

Recent Progress in the Development of Electrode Materials for Electrochemical Carboxylation with CO₂

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Abstract

The desire to reduce carbon emissions in chemical synthesis has spurred research interest in leveraging CO₂ as an abundant, non-toxic, and renewable carbon source. Electrochemical carboxylation, a strategy employing clean electricity for the sustainable synthesis of value-added carboxylic acids from CO₂, represents a promising avenue. In this context, the careful selection of electrode material emerges as an important factor influencing the efficiency and selectivity of electrocarboxylation reactions. This review delves into the current landscape of developing high-performing electrocatalysts, guided by fundamental mechanistic understanding. Additionally, it examines how the choice of cathode material impacts reaction regioselectivity and explores the role of the anode in elevating performance and sustainability. The review concludes with perspectives on the future directions of the field and proposes strategies for further improvements.

1. Introduction

Chemical manufacturing is an integral part of modern society, responsible for the production of fertilizers, fuels, medications, and consumer goods that contribute to improved life expectancy and quality of life. However, the industry's reliance on fossil fuels, both as an energy source to drive chemical reactions and feedstocks to synthesize commodity chemicals, has made it a dominant driver of global climate change. According to the International Energy Agency, the chemical industry is the largest industrial energy consumer and the third-largest industrial source of CO₂ emissions in the world [1]. Faced with these challenges, research efforts have focused on the valorization of CO₂ into fuels and chemical products, which would simultaneously decrease society's reliance on fossil fuels and help sequester a greenhouse gas from the atmosphere, allowing for the transition to a more sustainable carbon neutral economy.

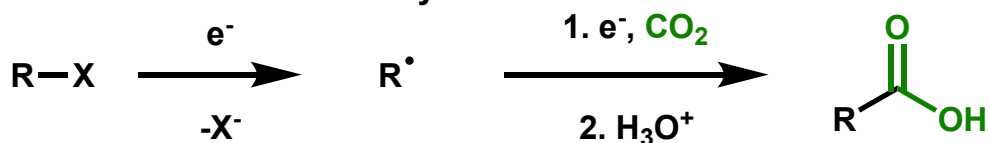
Despite these benefits, conversion of CO₂ into useful chemical products is challenging due to its thermodynamic stability and kinetic inertness. Consequently, previous strategies to activate CO₂ have often relied on harsh conditions, involving high temperatures and pressures. For instance, the industrial synthesis of urea from CO₂ and ammonia requires pressures of up to 350 bar and temperatures up to 220 °C [2,3]. The Kolbe-Schmidt reaction for the industrial synthesis of hydrobenzoic acid is performed with 100 bar of CO₂ pressure at 125 °C [4,5]. Even in instances where harsh conditions are avoided, the use of highly reactive reagents are required, such as organolithium and Grignard reagents, to drive C–C coupling with CO₂ [6–8].

Since then, milder and less-energy intensive conditions have been explored for the incorporation of CO₂ as a chemical building block in organic synthesis. These strategies have

focused on the development of improved thermo-[9], photo-[10,11], and electrocatalysts[12,13]. Out of these, thermocatalytic and photocatalytic methods still rely on homogeneous catalysts and stoichiometric chemical reductants, which are less ideal for industrial applications. Alternatively, electrochemical methods offer a milder route by providing the necessary energy in the form of voltage-driven electrons [14]. They can also be performed heterogeneously at the surface of an electrode, avoiding costly catalyst recovery and separation processes. And, as electricity becomes increasingly renewable in the future, electrochemical activation of CO₂ is shifting towards becoming a carbon-negative process.

To date, most literature reports on electrochemical conversion of CO₂ discuss electroreduction of CO₂ into useful C1 (CO, methanol, formate), C2 (ethylene, ethanol), and C3+ (propane, propanol) products. A great deal of progress has been made in the development of catalysts to improve selectivity, yield, and Faradaic efficiency (FE) towards the desired product [15–17], although achieving higher molecular weight products remains a challenge. One way to further increase molecular weights of products is to append CO₂ onto carbon scaffolds via a process called electrochemical carboxylation (or electrocarboxylation), generating carboxylic acids. The electrocarboxylation substrates range from organic halides (aryl and alkyl), carbonyls (ketones, aldehydes, imines), olefins, and alkynes. The diversity of substrate offers countless opportunities for the synthesis of industrially relevant carboxylic acids under mild conditions, using CO₂ as a renewable carbon feedstock and clean electricity as a driving force.

Substrate Reduction Pathway



CO₂ Reduction Pathway

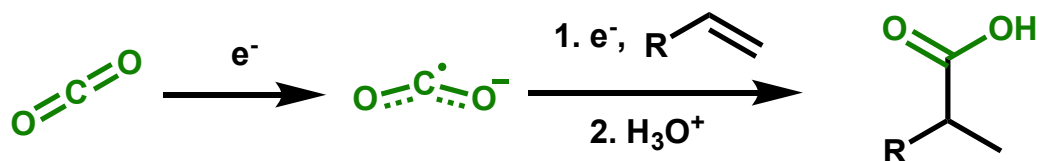


Fig. 1. Electrocarylation can either occur through a substrate reduction pathway (top) or CO₂ reduction pathway (bottom).

