheme 5, eq. 2).[26] This reaction was previously studied by the Mei group in 2018, when transition metal catalysts were employed.[27] Although electrochemical reactions played a role in enhancing the nucleophilicity of metal catalysts in Mei's work, Ackermann's method considerably reduces the need for transition metal catalysts as the electrochemical portion of the reaction serves as the required reducing agent. Moreover, the Ackermann group supported their proposed mechanism using cyclic voltammetry (CV), suggesting that the substrate electron density and steric hindrance affect the regioselectivity.

In 2022, the Qiu group reported a novel pathway for generating β-hydroxy acid derivatives via electrocarboxylation with carbon dioxide using epoxy aryl compounds as substrates (Scheme 5, eq. 3).[28] Previously, the synthesis of most β-hydroxy acid derivatives required multistep processes, and previous methods displayed limited functional group tolerance. Additionally, in almost all ring-opening carboxylation methods of epoxy compounds, the reactions were centered on O atoms, and electrochemical ring-opening carboxylation at the C center was unachievable. However, the Qiu group overcame this limitation and achieved high chemoselectivity, regioselectivity, yield, substrate scope, and functional group compatibility for the reaction. Remarkably, the magnesium anode as a sacrificial anode



Scheme 5 Monocarboxylation reactions of C–X (X = C, O, N) bonds and mechanisms

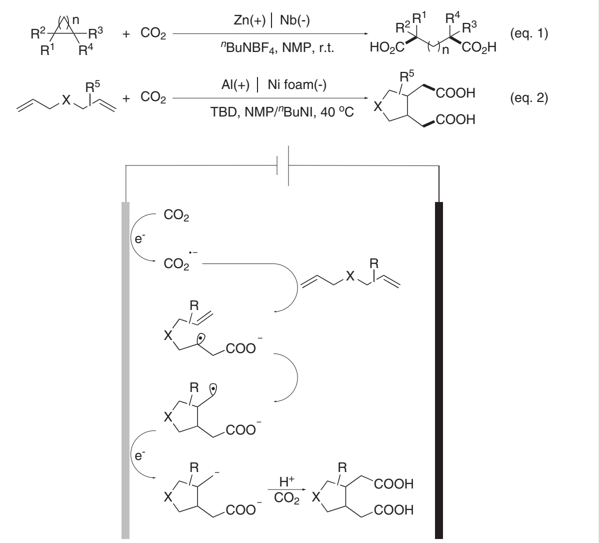
serves a dual purpose in the reaction, providing electrons and participating in intermediate formation. In a subsequent report, the Qiu group described electroreduced cross-electrophilic coupling of aziridines with aryl bromides (Scheme 5, eq. 4),[29] which also briefly mentioned the use of carbon dioxide and arylaziridines for cross-coupling to obtain β-amino acids.

In 2022, the Lu group developed a new strategy for generating amino acids through the electrocarboxylation of carbon dioxide with *N*-acylimines (Scheme 5, eq. 5).[30] This reaction is notably for its avoidance of sacrificial electrodes, using triethanolamine as an internal reducing agent, and for achieving high yields, chemoselectivity, and regioselectivity. Despite these advances, the mechanism did not present a novel discovery.

3 Electrocatalytic Dicarboxylation of CO_2

Since the discovery of carbon dioxide as an excellent carbon source, significant efforts have been made to explore its use in the monocarboxylation of various substrates.[31] Dicarboxylic acids are of substantial biological relevance and have been applied in various fields,[32] including medicine, materials science, and polymer industries.[33] Therefore, exploring the use of carbon dioxide as a carboxyl source for dicarboxylation modification is of great significance. Despite progress being made in the electrochemical dicarboxylation reactions for olefins,[3c,15,34] alkynes,[35] and aromatics,[36] there remains ample scope for improving the current pathways of electrochemical dicarboxylation reactions.

In 2022, the Yu group developed an innovative open-loop dicarboxylation method employing electrochemical techniques, breaking C–C bonds and achieving efficient selective cleavage and functionalization modification of C–C single bonds (Scheme 6, eq. 1).[37] This represented a significant leap forward from previous electrochemical oxidative ring-opening reactions that were confined to symmetrical substrates, as Yu's approach exhibited enhanced substrate adaptability and flexibility. Moreover, the group further demonstrated the cyclic dicarboxylation reaction between carbon dioxide and unactivated skipped dienes using electrochemical techniques in 2023 (Scheme 6, eq. 2).[38] While both reactions undergo dual single-electron transfers, the mechanisms differ significantly. In the ring-opening reaction, both single-electron transfers occur on the substrate, leading to the formation of radical anions and carbon anions that react with carbon dioxide. In contrast, for the cyclization reaction, the first single-electron transfer generates a free radical anion of carbon dioxide that attacks an olefin resulting in cyclization and a carbon radical; the second single-electron transfer then forms a carbon anion, and the nucleophile attacks carbon dioxide to form the corresponding carboxylate. This mechanism provides an exciting new strategy for the development of carbon dioxide dicarboxylation.



