

Recent Advances in Electrocatalytic Reduction of Carbon Dioxide Using Metal-Free Catalysts

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ABSTRACT: As part of the efforts to address the global energy issues, the identification of electrocatalysts for efficient and selective conversion of carbon dioxide to value-added products is a research topic of scientific and technological significance. Metal-free catalysts are considered next-generation, renewable materials that promise to be cost-effective, relative to their metal-containing counterparts, particularly relative to noble-metal-based catalysts. In this article, recent progress toward identification of metal-free catalysts for electrochemical reduction of carbon dioxide is reviewed. These catalysts are classified into four categories, including conducting polymers, pyridinium derivatives, aromatic anion radicals, and heteroatom-doped carbon materials. We provide a detailed investigation of the overall catalytic performance of each material, in terms of the product distribution, overpotential required, Faradaic yield, stability of the catalyst, and reaction mechanism. Several important factors that affect the catalytic performance, including the pH value, solvent type, carbon dioxide pressure/concentration, nature of the auxiliary electrode, and morphology of the catalyst, are discussed. The main issues and challenges associated with large-scale electrochemical reduction of carbon dioxide using metal-free catalysts are identified and analyzed, and future research directions for addressing these problems are suggested.

1. INTRODUCTION

Growing populations and technological advances have stimulated an unprecedented growth in energy consumption over the past century. The most common approach to meeting these global energy demands is through the combustion of fossil fuel resources such as petrol, coal, natural gas, and wood. However, utilization of these resources usually leads to the generation of a variety of species with negative environmental impacts, including nitrous oxides, sulfur oxides, and carbon dioxide (CO₂). Although it seems harmless on the surface, CO₂ is a potent greenhouse gas that has been found to be closely correlated with ocean acidification and global warming, which may cause catastrophic climate changes.^{1–3} Hence, it is of great interest to limit the emission of carbon dioxide (particularly from anthropogenic sources) and reduce its atmospheric concentration.

Currently, CO₂ capture and storage (CCS) is considered a promising technology for the significant reduction of carbon dioxide emissions while simultaneously permitting the use of fossil resources to meet the ever-increasing energy demands worldwide.^{4,5} However, the capabilities for reduction of CO₂ emissions must be on the scale of billions of metric tons in order for any technology to be deemed as a practical option for climate change mitigation.⁵ Scaling up CCS requires careful consideration of several key factors, including cost, regulatory/legal issues, subsurface uncertainty, and transportation infrastructure. The captured CO₂ can be used effectively for enhanced oil recovery (EOR) operations, which perhaps affords the only truly viable large-scale utilization of the captured gas at this time. There has been a great deal of interest, however, in exploiting the large-scale availability of CO₂ to use it as a feedstock for conversion to value-added products, such as fine and commodity chemicals, which could provide a revenue stream, and low-carbon fuels for a variety of needs. However,

CO₂ is an extremely stable molecule, the chemical conversion of which is energy-intensive. Therefore, it is highly desirable to search for novel catalytic systems capable of efficient conversion of carbon dioxide to target chemicals. CO₂ conversion can be achieved by a variety of methods, such as chemical conversion^{6–8} and electrocatalytic reduction.^{9–11} It is noteworthy that these approaches are not implemented on an industrial scale and cannot provide commodity chemicals in large quantities, primarily because of the high energy requirements and/or low efficiencies for CO₂ chemical/electrochemical conversion, insufficient industrial interest in CO₂-based products, lack of investment incentives, and social-economic driving forces.^{12,13} However, despite these challenges, CO₂ conversion, particularly in a highly selective and energy-efficient manner, is still considered an extremely important topic worthy of exploration and careful examination in energy and environmental sciences.

In this review, we focus on the conversion of CO₂ to useful products using electrochemical catalytic approaches. These methods are of great interest because they have advantages in that (i) the process can be controlled elegantly by electrochemical potentials, and (ii) the background electrolytes can be reused to reduce the overall chemical consumption to solely that of water. In addition, the electricity required to drive these electrochemical processes can be obtained through solar, wind, tidal, and geothermal processes, thereby avoiding the generation of new CO₂. Furthermore, the electrochemical

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setups are generally modular, compact, and can be easily scaled up.¹⁴

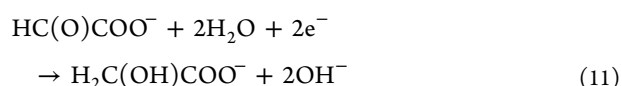
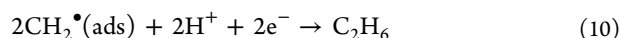
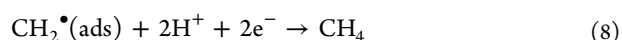
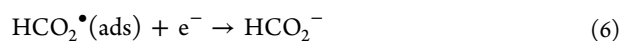
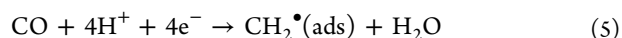
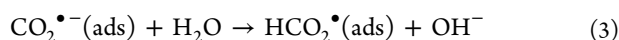
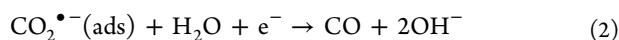
We first examine electrochemical fundamentals that are generally useful in the design of catalytic systems capable of driving the electrochemical conversion of CO₂. Second, we review the common types of catalytic materials, with an emphasis on metal-free catalysts that have been explored for electrochemical reduction of CO₂. Metal-free catalysts are considered new-generation, renewable materials that promise to be cost-effective, relative to their metal-containing counterparts, particularly relative to noble-metal-based catalysts. We provide a detailed discussion on metal-free electrocatalysts that have been developed and discovered to date for CO₂ reduction. These catalytic systems include conducting polymers, pyridinium derivatives, radical anions, and heteroatom-doped carbon materials.