The choice of electrode material plays a key role in controlling the selectivity and efficiency of electrocarboxylation reactions. On the cathodic side, there are two generally accepted classes of mechanism for the electrocarboxylation of organic substrates [18,19]. Mechanism 1 (**Figure 1, top**) involves cathodic reduction of the organic scaffold, forming a nucleophilic species that can react with the electrophilic carbon in CO₂. Activation of the substrate can either involve a one or two electron transfer, depending on the identity of the substrate. Alternatively, CO₂ can be reduced in mechanism 2 (**Figure 1, bottom**), forming a radical anion, CO₂^{•-}, that reacts with an electrophilic substrate. Due to the inertness of CO₂, it was generally accepted that substrate activation was the dominant route towards electrocarboxylation. However, advances in the CO₂ reduction literature have dramatically lowered the overpotential for CO₂ reduction, making

mechanism 2 a more viable strategy, and in certain cases, a preferred strategy. This review highlights the current state of the art in the development of high performing electrocatalyst guided by the mechanistic understanding. There will also be brief discussions about the role of the cathode material in controlling reaction regio- and stereoselectivity, as well as the role of the anode in improving performance and sustainability. Finally, our perspectives on the outlook for the field and proposed strategies for further improvements will be discussed.

2. Mechanistically Informed Catalyst Design

2.1 Substrate activating catalysts

Given the relative kinetic inertness of CO₂, the electrocarboxylation substrate is often more readily activated under an applied reduction potential. In a substrate activation mechanism, the substrate can either be singly or doubly reduced, generating a nucleophilic species that subsequently reacts with CO₂. Efforts in electrocatalyst design have predominantly focused on lowering the onset reduction potential required to activate these substrates.

An example of a substrate that predominantly goes through the substrate activation pathway are organic halides. For these species, silver has traditionally been used as an electrocarboxylation cathode[18]. This is because the reduction potential of organic halides on silver is more positive relative to other cathode materials due to the strong X–Ag interaction, driving formation of the radical anion species. However, recent efforts have attempted to move away from using expensive, pure silver as an electrocatalyst, with focus shifting toward transition metal catalysts made from cheap and abundant materials.

One such strategy is the alloying of Ag with transition metals. Suryanarayanan et al. [20] synthesized trimetallic alloy nanomaterials made of different ratios of silver, copper, and nickel (Ag_xCu_yNi_z) and electrodeposited their materials on glassy carbon electrodes. They found that for the electrocarboxylation of benzyl bromide, a common electrocarboxylation model substrate, the best performing alloy was Ag₄₆Cu₄₀Ni₁₄, giving a yield of 95% under constant potential electrolysis with a charge of 2.1 F/mole. In general, it was observed that the alloy materials produced yields between 75-95%, which was comparable or better than the best performing monometallic system (Ag₁₀₀, with yield of 75%). X-ray diffraction and atomic force microscopy analysis (AFM) showed that the presence of Cu and Ni in the alloy generated a more porous structure that had greater surface roughness. This, in turn, led to lower reduction potentials for the benzyl bromide substrate and improved carboxylation performance, as confirmed by voltammetry data.

Research efforts have also focused on completely moving away from silver. Yimin et al. [21] showed that a Cu-Ni alloy electrode led to improved carboxylation performance over monometallic Ag, also citing greater porosity as the cause of improved performance. Using benzyl bromide as the substrate, the best performing Cu-Ni alloy produced a product yield of 39.4%, compared to 28.7% on Ag alone. The lower yield compared to work by Suryanarayanan [20] might be attributed to differences in electrolysis conditions (electrolyte solvent, run time, anode material). However, these works demonstrate the promise of using transition metals as carboxylation cathodes, with work by Yimin et al. showing potential for systems that only contain transition metals.

Considering the importance of high surface area electrocarboxylation catalysts, more recent catalyst design efforts have focused on increasingly porous catalyst materials. A carbazole-derived

porous organic polymer embedded with Cu (Cu@Cz-POP) showed promising performance towards the electrocarboxylation of benzyl bromide, delivering yield of 65% with a current density of 120 mA/cm² [22]. It was proposed that the porous structure help to promote mass and electron transport to the catalytically active Cu sites. Additionally, the electron-rich carbazole functionalization has high CO₂ affinity that is thought to promote CO₂ transport and coupling with the reduced benzyl bromide species, making carboxylation more favorable compared to side reactions such as hydrogenation.

These examples highlight some of the guiding principles that have allowed for the design of improved electrocarboxylation catalysts. Since then, research efforts have also expanded to the electrocarboxylation of substrates that are more challenging to activate compared to benzyl bromide, such as aryl chlorides and alkyl bromides. Due to the high onset reduction potentials of these substrates, direct reduction routes are often unviable. To that end, research efforts have focused on indirect reduction routes, either with the use of transition metal complexes or organic mediators.

