

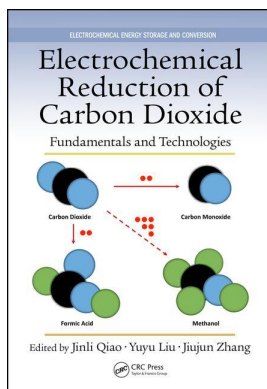
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Electrochemical Reduction of Carbon Dioxide Fundamentals and Technologies

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Introduction to CO Electroreduction

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1 Introduction to CO₂ Electroreduction

Yuyu Liu and Jinli Qiao

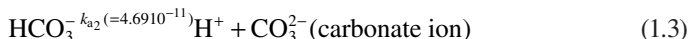
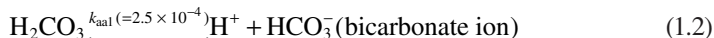
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1.1 CHEMICAL AND PHYSICAL PROPERTIES OF CO₂

Carbon dioxide (CO₂) (mole weight 44.0) is a linear molecular (O=C=O), in which two oxygen (O) atoms are each covalently double bonded to a single carbon (C) atom. With an average C=O bond energy $E_{\text{C=O}} [=187 (2 \times 93.5) \text{ kcal/mole}]$ being much

higher than $E_{O=O}$ [=116 (2 × 58)] and $E_{C=C}$ [=145 (2 × 72.5)], CO_2 is rather chemically stable unless chemically,¹⁻¹⁰ electrocatalytically, and photocatalytically¹¹⁻¹⁹ treated under vigorous conditions. It usually exists as a colorless and odorless gas in air with a mean atmospheric concentration of 0.039% (v/v), and is well known as one of the most notorious greenhouse gases. It forms solid dry ice at $-78.5^\circ C$ and it partially dissolves and is even dissociated in water (1.45 g/L at $25^\circ C$, 100 kPa).



where

$$k_{a1} = \frac{[H^+] \times [HCO_3^-]}{[H_2CO_3]}, \quad k_{a2} = \frac{[H^+] \times [CO_3^{2-}]}{[HCO_3^-]} \quad (1.4)$$

More information of CO_2 can be found when necessary.⁶

1.2 CO_2 PRODUCTION AND CONSUMPTION

Global CO_2 is released from both nature and anthropogenic sources. Nature sources include soils,²⁰ inland waters,²¹ the ocean,²² and even volcanic activity,²³ whereas anthropogenic sources include cement industry²⁴ (responsible for 8% of the world's CO_2 emissions²⁵), metrics²⁶ (approximately 5% from steel²⁷), land transport,²⁸ aviation,²⁹⁻³² shipping,³³ and compost reactors.³⁴ The combustion of fossil fuels (primarily coal, fuel oil, and natural gas) is the main reason of long-term climate change.³⁵ With the carbon balance being broken, the atmospheric concentration of CO_2 is gradually rising,^{30,36-38} also causing carbon accumulation in land and oceans³⁹ and irreversible climate change.^{40,41} It is predicted that the daily atmospheric concentration of CO_2 will soon surpass 400 ppm at the sentinel spot of Mauna Loa, Hawaii, a value not reached at this key surveillance point for a few million years,⁴² and rise to above 750 ppm by 2100.⁴³

The CO_2 emission varies according to each country and region (Table 1.1).⁴⁴ The United States is one of the largest CO_2 -emitting countries of the world,^{45,46} although the emission decreased by 4% to 5.19×10^9 t in 2012, following a 2% decrease in 2011. In 2006, China exceeded the United States in CO_2 emission, and became the world's largest emitting country due to its economic growth and high energy consumption.^{44,47} In Asian countries, China, India, and Japan emitted 9.86, 1.97, and $1.32(\times 10^9)$ t CO_2 in 2012, respectively, increased from 9.55, 1.84, and 1.24 in 2011, accounting for 38% of the total emission (34.5) of the world in 2012. In EU countries, Germany is the largest CO_2 -emitting country; the CO_2 emission was $0.81(\times 10^9)$ t in 2012, accounting for 22% of EU countries' total emissions.

TABLE 1.1
The 1990–2012 CO₂ Emissions per Region/Country (×10⁹ t)

Countries	1990	1995	2000	2005	2010	2011	2012
United States	4.99	5.26	5.87	5.94	5.50	5.39	5.19
EU27	4.32	4.08	4.06	4.19	3.91	3.79	3.74
• France	0.39	0.39	0.41	0.41	0.39	0.37	0.37
• Germany	1.02	0.92	0.87	0.85	0.82	0.80	0.81
• Italy	0.43	0.44	0.46	0.48	0.42	0.41	0.39
• Spain	0.23	0.25	0.31	0.36	0.28	0.29	0.29
• United Kingdom	0.59	0.56	0.55	0.55	0.51	0.47	0.49
• Netherlands	0.16	0.17	0.17	0.18	0.18	0.17	0.16
Japan	1.16	1.25	1.28	1.32	1.24	1.24	1.32
Australia	0.27	0.30	0.36	0.41	0.43	0.44	0.43
Canada	0.45	0.48	0.55	0.57	0.55	0.56	0.56
Russian Federation	2.44	1.75	1.66	1.72	1.71	1.78	1.77
China	2.51	3.52	3.56	5.85	8.74	9.55	9.86
India	0.66	0.87	1.06	1.29	1.78	1.84	1.97
Total	22.7	23.6	25.4	29.3	33.0	34.0	34.5

Source: Selected from Olivier, J. G.; Janssens-Maenhout, G.; Peters, J. A., *Trends in Global CO₂ Emissions: 2012 Report*. PBL Netherlands Environmental Assessment Agency: **2012**.