2. FUNDAMENTALS OF ELECTROCATALYSIS OF CO₂

In this section, we recall the fundamentals underlying the electrocatalysis of CO₂ that are necessary for the mechanistic investigation of CO₂ conversion pathways. The electrochemical conversion of CO₂ can result in a variety of products, with corresponding reactions that occur over a wide range of standard electrochemical potentials. Hence, a brief review of these reactions and their associated thermodynamics is the objective of this section.

The electrochemical conversion of CO₂ has been investigated under a variety of conditions, in both gas and liquid phases and over widely different temperature ranges. Various reduction products can be formed via different reaction pathways; the main products include formic acid (HCOOH), or formate (HCOO⁻) in basic solution, oxalic acid (H₂C₂O₄) or oxalate (C₂O₄²⁻) depending on solution pH, carbon monoxide (CO), formaldehyde (CH₂O), ethanol (CH₃CH₂OH), ethylene (CH₂CH₂), methane (CH₄), and many others. Solid oxide fuel cells (SOFCs) are the typically used for performing CO₂ conversions at high temperatures, while transition metal-based electrodes combined with conventional electrochemical cells constitute the low-temperature systems.¹² Low-temperature CO₂ conversions usually afford a broader scope of products, whereas SOFC operations at high temperatures permit a higher selectivity. In addition, low-temperature CO₂ conversions in liquids (including both aqueous and nonaqueous systems) require large overpotentials of around several volts and, thus, high power demands.

The reaction mechanism in the electrochemical reduction of CO₂ governs the product distribution; a wide variety of products can be obtained through various reaction pathways or combinations of several pathways. Generally, the type and number of pathways required for the electrocatalytic reduction process are strongly affected by experimental conditions, such as the nature of the catalyst, electrode potential, electrolyte, pH, temperature, and CO₂ concentration. Several possible pathways have been proposed previously,^{15–18} including



Electrocatalytic reduction of carbon dioxide can occur via two-, four-, six- and eight-electron transfer processes; the corresponding thermodynamic electrochemical half-reactions of CO₂ reduction, the number of electrons transferred, and the associated standard electrode potential (V versus standard hydrogen electrode, SHE) are summarized in Table 1.¹⁹ Note

Table 1. Selected Standard Potentials of CO₂ Reduction Reactions (Potential Versus Standard Hydrogen Electrode, SHE) at 1.0 atm and 25 °C

electrochemical thermodynamic half-reactions	standard potential (V vs SHE)
CO ₂ (g) + 4H ⁺ + 4e ⁻ = C(S) + 2H ₂ O(l)	0.210
CO ₂ (g) + 2H ⁺ + 2e ⁻ = HCOOH(l)	-0.250
CO ₂ (g) + 2H ⁺ + 2e ⁻ = CO(g) + H ₂ O(l)	-0.106
CO ₂ (g) + 4H ⁺ + 4e ⁻ = CH ₂ O(l) + H ₂ O(l)	-0.070
CO ₂ (g) + 6H ⁺ + 6e ⁻ = CH ₃ OH(l) + H ₂ O(l)	0.016
CO ₂ (g) + 8H ⁺ + 8e ⁻ = CH ₄ (g) + 2H ₂ O(l)	0.169
2CO ₂ (g) + 2H ⁺ + 2e ⁻ = H ₂ C ₂ O ₄ (aq)	-0.500
2CO ₂ (g) + 12H ⁺ + 12e ⁻ = CH ₂ CH ₂ (g) + 4H ₂ O(l)	0.064
2CO ₂ (g) + 12H ⁺ + 12e ⁻ = CH ₂ CH ₂ (g) + 3H ₂ O(l)	0.084

that the reactions shown in Table 1 merely indicate the thermodynamic tendency of each reaction, and do not imply a knowledge of the reaction mechanism or kinetics. In fact, the electrochemical reduction of CO₂ consists of complicated reaction mechanisms and usually exhibits very slow kinetics, even with catalysts present. In addition, the standard potentials shown in Table 1 are only for aqueous systems; the values for nonaqueous systems are significantly different. Note that the standard potentials listed in Table 1 correspond to a H⁺ concentration of 1 M (i.e., pH = 0); at other pH values, the electrochemical potential under identical conditions can be calculated from $E(\text{pH}) = E(\text{pH} = 0) - (2.303RT/F) \text{pH}$. In the following discussion, the pH value, as well as the reference electrode to which the potential value refers, in each example is stated explicitly.