In 2021, Yu et al. [23] studied the electrocarboxylation of a series of unactivated organic halides, using nickel as their catalyst. The optimized Ni-catalyst, containing a combination of ditertbutylbipyridine (L, dtbbpy) and 4-dimethylaminopyridine (DMAP) ligands, was able to perform electrocarboxylation of 4-chlorobiphenyl in 70% yield. They also performed electrocarboxylation of a wide range of aryl chloride, bromides, iodine and sulfonate substrates with yields reaching up to 90%. Mechanistic investigation found that rather than being directly reduced by the cathode, the organic halide substrate undergoes an oxidative addition step to the reduced Ni-catalyst. Consequently, the presence of the catalyst allows for the carboxylation of difficult to reduce species that have previously been inaccessible.

More recently, there has been a shift towards metal-free electrocarboxylation, especially for applications in the pharmaceutical industry that has strict limits on metal impurities. Work by Xue and Qiu et al. [24] demonstrated that naphthalene could act as an organic mediator for the electrocarboxylation of a wide range of aryl and alkyl bromide and aryl chloride substrates. Specifically, aryl chlorides containing electron-donating groups, which are especially challenging to reduce, showed respectable yields between 30-60%. Cyclic voltammetry data indicated that the naphthalene is first reduced, generating a radical anion that goes on to reduce the organic halide species. Density functional theory (DFT) was performed to confirm the thermodynamic viability of this process.

2.2 CO₂ activating catalysts

It was previously proposed that under electrocarboxylation conditions, CO₂ could also be reduced to generate the radical anion CO₂^{•-} that goes on to react with the organic scaffold. However, it was believed that this CO₂ reduction route was the minor pathway due to high overpotentials required for CO₂ reduction. More recently, as CO₂ reduction catalysts become increasing efficient and selective, there has been emerging interest in applying these catalysts towards electrocarboxylation.

In 2022, Zheng et al. [25] reported on a double activation strategy for the electrocarboxylation of acetophenone via silver-doped CeO₂ nanowires (Ag-CeO₂ NWs). They observed that compared to its monometallic counterparts (Ag foil, Ag nanoparticles, and CeO₂ nanowires), the Ag-CeO₂ NWs produced the 2-phenyllactic acid product at 91% Faradaic efficiency and 83% yield. In the CO₂ reduction literature, Ag has been shown to promote the formation of the adsorbed CO₂^{•-} radical

anion [26,27]. Under aqueous conditions, $\text{CO}_2^{\cdot-}$ is protonated, subsequently forming CO. In contrast, under the non-aqueous conditions typically employed in electrocarboxylation, the highly reactive $\text{CO}_2^{\cdot-}$ intermediate is expected to react with other species in solution, including the ketones employed in this work. Additionally, the authors found that using CeO_2 as a support further lowered the onset reduction potential of CO_2 , such that the difference in onset reduction potential between CO_2 and acetophenone was only 0.13 V (compared to a difference of 0.95 V with the use of Ag foil). By bringing the onset reduction potential of CO_2 closer to that of acetophenone, the authors were able to optimize a double activation strategy by promoting the CO_2 reduction mechanism on top of the existing ketone reduction mechanism.

Performing electrocarboxylation via CO_2 reduction is also a promising strategy for substrates that have high reduction potentials. One such substrate is styrene, which has a reduction potential similar to that of CO_2 [28,29]. Previous studies of styrene carboxylation have employed bulk metal cathodes such as nickel or titanium [29–31], but yields remained low due to the high onset reduction potentials of both starting materials. To circumvent this issue, Zheng and coworkers [32] proposed to use nitrogen-coordinated single atom Cu catalysts, which had also been shown to lower the overpotential of CO_2 reduction to $\text{CO}_2^{\cdot-}$ [33–35], towards the electrocarboxylation of styrene. Under optimized conditions, the reaction achieved a FE of 92%, with the rest of the current density going towards CO_2 reduction products (CO and CH_4). More impressively, the performance of the single atom catalyst was dramatically better than that of Cu foil alone (34% FE). The findings of this work pave the way towards rational catalyst design, drawing inspiration from the CO_2 reduction literature to improve carboxylation performance.

Similarly, Mita et al. [36] proposed a strategy to carboxylate heteroaromatic compounds that exhibit high reduction potentials (-2.50 to -2.94 V vs. SCE) by taking advantage of the less negative reduction potential of CO_2 (-2.2 V in DMF and -2.3 V in MeCN vs. SCE). They were able to perform dicarboxylation of a wide range of heteroaromatic compounds with up to 90% yield. Prior to this work, electrochemical dicarboxylation was limited to styrene and 1,3-diene derivatives. Furthermore, they were able to apply their optimized conditions towards the synthesis of bioactive compounds, demonstrating the viability of electrocarboxylation for a wide range of applications.

Performing electrocarboxylation via CO_2 reduction is also a viable strategy to avoid unwanted side products. For instance, previous routes to activate benzyl halides for carboxylation would often lead to side reactions such as hydrogenolysis or reductive coupling of the radical halide [37]. However, Mellah et al. [38] showed that by using a Sm(II)-catalyst to activate CO_2 for electrocarboxylation, they were able to avoid the formation of these side products. They reported the highest to date yield for the electrocarboxylation of benzyl chloride at 99%. This strategy is also viable for substrates that are challenging to reduce, as demonstrated by their substrate scope study of a wide range of benzyl chlorides and bromides.