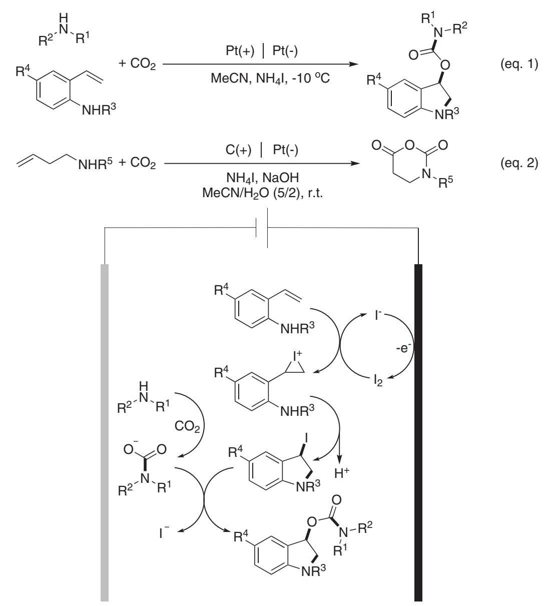
Scheme 6 Electrocatalytic dicarboxylations of CO_2 and mechanism

While significant advancements have been made in the field of electrochemical dicarboxylation of carbon dioxide, several challenges still remain to be addressed, such as overcoming the limitations of substrates and minimizing the use of electrodes and metals. Addressing these issues is crucial for advancing the field and necessitates more comprehensive research. Therefore, there is a need for more extensive research to enhance our understanding of the underlying mechanisms and improve the efficiency of these reactions.

4 Electrocatalytic Esterification of CO_2

Carbon dioxide has been extensively recognized as an excellent carbon source, and its potential has been extensively explored in electrochemical carboxylation. Another promising application of carbon dioxide is its use in electrochemistry-based esterification. However, it is worth noting that the current research focus remains largely on electrochemical carboxylation, while relatively less attention has been given to electrochemical esterification. Therefore, given the potential benefits, shifting research focus towards electrochemical esterification could yield valuable insights and practical applications.

In 2021, the Liang group reported a novel reaction strategy for the esterification of carbon dioxide, an amine, and an enyl sulfonamide to form a carbamate using electrochemistry (Scheme 7, eq. 1).[39] The success of this method can be attributed to the suppression of competing reactions under controlled low-temperature conditions. The Pan group reported a similar approach in 2022, where C–C coupling of an allylamine or homoallylamine and carbon dioxide was achieved to produce oxazolidinones or 1,3-oxazinanones, respectively (Scheme 7, eq. 2).[40] In this case, the addition of iodized salt as an electron transfer agent eliminates the requirement for sacrificial anode and metal catalysts. Both methods achieved excellent yields and regioselectivity. Furthermore, the Nam group also developed a unique reaction strategy for the synthesis of methyl formate in 2022.[41] They utilized Ti as the anode, Sn as the cathode, methanol as the electrolyte, and $NaBF_4$ as the electrolyte. The key to this approach is generating a strong Lewis acid at the anode, facilitating the reduction of carbon dioxide at the cathode to formate, which is coupled with methanol to form methyl formate. These studies demonstrate the potential for electrochemical esterification as a promising research area with multiple practical applications.



Scheme 7 Electrocatalytic esterifications of CO_2 and mechanism

After analyzing the above discussion, it is apparent that electrochemical esterification of carbon dioxide still faces significant challenges. The successful coupling of three components and the self-cyclization reactions require further refinement to enhance efficiency and overall success rates. Consequently, it is evident that continued investigation into the electrochemical esterification of carbon dioxide is imperative to fully exploit this technology for broader applications.

5 Conclusions

In summary, while electrochemical methods offer certain advantages over traditional transition metal catalysis and photocatalysis, they also come with some drawbacks, such as the requirement for sacrificial electrodes and weak selectivity in some cases. Despite these challenges, significant strides have been made in addressing these issues and broadening the range of substrates amenable to electrochemical transformations. Notably, the field of electrochemistry has enormous potential for the carboxylation reaction after C–H activation, an area that has yet to be fully explored. Moving forward, it is essential for researchers to persist in their efforts to refine electrochemical techniques, address the current challenges, and uncover innovative strategies to realize the full potential of electrochemical methods.

Conflict of Interest

The authors declare no conflict of interest.

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