3. CATALYST MATERIALS FOR THE ELECTROCHEMICAL REDUCTION OF CO₂

Metal-based materials have dominated the published work on electrocatalysts for CO₂ reduction. The most widely employed electrocatalysts for CO₂ conversion are transition metal-related materials, such as titanium,²⁰ molybdenum,^{21,22} chromium,²³ tungsten,²⁴ rhenium,²⁵ manganese,^{26,27} iron,²⁸ cobalt,²⁹ nickel,³⁰ ruthenium,³¹ palladium,³² platinum,³³ copper,^{34,35} silver,³⁶

and gold.³⁷ Other types of metallic elements that have been utilized for the development of electrocatalysts for electrochemical reduction of CO₂ include aluminum,³⁸ indium,³⁹ thallium,⁴⁰ tin,⁴¹ lead,⁴² alkaline metals,^{43,44} and alkaline-earth metals.⁴⁵ The rising costs of several types of metals, in particular, noble metals such as Ag, Au, Cu, and Pt, are the main hindrance toward large-scale practical applications. Recently, progress has been made toward the enhancement of the catalytic efficiencies of noble metals, for example, through the use of silver⁴⁶ or oxide-derived nanocrystalline copper.^{47,48} With these new material systems, the quantities of metals and the associated costs required to achieve a certain level of catalytic efficiency may be reduced significantly. However, it is still of great interest to seek alternative, nonmetallic systems that may be potentially useful for the development of cost-effective catalysts. Several excellent reviews^{10,49–51} are already available that focus on the CO₂ reduction properties of metal electrode- and transition metal-based catalytic systems, whereas only one monograph⁵² discusses the use of small organic molecules as mediators and catalysts for photocatalytic/electrocatalytic CO₂ reduction. In this review, we devote our attention to nonmetallic catalysts, presenting a comprehensive overview of these materials and providing a detailed evaluation of their electrocatalytic properties toward CO₂ reduction.

Conducting Polymers. Electronically conducting polymers enjoy several promising characteristics for use as electrocatalysts such as ease of synthesis, low cost, and high conductivities (in particular upon doping or incorporation of other conducting components).^{53–59} Because of the highly conjugated polymeric backbones, a variety of conducting polymers can usually undergo rapid and reversible redox processes.^{60–63} Polyaniline (PAn) and polypyrrole (PPy) are two of the most commonly researched conducting polymers because they exhibit high electrical conductivities, can accommodate different doping states, enjoy reasonable environmental stability, and are less expensive, compared to other types of conducting polymers.^{64–66}

Aydin et al.⁶⁷ investigated the electrocatalytic performance of a PPy electrode for CO₂ reduction in a methanol/LiClO₄/H₂O/H⁺ (pH = 1) electrolyte system under both ambient and high-pressure conditions. Their cyclic voltammogram (CV) curves for the PPy electrode with and without CO₂ are shown in Figure 1. Without carbon dioxide, the authors observed a reduction peak for the LiClO₄ electrolyte, which may have resulted from hydrogen evolution under their

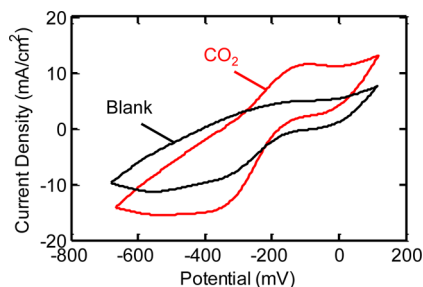


Figure 1. Cyclic voltammograms recorded on a PPy electrode with (red curve) and without (black curve) CO₂ in methanol/LiClO₄/H₂O/H⁺ (pH = 1). The potential is referred to Ag/AgCl. The scan rate is 50 mV/s. Reprinted with permission from ref 67. (Copyright Elsevier, Amsterdam, 2004.)

experimental conditions. In the CO₂-saturated electrolyte solution, a broad peak with significantly higher current densities was observed between -0.3 V to -0.6 V versus Ag/AgCl, consistent with the desired catalytic activity of the PPy electrode toward CO₂ reduction.⁶⁷ It is interesting to note that, in the presence of CO₂, there existed a pronounced peak at around -0.2 V versus Ag/AgCl during the anodic scan. This observation indicates that the reduction products or intermediates formed during the cathodic scan were reoxidized. The reason for this behavior is not clear. It might possibly be due to generation of surface-bound species such as CO₂^{•-}(ads) during the electrocatalytic reduction of CO₂ that might still have been attached to the catalyst surface when the scan was reversed, and therefore became oxidized again.

Constant potential electrolysis of CO₂ was performed at -0.4 V versus Ag/AgCl for a period of 5 h. The main products were found to be HCOOH, HCHO, and CH₃COOH. The electrolysis results at ambient pressure are summarized in Table 2. The Faradaic efficiencies (i.e., the ratio between the number

Table 2. Summary of the Results for the Electrochemical Reduction of CO₂ at Ambient Pressure on a PPy Electrode^a

electrode potential, E (V)	time, t (h)	total charge passed during electrolysis, Q (C)	Faradaic Efficiency, η (%)		
			HCOOH	HCHO	CH ₃ COOH
-0.4	1	1.7	41.3	11.6	33.7
-0.4	2	2.9	37.1	9.7	29.8
-0.4	3	4.0	32.3	7.6	25.5
-0.4	4	5.2	26.3	8.2	21.4
-0.4	5	6.1	23.4	6.1	19.3

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of electrons used to generate a specific product and the total number of electrons transferred during electrolysis) for the formation of formic acid, formaldehyde, and acetic acid decreased gradually with electrolysis time, attributed to the hydrogen evolution side reaction that occurred on the electrode surface. In addition, these authors performed electrolysis experiments under high CO₂ pressures, ranging from 5 bar to 20 bar. They found that the Faradaic efficiencies for the formation of HCOOH and HCHO increased with increasing pressure, whereas the efficiency for the formation of CH₃COOH remained almost unchanged with varying pressure.