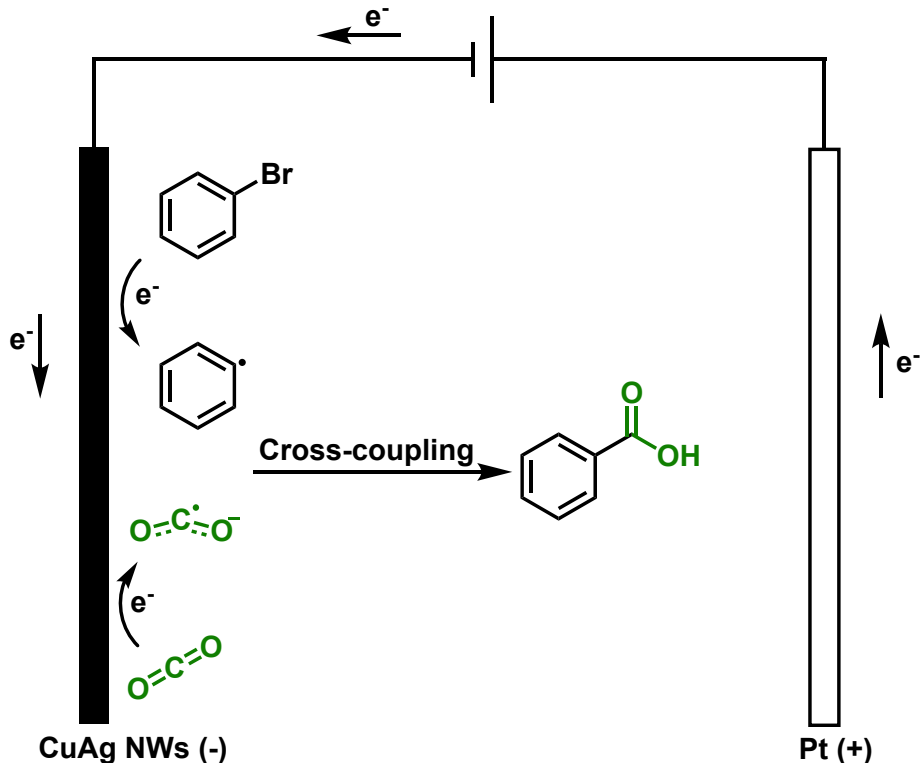


Fig. 1. Proposed electrocarboxylation mechanism via the double activation of CO₂ and bromobenzene with the use bimetallic CuAg NWs. Reproduced from [39] with permission from American Chemical Society.

One shortcoming of the CO₂ activation strategy is the formation of CO₂ reduction side products. To address this issue, a bimetallic copper–silver catalyst was recently developed for the electrocarboxylation of aryl bromide, using bromobenzene as the model substrate [39]. Mechanistic studies revealed that both bromobenzene and CO₂ undergo a one-electron reduction, followed by a radical cross-coupling step to form the desired product (**Figure 2**). Control experiments suggest that Cu was responsible for CO₂ activation, while Ag both activated the aryl bromide and promoted radical cross-coupling step. The use of this bimetallic system helped to suppress electroreduction side reactions, leading to a high FE of 98%. However, further improvements are required as yields remained at around 60%.

2.3 Regioselectivity

The catalyst material can also play a crucial role in controlling reaction regioselectivity. The electrocarboxylation of styrene derivatives is a well-studied reaction [28–31,40]. One of the challenges of styrene carboxylation is controlling reaction regioselectivity, as carboxylation at either α - or β -position, as well as dicarboxylation, have all been observed. Previous attempts to perform carboxylation of styrene have mainly produced the branched product, via carboxylation at the α -position. This is because activation of styrene with metal catalysts lead to the formation of stable η^3 -benzylic metal intermediates that produce the branched product [41–44].

Recently, Mellah and co-workers [45] developed an alternative route to carboxylate styrene and its derivatives, producing exclusively the β -carboxylated product. Rather than activating styrene, their Sm(II)-catalyst was used to activate CO_2 , forming a samarium carboxylate species (**Figure 3a**). This radical species then adds to the olefin at the β -position, forming the more stable benzylic radical species that is subsequently reduced. Using this strategy, they were able to exclusively synthesize the linear, β -carboxylated product.

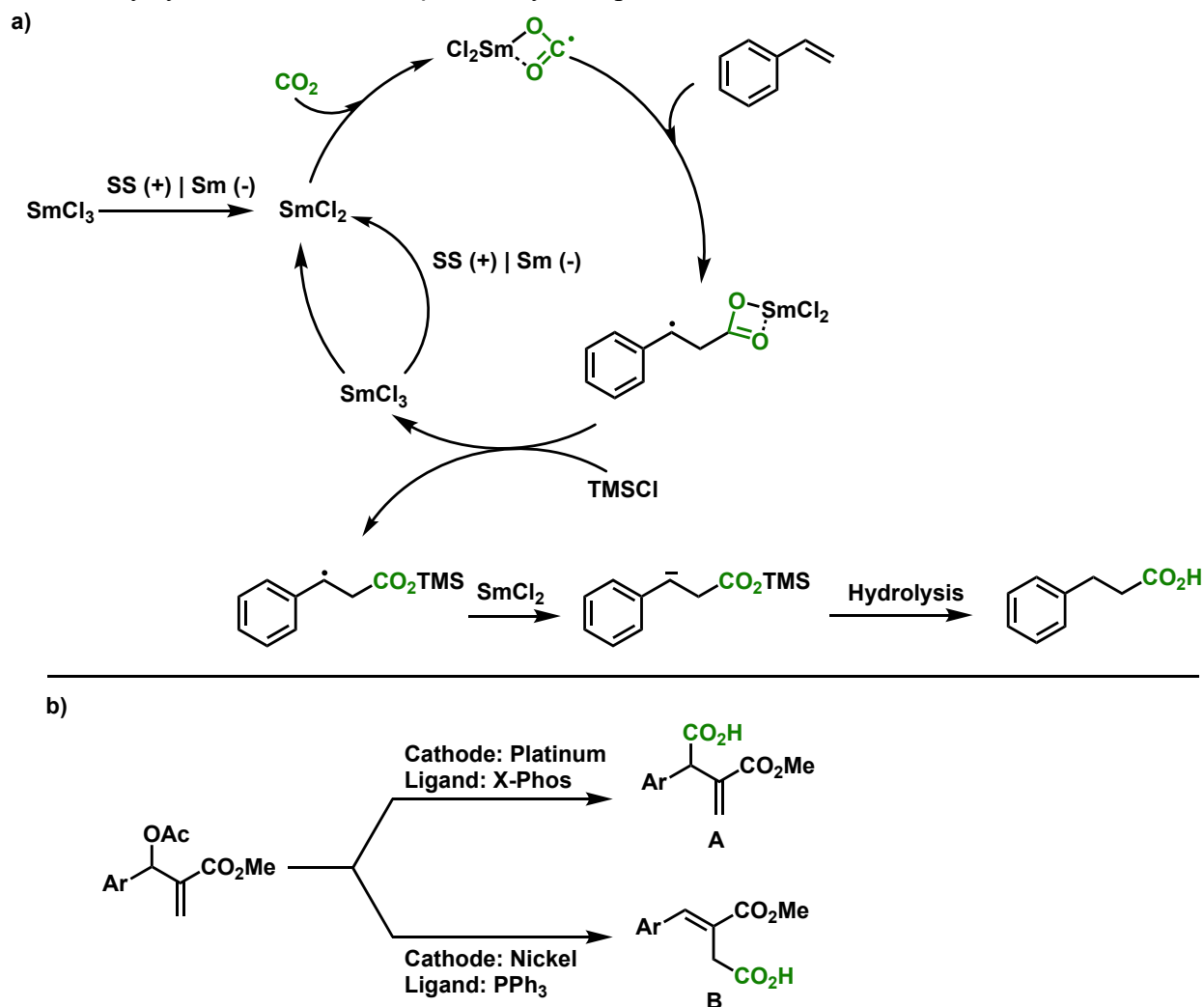


Fig. 2. Regioselective electrocarboxylation reactions. **(a)** Proposed mechanism for the Sm-catalyzed regioselective electrocarboxylation of styrene with CO_2 . Reproduced from [45] with permission from American Chemical Society. **(b)** Switchable regioselectivity of Baylis-Hillman acetates carboxylation with the choice of cathode material. Reproduced from [46] with permission from Elsevier.

The choice of electrode material can also lead to a switch in reaction regioselectivity. Tummanapalli and coworkers [46] studied the electrocarboxylation of Baylis-Hillman acetates and found that a Pt cathode predominantly led to carboxylation at the benzylic position. Meanwhile, the use of a Ni cathode produced the *E*-isomer as the major product (**Figure 3b**). The team proposed that this observed switch in regioselectivity, was due to a difference in mechanism favored by each electrode. Mechanistic studies found that the Pt cathode favored a direct two

electron reduction of the acetate, generating an allyl carbanion that goes on to attack CO₂. Meanwhile, the Ni cathode favors two single electron reductions of both the acetate and CO₂. In this case, the product is formed via a radical coupling step. This was the first report of a regioselectivity switch due to the choice of electrode material alone.

2.4 Stereoselectivity

When synthesizing chiral compounds, the ability to selectively produce the desired stereoisomer is highly desirable as it avoids costly separation processes during the production of pharmaceuticals and agrochemicals, among other applications [47]. Asymmetric electrocarboxylation is inherently challenging due to the achiral nature of the electron. Some of the earliest strategies employed to perform asymmetric electrocarboxylation was by using chiral starting materials to produce the desired chiral products. However, this chemistry is limited by the substrate, and strategies to perform enantioselective carboxylation of achiral substrates must be explored. This section will focus on the progress that has been made towards developing electrocatalysts that can perform enantioselective electrocarboxylation at high yields and FEs.

In 2014, Wang and Lu et al. [48] reported on the use of a chiral Co(II)salen complex for the electrocarboxylation of 1-phenylethylchloride. When the Co(II)salen complex was present, they were able to synthesize the chiral 2-phenylpropionic acid product at 83% enantiomer excess (ee), though only with a yield of 16%. Furthermore, they were able to invert the favored stereoisomer by the choice of chiral catalyst Co(II)-(R,R)(salen) versus Co(II)-(S,S)(salen).