Koleli et al.⁶⁸ developed a PAn-based electrode and tested its performance for electrocatalytic reduction of carbon dioxide under ambient conditions, using methanol as the solvent. In cyclic voltammogram measurements, no reduction wave was observed in the absence of CO₂, whereas a pronounced peak between 0.0 and -0.2 V (vs SCE) was observed when the solution was saturated with CO₂ (see Figure 2). The authors found that the maximum Faradaic efficiencies for the formation of formic acid and acetic acid were 12% and 78%, respectively.

Pyridinium Derivatives. Several studies^{52,69–74} have shown that electrocatalytic reduction of CO₂ can be achieved with pyridinium as the catalyst when it is coupled to different types of electrodes, such as palladium (Pd), platinum (Pt), and carbon. Although the nature of the electrode materials has some effects on the overall performance of the system (e.g., product selectivity, Faradaic efficiency), the pyridinium species has been identified to be the active catalytic component. Seshadri et al.⁶⁹ found that the pyridinium/Pd-catalyzed

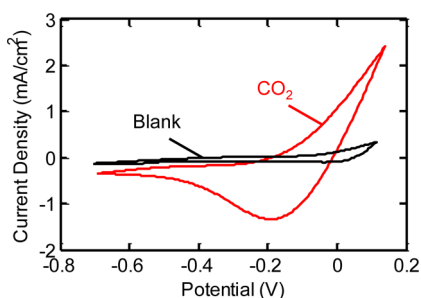


Figure 2. Cyclic voltammograms in a blank electrolyte solution (black curve) and in a CO₂ saturated solution (red curve), recorded on a PAN electrode in methanol/LiClO₄/water/H⁺ (pH = 0): (a) blank electrolyte solution and (b) CO₂ saturated solution. The potential is referred to SCE. The scan rate was 50 mV/s. (Reprinted with permission from ref 68. Copyright Elsevier, Amsterdam, 2004.)

electrochemical reduction of CO₂ could be achieved at a Faradaic efficiency of 30% in an aqueous solution with a pH value of 5.4. The reduction product was methanol with hydrogen evolution as the side reaction, probably originating from the hydrogen-production ability of the Pd electrode. The stability of the catalytic system was found to be ~19 h, based on constant-potential (overpotential = 200 mV) electrolysis experiments (current density = 40 mA/cm²). It was later found by the Bocarsly group that the pyridinium ion and its associated substituted derivatives, when combined with Pt electrodes, can be used as effective catalytic systems for electrochemical CO₂ reduction.⁷⁰ HCOOH and CH₃OH were observed to be intermediate products; relatively low Faradaic efficiencies for the generation of two products were obtained (11% for HCOOH and 22% for CH₃OH, pH = 4.7–5.6) from constant-current electrolysis experiments at a current density of 40 mA/cm². Similar to the case wherein the Pd electrode was used,⁶⁹ the low Faradaic yields in the pyridinium/Pt system may also have been a result of the hydrogen evolution side reaction catalyzed by the Pt electrode.

It should be noted that when the pH value of the pyridine-containing electrode solution was >7, the electrocatalytic reduction of CO₂ did not occur.⁶⁹ This observation suggests that the active catalytic species was the protonated pyridine (i.e., pyridinium), and thus the pH of the reaction mixture was typically maintained at ~5, such that the majority of pyridine molecules were converted to pyridinium. Furthermore, no catalytic activity was observed during a long electrolysis period of 50 h when using the *N*-methylpyridinium cation instead of the protonated pyridine, confirming the important role of the latter.⁶⁹ While the observation that the use of a Pd electrode preloaded with hydrogen led to an increased Faradaic yield of CH₃OH might suggest that the Pd electrode, instead of pyridinium, acted as an active catalytic component to facilitate the transfer of surface-bound hydrogen atoms to carbon dioxide, this latter conclusion was considered unlikely, since the reduction products at an hydrogenated palladium electrode were found to be either formic acid or carbon monoxide, not methanol.⁷¹

An important observation from the study by the Bocarsly group is that, when using an inert electrode that does not catalyze hydrogen evolution, the electrochemical reduction of carbon dioxide did not occur.⁷⁰ Such an observation suggests the importance of surface-bound hydrogen molecules during CO₂ reduction. Another study by the same group further showed that, mechanistically, it was indeed carbon dioxide, not