While the findings of this work were promising for advancing asymmetric synthesis in electrochemistry, there were improvements that needed to be made. One shortcoming was the use of a homogeneous catalyst, which presents challenges in separations and recyclability. To address this issue, Wang and Lu et al. [49] proposed to incorporate their chiral cobalt complex into silver nanoparticles (**Figure 4**). Their [Co]@Ag composite was used as the cathode for their system, performing both carboxylation and asymmetric synthesis on one heterogeneous surface. With this system, they were able to carboxylate 1-phenylethylchloride at 73% ee and 58% yield. Compared

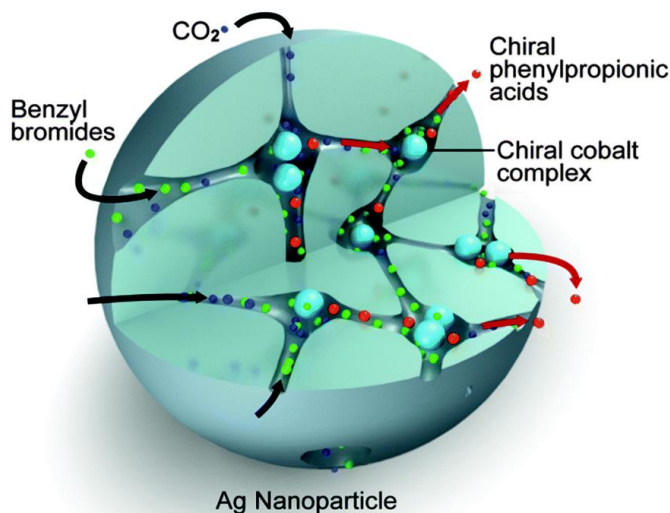


Fig. 3. [Co]@Ag composite for the asymmetric carboxylation of benzyl bromides. Reprinted from [49] with permission from Royal Society of Chemistry.

to their original work, the ee was lower but the yield was a lot higher, due to the use of silver as the cathode material instead of glassy carbon. The composite material also exhibited great recyclability, lasting through seven cycles without Co leaching.

Since then, the incorporation of chiral metal complexes into electrode materials have been employed to perform electrocarboxylation of other types of substrates, such as ketones [50–52]. More recently, this work has been improved upon through further screening of metal centers and chiral ligands. The most optimized catalyst was a Ni(II)L1 complex (L1 = salen functionalized with tBu groups), which could perform electrocarboxylation of acetophenone with an ee of 90% and yield of 59% [53].

3.0 Sacrificial Anode-free Carboxylation

One major drawback to electrocarboxylation reactions is that most systems rely on the use of sacrificial anodes. The metal cation generated oxidatively provides a stabilizing effect for the carboxylate product, preventing further nucleophilic reactions or reverse decarboxylation. Additionally, preferential oxidation of the anode prevents undesirable oxidation of the substrate, product or other organic species that would generate protons that are harmful to carboxylation performance. However, the constant need for anode regeneration prevents these systems from use in a continuous reaction setting and is often costly and non-environmentally friendly. Thus, the ability to perform electrocarboxylation reactions without the need for a sacrificial anode represents a positive step towards incorporating these processes in an industrial setting.

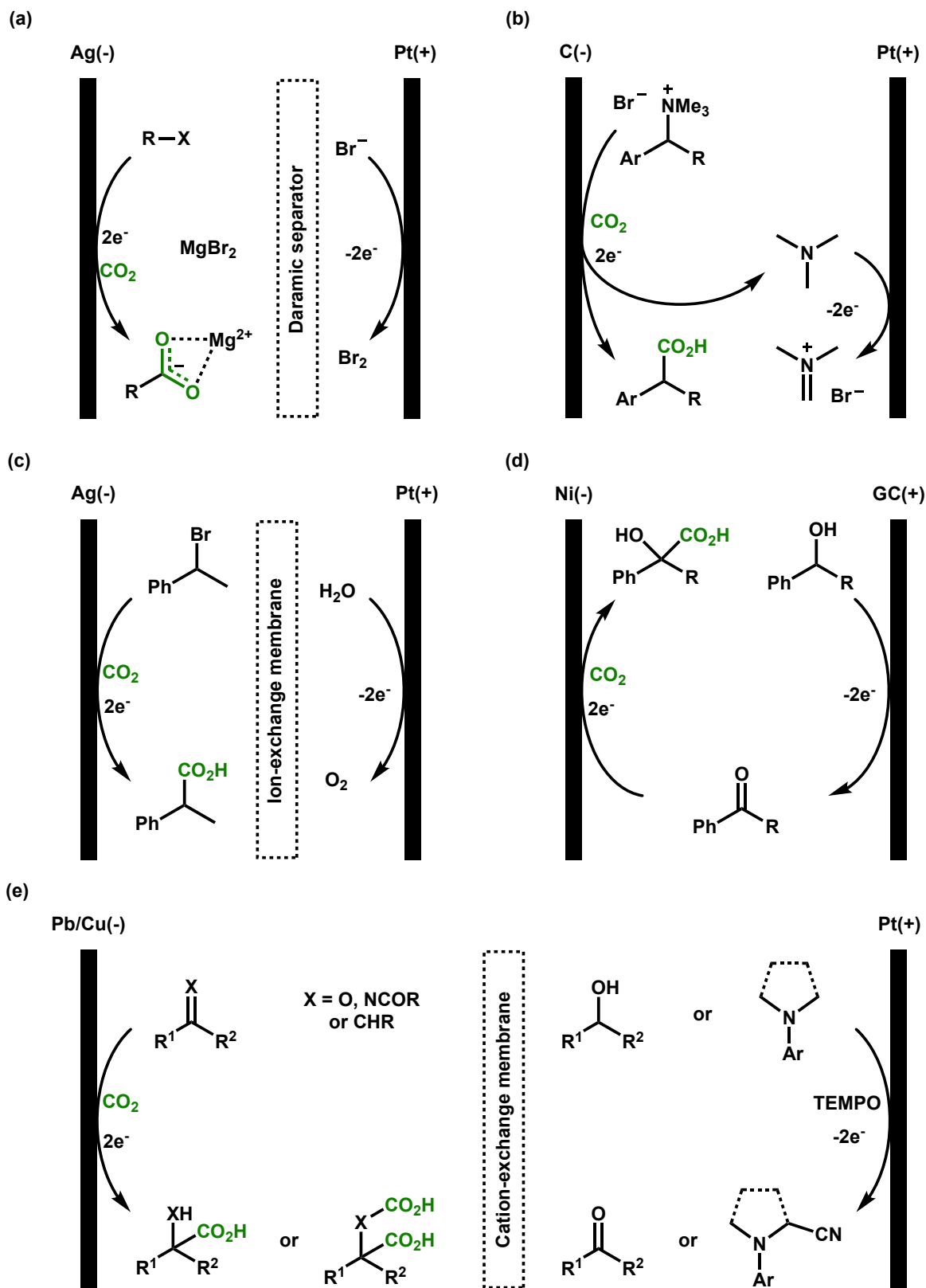


Fig. 4. Sacrificial anode free electrocarboxylation. (a) Addition of exogenous Mg salts replaces cations generated by a sacrificial anode, allowing for carboxylate protection without the use of a sacrificial anode. (b) The choice of substrate can circumvent the need for a sacrificial anode, such as the use of benzyltrimethylammonium salts. (c) Cell design strategies, such as the choice of membrane in divided cells, offer opportunities to explore the use of aqueous analytes. (d, e) Paired electrosynthesis is a viable strategy to synthesize useful products at both electrodes.

3.1 Electrolyte design

Rather than rely on the cation generated by the sacrificial anode for carboxylate protection, Manthiram et al. explored the ability to use exogenous Mg salts to control selectivity (**Figure 5a**) [12]. When conducted in the absence of a sacrificial anode, facile bromine oxidation served as the counter reaction on the Pt anode, which avoids the generation of protons in the anodic counter reaction. Interestingly, inexpensive MgBr_2 served to match or improve process yields relative to the reaction in which a Mg anode was used across a variety of alkyl and aryl halides. A variety of spectroscopic techniques were used to reveal the ability of the carboxylate anion product to protect the cathode against detrimental passivation of insoluble MgCO_3 formed from CO_2 reduction.

3.2 Substrate Design

In addition to alkyl halides, benzyltrimethylammonium salts have been demonstrated as successful substrates for electrocarboxylation without the need for a sacrificial anode (**Figure 5b**) [13]. A wide substrate scope was demonstrated for both primary and secondary starting materials, including the synthesis of racemic ibuprofen. The simple setup and reaction conditions avoid the need for complicated reaction purification procedures such as column chromatography, and the reaction was shown to proceed with similar yields on gram scale as on small scale. Although the starting materials required synthesis from the alkyl halides, a one-pot method was demonstrated using benzyl bromide and trimethylamine to yield the acid product without much loss in yield. Mechanistic studies using techniques such as Differential Electrochemical Mass Spectrometry (DEMS) supported the proposed mechanism, which included reductive cleavage of the C–N bond to form the carbon-based radical, followed by addition of the second electron and trapping with CO_2 to form the acid product, with trimethylamine oxidation at the anode.

3.3 Cell Design

Medvedev and coworkers investigated the use of aqueous anolytes in divided cells for sacrificial anode-free carboxylation (**Figure 5c**) [54]. A cation exchange membrane (CEM), anion exchange membrane (AEM) and bipolar membrane (BPM) were studied at various potentials, and the AEM generally gave better yield and selectivity for the carboxylated product due to cathodic passivation with KBr when CEM or BPM were used. Three potential ranges were explored based on the dominant species identified by CV: (1) less negative than -1.0 V, where R–Br reduction to $\text{R}^\bullet$ is dominant, (2) between -1.0 and -1.5 V, where $\text{R}^\bullet$ reduction to R^- is dominant, and (3) more negative than -1.5 V, where CO_2 reduction is dominant. Concentration dependence studies revealed that a high $\text{CO}_2/\text{R–Br}$ ratio was necessary for high selectivity for carboxylated product relative to dimerized product, and that lower temperatures favored carboxylated product due to the increased solubility of CO_2 . DFT calculations were used to support the experimental results illustrating that at potentials more negative than -1.8 V, the barrier to CO_2 reduction is lower than that for alkyl halide reduction, whereas the trend switches above -1.8 V. The highest overall yields for carboxylated product were obtained using an AEM at -1.4 V in a dilute solution of alkyl halide.