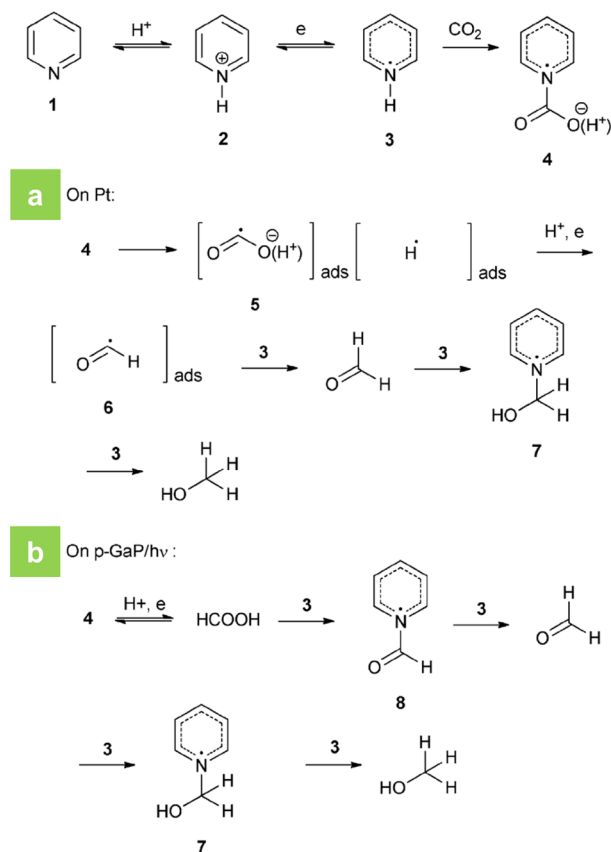
bicarbonate, that was being reduced during electrolysis with a pyridinium/Pt system.⁷² This study also suggests that the electrochemical reduction of carbon dioxide proceeds via a surface-active, rate-limiting step that is first-order, with respect to both pyridinium and carbon dioxide.

In another study, by Smith et al.,⁷³ two types of organic polymers containing benzimidazole and pyridine or bipyridine units were synthesized and examined as electrocatalysts for the electrochemical reduction of CO₂. The authors functionalized carbon fiber papers with these polymers and tested the catalytic performance of the resulting polymer/carbon fiber composite electrodes. It was found that both types of polymers, upon protonation to pyridinium, exhibited electrocatalytic activities toward CO₂ reduction. These results are claimed to be the first demonstration of heterogeneous organic polymer-based catalysts for CO₂ reduction. More interestingly, the bipyridine-based electrode system displayed significantly higher catalytic currents than did the pyridine-based system. It was suggested in this study that the pyridine-containing polymer may form an adduct with CO₂ that is too stable to exhibit high catalytic activities, while the less-stable adduct with the bipyridine-containing polymer may favor the release of the reduction products.

The use of a semiconducting electrode, combined with the pyridinium-based homogeneous catalytic system, resulted in a remarkable enhancement in selectivity for CO₂ reduction reactions. Barton et al.⁷⁴ showed that the Faradaic efficiency for the formation of CH₃OH was almost 100% when using the pyridinium/p-GaP system under illumination. Notably, the potential (−0.22 V versus SCE, pH = 5.2) required to drive the reaction was significantly less negative than the standard thermodynamic potential (−0.52 V versus SCE, pH = 5.2) without illumination. When applying a potential of −0.20 V versus SCE, the quantum efficiency for the generation of methanol was 11% and 1.3%, respectively, under 365-nm and 465-nm illumination. A more negative potential (−0.50 V versus SCE) led to higher efficiencies (44% under 365-nm illumination and 2.6% under 465-nm illumination). However, such solar-to-fuel quantum efficiencies were deemed insufficient for commercialization of this technology. The reason for this inefficient conversion process was attributed to the band structure of the p-GaP photoelectrode that results in an energy-level mismatch with the solar spectrum. Nonetheless, this photoelectrochemically driven process is of great interest, since it allows CO₂ reduction at very low overpotentials and exhibits an extremely high Faradaic efficiency for methanol production, because of the very low catalytic activity of the photoelectrode toward the hydrogen evolution side reaction.⁷⁴

There has been increasing interest in the mechanistic steps involved in the pyridinium-catalyzed CO₂ reduction process. A plausible mechanism for six-electron reductive conversion process from carbon dioxide to methanol has been proposed (see Scheme 1).^{52,70} First, pyridine (1) in an acidic aqueous solution accepts a proton to generate pyridinium (2) (i.e., protonated pyridine), which is subsequently reduced via a one-electron transfer process to form the pyridinyl radical (3). The radical 3, in turn, is expected to have a strong reduction ability and, hence, to react with carbon dioxide to form a radical carbamate species (4), which is considered a key intermediate in the mechanism. On a Pt electrode (Scheme 1a), 4 is converted to a surface-bound hydroxyformyl radical species (5), which subsequently reacts with a surface-adsorbed proton to generate a formyl radical species (6). Next, 6 reacts with the

Scheme 1. Proposed Mechanism for the Pyridinium Catalyzed Reduction of CO₂ to Methanol on (a) a Pt Electrode and (b) an Illuminated p-GaP Electrodes^a

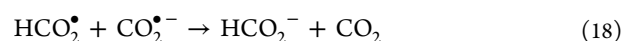
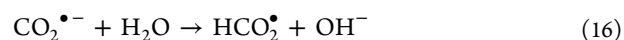
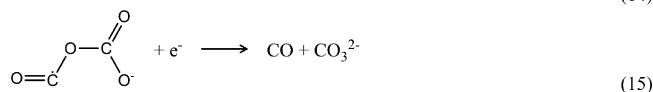
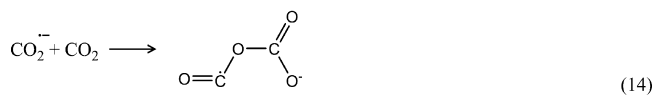