3.4 Paired Electrosynthesis

The use of a linear paired electrosynthesis technique for α -hydroxycarboxylic acid synthesis was demonstrated by Muchez and coworkers in 2019 [55]. A proposed mechanism involved TEMPO-mediated oxidation of the alcohol to the aldehyde or ketone, followed by reduction of the carbonyl and trapping with CO₂ (**Figure 5d**). Not only did this method allow for sacrificial anode-free synthesis, but the use of alcohols represent a greener starting material than aldehydes or ketones. Both primary and secondary benzylic alcohols could be used, with bulkier secondary alcohols leading to higher yields due to minimized dimerization. For electrolyte conditions, the basic supporting electrolyte salt was used for deprotonation of the alcohol during oxidation, while water inclusion was explained by alcohol-to-TEMPO proton transfer, also during oxidation. Investigating various cathode materials led to the observation that for 1-phenylethanol and benzyl alcohol, catalysts with higher metal-hydrogen bond strengths led to higher yields.

Zhang et al. showed how the mono- or dicarboxylation of unsaturated bonds could be paired with TEMPO-mediated alcohol or amine oxidation, separated by a CEM (**Figure 5e**) [56]. With ketones or *N*-acyl imines in the cathodic chamber α -hydroxy- or aminocarboxylic acids were obtained, while alkenes and dienes led to the dicarboxylated products. On the anodic side, primary and secondary alcohol oxidation to aldehydes and ketones was explored, in addition to α -cyanation of tertiary amines. The ability to synthesize racemic Naproxen and Ibuprofen with one additional step following the electrocarboxylation was demonstrated. Mechanistic studies were conducted for the carboxylation reaction using CV and DFT revealed that while substrate reduction occurred prior to electrophilic attack of CO₂ for the ketone, CO₂ reduction followed by electrophilic attack of the substrate occurred for the alkene. For the model system, most of the >10 V cell potential was accounted for by ohmic resistance, with ~2.5 V being used to drive the reactions during constant current electrolysis.

4.0 Conclusions and Outlook

Much progress has been made on catalyst design efforts that allow for the electrocarboxylation of organic substrates at improved yields, FEs, and selectivity. While earlier catalyst design efforts have focused on the substrate activation mechanism, advances in the development of CO₂ reduction catalysts have led to emerging interest in performing electrocarboxylation via the CO₂ reduction route. Understanding of these two pathways is still nascent and further insight how to differentiate these pathways must be acquired. Developing this understanding will allow for the rational design of electrocatalysts with high activity, selectivity, and recyclability. Furthermore, understanding the anodic half-reaction of this system will be important in developing a truly sustainable electrocarboxylation system.

For electrocarboxylation to become industrially viable, the following challenges remain to be addressed:

1. *Better understanding of the two different types of electrocarboxylation mechanisms and how they vary with different types of electrocatalysts:* Experimental and computational methods should be used to better understand the different mechanistic pathways observed and favored on a wide range of electrocatalysts, such as metal foils, mixed metal alloys, metal oxides, and nanostructured catalysts. Specifically, there is little precedent of theoretical studies performed to better understand key intermediates observed in the different mechanistic pathways and how these intermediates might be favored or disfavored with the choice of catalyst. Additionally, advances in characterization techniques such as X-ray photoelectron spectroscopy (XPS), X-ray absorption

spectroscopy (XAS), and vibrational spectroscopy may allow for *in situ/operando* characterization. To that end, these techniques should be used towards better understanding the relationship between electrocarboxylation catalyst and performance. Ultimately, this insight will allow for the electrocarboxylation of a wider range of substrates, producing carboxylic acids for applications in the pharmaceutical, polymer, and agrochemical industries.

2. *Asymmetric catalysis*: As previously mentioned, performing enantioselective electrocarboxylation is extremely challenging due to achiral nature of the electron. While there has been some progress made towards improving the enantioselectivity of electrocarboxylation reactions, many of these works involve the use of homogeneous catalysts that require costly separations. The development of a heterogeneous catalyst that is able to selectively produce the desired stereoisomer at high yields and FEs would dramatically improve the industrial capability of this process. To achieve this goal, further insight on the tradeoff between selectivity and activity must be developed, allowing for the development of hybrid catalysts that optimize both.
3. *Development of flow electrocarboxylation systems*: Flow systems offer the benefits of being more efficient, more scalable, and higher quality compared to batch systems. To make flow electrocarboxylation systems a reality, more robust electrocatalysts must be designed and studied. Additionally, passivation of the cathode material is a common issue that must be addressed to improve the lifespan of the electrode. On the anodic side, the development of sacrificial anode free systems is promising, but greater understanding of anodic processes must be developed.

In conclusion, while many challenges remain to be addressed in the development of active, selective, and scalable electrocarboxylation catalysts, a great deal of progress has also been achieved to drive this technology towards industrial applications. We envision that with continued innovation informed by fundamental understanding, electrocarboxylation could contribute to a more sustainable carbon cycle.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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