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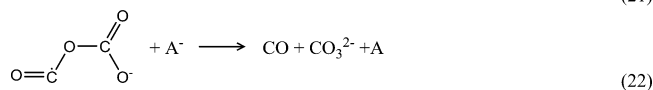
pyridinyl radical, forming HCOH and finally CH₃OH. In contrast, on a p-GaP photoelectrode under illumination (Scheme 1b), the CO₂ reduction process is likely to occur via the generation of HCOOH as the intermediate, because of the lack of surface-adsorbed hydrogen. Notably, the pyridinyl radical species (3) is considered to be the crucial intermediate in the postulated mechanism shown in Scheme 1. The electrocatalytic generation of 3 has been claimed to be associated with a cyclic voltammetric peak at -0.58 V versus SCE using a pyridinium/Pt system with pH = 5.2.⁷⁰ However, a recent computational study by Keith et al.⁷⁵ in 2012 predicts that the redox reaction between pyridine and pyridinium radical should actually occur at -1.47 V versus SCE (pH = 5.3). Coincidentally, this value is very similar to the redox potential obtained from another independent computational study by Tossell (-1.44 V versus SCE) in 2011.⁷⁶ It should be noted that these two studies utilized significantly different computational methods. Tossell's calculations⁷⁶ are based on the CBS-QB3 method combined with the conductor-like polarizable continuum model (CPCM), whereas Keith et al.⁷⁵ used unrestricted density functional theory with the B3LYP functional and the aug-cc-pVDZ basis set. To confirm the validity of their theoretical approach, Keith et al. calculated the redox potentials of a variety of N-substituted pyridinium species with experimentally determined redox potentials available, and excellent agreement was found for all compounds, except the unsubstituted pyridinium species. These computational results

disfavor the role of the pyridinyl radical in the electrochemical reduction of CO₂, and they have altered the mechanistic view of pyridinium-based electrocatalysis substantially.

Aromatic Radicals. Anion radicals of aromatic esters and nitriles, which can be generated readily by electrochemical means, exhibit strong electrocatalytic characteristics for the reduction of CO₂ in an aprotic medium such as dimethylformamide (DMF).^{52,77,78} These studies demonstrated a striking difference in product selectivity between direct, noncatalyzed electrolysis on inert electrodes and anion radical-catalyzed electrolysis. Aromatic anion radicals were found to be able to reduce CO₂ solely to oxalate with negligible formation of CO and other carboxylated products, while direct electrolysis yields various quantities of CO and oxalate, depending on the CO₂ concentration and reaction temperature. Based on the product distribution obtained in DMF at inert electrodes such as Hg and Pb, as well as its variation with current density and carbon dioxide concentration, the mechanism of direct electrolysis in the absence of aromatic anion radicals was postulated to be the sequence of reactions given by eqs 12–18.^{52,77,78}



First, one electron reduction of CO₂ results in the formation of a carbon dioxide anion radical (eq 12). Oxalate is considered to be generated from the coupling of the two CO₂ anion radicals (eq 13). The generation of CO, together with an equimolar quantity of carbonate, involves the reaction of the anion radical with carbon dioxide to form an adduct (eq 14) and subsequent reduction of this adduct (eq 15). Protonation of the CO₂ anion that gives rise to a HCO₂ radical occurs in the presence of water molecules in the reaction mixture (eq 16). Finally, the HCO₂ radical accepts another electron to produce formate (eq 17 or 18). The mechanism of homogeneous catalysis by aromatic anion radicals is



First, ester or nitrile (denoted as A) is reduced to generate a stable aromatic anion radical (eq 19). Next, this radical donates the electron to carbon dioxide, leading to the production of a

CO₂ anion (eq 20). Dimerization of CO₂ anions results in the formation of oxalate (eq 21). In competition with the dimerization step, the CO-forming path (eq 22) is disfavored, because the reaction between CO₂ and its anion radical to form an intermediate adduct (eq 14) is not thermodynamically favorable, and the reduction of this adduct (eq 22) is very slow.

Aromatic anion radicals generated from other polycyclic aromatic hydrocarbons, such as chrysene and picene, can also function as homogeneous catalytic systems for the electrochemical reduction of carbon dioxide.^{79,80} Moreover, photochemical reduction of carbon dioxide has been achieved in a nonaqueous polar solvent by using oligo(*p*-phenylenes) or *p*-terphenyl as the catalyst and triethylamine as a sacrificial electron donor under >290 nm illumination.^{81,82} These studies found that photocatalysis in DMF results in highly efficient formation of formate and CO. The aforementioned anion radicals are considered real catalysts, since these species can be regenerated continuously upon donating electrons to carbon dioxide. Large overpotentials are usually necessary in most of these aromatic radical-catalyzed reactions. Still, the controllability in product distribution is desirable.

Heteroatom-Doped Carbon Materials. Carbon is well-known to form several allotropes with a great variety of structures and properties.⁸³ Carbon nanotubes can be viewed as one-dimensional cylinders composed of a single layer or a few layers of graphene with high length-to-diameter ratios ranging from 10² to 10⁷. Carbon fibers, which have also attracted widespread attention, both fundamentally and for practical applications,^{84,85} can be synthesized easily from spinnable polymer precursors, such as polyacrylonitrile (PAN).⁸⁶ Doping of carbon materials with heteroatoms can improve their electronic and mechanical properties.⁸⁷ Doping with other elements with electronegativity lower than that of carbon, such as boron, phosphorus, and sulfur, has also been demonstrated to give rise to high electrocatalytic performance for the oxygen reduction reaction (ORR).^{88–90} Co-doping with more than one type of element has been found to bring about synergistic effects toward ORR.^{91,92} Electron-accepting polyelectrolyte-modified CNTs have been demonstrated to be efficient metal-free electrocatalysts with strong ORR activities.⁹³ However, there have been very few studies dealing with CO₂ reduction using metal-free carbon materials.

Recently, Kumar et al.⁹⁴ reported the ability of PAN-based heteroatomic carbon nanofiber (CNFs) to catalyze carbon dioxide reduction into carbon monoxide. These PAN-derived CNFs are considered to be next generation, inexpensive, and renewable, metal-free catalyst materials. These authors prepared integrated mats composed of nanoscale fibers (Figure 3) from

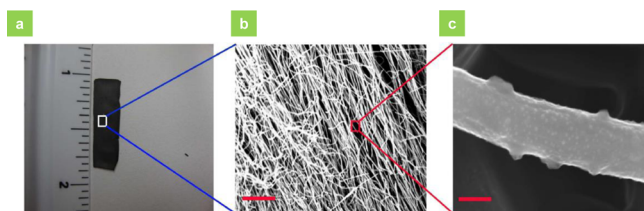


Figure 3. (a) Digital image of the CNF mat used as the electrocatalyst. (b) Scanning electron microscopy (SEM) image of the CNF mat showing the intertwined fibers. Scale bar = 5 μm. (c) High-resolution SEM image of an individual carbon nanofiber. Scale bar = 200 nm. (Reprinted with permission from ref 94. Copyright MacMillan, New York, 2013.)

an electrospinning process. The digital image (Figure 3a) shows that the as-electrospun fibers formed an integrated macroscopic mat. The scanning electron microscopy (SEM) image (Figure 3b) shows that the sample contained randomly oriented fibers in the mat. A high-resolution SEM image (Figure 3c) shows that the fiber was generally of submicrometer or nanoscale size, with surface corrugation to a certain degree.

The CO₂ reduction efficiency was evaluated by examination of the CV response (Figure 4a). The CV curve for CNFs

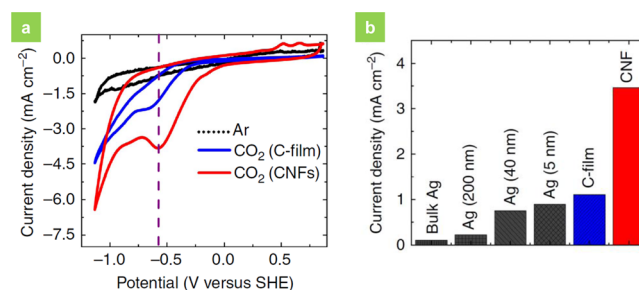


Figure 4. (a) CV curves for the CNF mat and the carbon film with and without CO₂. Electrolyte: 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIN-BF₄). The potential is referred to SHE. (b) Current densities of different catalysts (bulk Ag, Ag nanoparticles with varying sizes, carbon film, and CNFs). (Reprinted with permission from ref 94. Copyright MacMillan, New York, 2013.)

acquired in the presence of CO₂ showed a well-defined peak at −0.57 V versus SHE in 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIN-BF₄), characteristic of CO₂ reduction. The authors further performed experiments whereby a constant potential of −0.57 V versus SHE was applied and the electrolysis products were collected and analyzed by gas chromatography. A very high Faradaic efficiency of 98% was observed for the formation of CO. Additional CV experiments were also carried out using a carbon film without fibrous structures (C-film) prepared by PAN under similar carbonization conditions. The C-film exhibited a much smaller CO₂ reduction peak at −0.63 V versus SHE with significantly lower current densities. The performance comparison between the CNF mats and the C-film highlighted the important role of nanofibrous structures for electrocatalysis of CO₂ reduction.

These authors also compared the CNF mats with other Ag-based electrocatalysts (Figure 4b). They found that the CNF mat displayed a much higher current density under similar electrolysis conditions for CO₂ reduction. Such high current responses were attributed to the electronic structure modulation by remaining N atoms in the carbon fibers. However, caution should be used when comparing catalysts with different morphologies. In this study, the authors used the geometric surface area of the mat, instead of the real surface area determined by nitrogen adsorption/desorption isotherms. Therefore, it remains to be seen which material exhibited a higher amperometric response once the current is normalized to the real surface area. In particular, for electrospun CNF mats, various processing conditions could affect the total microscopic surface areas.^{95,96} Nonetheless, this study points to an exciting direction that may lead to discoveries of the next generation of metal-free electrocatalysts possessing higher catalytic efficiencies than conventional noble-metal systems.

4. CONCLUSIONS

Electrochemical conversion of CO₂ to industrially relevant value-added products is a research field that has recently attracted global attention; development of cost-effective, highly efficient catalysts for CO₂ reduction is a promising strategy to address the CO₂ issue. However, most of the previous efforts have been devoted to metal-based catalytic systems. This review concentrates on next-generation metal-free electrocatalysts for CO₂ conversion, which can be divided into four classes: conducting polymers, pyridinium derivatives, radical anions, and heteroatom-doped carbon materials. These material systems, which can be obtained via relatively inexpensive means, show comparable catalytic current densities during electrolysis relative to their metal-containing counterparts, and thus point to a new exciting direction for further studies by the energy/environmental community. Pyridinium derivatives and radical ions generally are homogeneous catalysts, whereas conducting polymers and heteroatom-doped carbon materials function as heterogeneous catalysts. For the homogeneous catalysts (i.e., pyridinium derivatives and radical ions), the identity of the electrode is important, because, in most cases, the electrode is in direct contact with the electrolyte solution. The type of electrode affects the Faradaic efficiencies and product selectivity because (1) different electrodes show varying activities toward hydrogen evolution, a major side reaction during the electrocatalytic reduction of CO₂, and (2) the nature of the electrode materials may change the catalytic mechanism, leading to formation of different products. Heterogeneous conducting polymer catalysts are usually prepared from direct electrochemical polymerization of precursor monomers (e.g., aniline and pyrrole) onto conductive substrates (i.e., electrodes). The resulting polymer film covers the conducting substrate conformally in most cases, thereby leading to almost no exposure of the substrate to the electrolyte solution. Hence, the nature of the substrate shows negligible effects on the catalytic performance. A major issue associated with conducting polymer catalysts is the stability. The conjugated backbones of these polymers undergo significant morphological changes during charging, thereby causing degradation and reduced catalysis efficiencies during long-term electrolysis. Hybridization of conducting polymers with other materials such as graphene and carbon nanotubes may provide enhancements in catalyst stability. Heteroatom-doped carbon materials appear to be promising systems for electrocatalytic reduction of CO₂, because they are extremely stable during electrocatalysis and can be used in nonaqueous media such as ionic liquids, thus eliminating the hydrogen evolution side reaction and improving Faradaic efficiencies of desired products significantly. In addition, a variety of established strategies are available for manipulating the electronic properties of carbon materials, further providing a high degree of flexibility to improve the catalytic performance, since the electronic structure of carbon governs its molecular level interaction with CO₂.

An important question for electrocatalysis of CO₂, the product selectivity, has not been examined carefully in these metal-free systems. There are a variety of pathways and reactions for electrochemical CO₂ reduction that can result in different products. Thus, it would be interesting to, for instance, examine the effects of cations/anions in the electrolyte solution and CO₂ concentration on the product selectivity using these metal-free catalysts previously developed. In addition, turnover

frequency and turnover number, as well as the dependence of the two parameters on the overpotential, have not been explicitly calculated or specified in these systems. Clarification of this question would be important in order to achieve a fair and accurate comparison of these systems to the previously developed metal-based catalysts. Furthermore, detailed investigations on these metal-free systems should be performed, such as to employ different electrochemical techniques to evaluate catalytic performance, investigate a variety of electrolysis conditions to determine the optimum for the use of these catalysts, and implement judicious design of the electrolysis cells to eliminate self-inhibition, catalyst deactivation, ohmic losses, and uncompensated solution resistance. Last but not least, among currently studied metal-free electrocatalysts of CO₂ reduction, only the mechanism of pyridinium-based systems has been examined carefully by computational studies. Mechanistic insights into the catalytic performance of the other systems have yet to be revealed; development of theoretical approaches in this regard is thus of interest for the rational design and further performance improvement of these catalysts.

In summary, the major issues and challenges associated with electrochemical CO₂ reduction include an inability to control product distribution, high operation cost, low catalyst activity, insufficient catalyst durability, and a lack of mechanistic understanding. Hence, breakthroughs in the development of new generations of catalytic processes are desired and indispensable for large-scale practical applications. The priority is the development of novel material synthesis technologies to generate high-performance catalysts, two important types of which are (1) organic/inorganic hybrid materials with specific binding sites for CO₂ thereby exhibiting remarkable synergistic effects, and (2) nanostructured materials that can facilitate electron/ion transport and prevent active components from mechanical and chemical degradation. In addition, the development of new catalytic materials should be accompanied by concomitant theoretical investigation (e.g., molecular dynamics simulation and electronic calculation) to elucidate the structure–property relationship and the detailed mechanisms for CO₂ reduction. Furthermore, significant advances in technologies and related process engineering are still required for the industrial-level deployment of electrochemical approaches for CO₂ conversion into fuels and commodity chemicals. For example, electrode systems that allow operation at high current densities comparable to those of commercialized H₂O electrolyzers need to be developed. In addition, more-efficient fabrication of catalyst materials (e.g., multiple-nozzle electrospinning followed by carbonization to generate carbon nanofibers) is desirable to reduce the cost and realize practical applications of these materials. Moreover, special attention should be devoted to the management of power and heating devices in order to develop large scale electrochemical processes. In addition, it might be advantageous to explore the synergies by coupling the electrochemical processes with catalytic routes; such an integrated method, compared to the two individual approaches alone, may enhance the productivity and improve the economy of the overall process.

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Notes

The authors declare no competing financial interest.

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