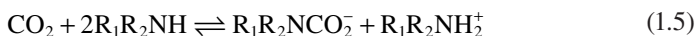
Carbonate precipitation in soils is a sink for atmospheric CO₂.⁴⁸ Carbon is transferred into the soil through dissolution in rainwater ($\text{Ca}^{2+} + 2\text{HCO}_3^- = \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2$). Photosynthesis also utilizes the sun's energy with chlorophyll in plants as a catalyst to recycle CO₂ and water into new plant life.⁴⁹ The oceans also take up a considerable amount of CO₂.^{39,50,51} It was reported that between 1959 and 2008, 43% of each year's CO₂ emissions remained in the atmosphere on average and the rest was absorbed by carbon sinks on land and in the oceans.⁵⁰

1.3 CO₂ CAPTURE, CONVERSION, AND UTILIZATION

At present, certain barriers still hinder the practical application of CO₂ capture, conversion, and utilization. These barriers include: (1) the high costs of CO₂ capture, separation, purification, and transportation to user sites; (2) the high energy requirements for CO₂ chemical/electrochemical conversion; (3) limitations in market size and investment incentives; (4) lack of industrial commitment to enhance CO₂-based chemicals; and (5) insufficient socioeconomic driving forces.^{52,53} Despite such challenges, CO₂ capture, conversion, and utilization are still recognized as feasible and promising cutting-edge areas of exploration in energy and environmental research.

1.3.1 CO₂ CAPTURE

CO₂ may be chemically and physically captured from either fuel gas (precombustion capture) or flue gas (postcombustion and oxy-combustion capture).^{54–59} Precombustion CO₂ capture is normally carried out to remove CO₂ from H₂–CO₂ mixture gas, and the resultant H₂ is supplied to power generation devices which may be fuel cell and power plants. Postcombustion capture is a mature technology. Solvent adsorbents frequently used contain monoethanolamine (MEA), 2-amino-2-methyl-1-propanol, diethanolamine, and methyldiethanolamine, which work based on the following reactions:



Selexol (dimethylether polyethylene glycol), Rectisol (chilled methanol), Fluor (propylene carbonate), and Purisol (*N*-methyl-2-pyrrolidone) have often been used for physical adsorption of CO₂.

Carbonate looping processes are also a postcombustion technology using limestone called dry sorbents.⁶⁰ As shown in Figure 1.1, calcium oxide (CaO) is carbonized in a reversible and exothermic reaction “CaO_(s) + CO_{2(g)} ⇌ CaCO_{3(s)}” at 600–700°C and the formed calcium carbonate (CaCO₃) calcination in an endothermic reaction at 900°C. The regeneration of CaO is enhanced under reduced pressure.

Oxy-combustion capture is an alternative to postcombustion capture.⁶¹ Pure oxygen is provided instead of air for combustion, producing flue gas streams with high CO₂ concentrations. This is beneficial to CO₂ condensation (cryogenics separation).

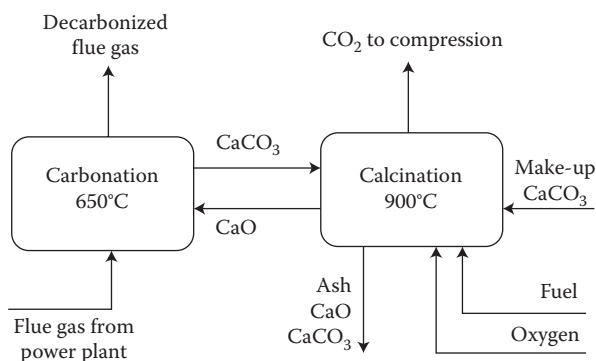


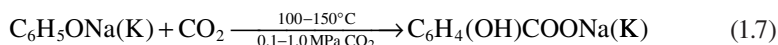
FIGURE 1.1 Carbonate looping process. (Markewitz, P. et al., Worldwide innovations in the development of carbon capture technologies and the utilization of CO₂. *Energ Environ Sci* **2012**, 5, (6), 7281–7305. Reproduced by permission of The Royal Society of Chemistry.)

However, oxy-combustion capture is not considered as a practical means to separate CO₂ from flue gases because of the high energy costs involved.

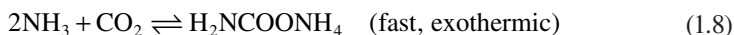
1.3.2 CO₂ CONVERSION

CO₂ can be converted to other chemicals by chemical, photochemical, electrochemical, and photoelectrochemical methods, which break the C=O bond.

CO₂ recovery started early in the late nineteenth century. It was reported that in 1860, Kolbe succeeded in preparing salicylic acid by heating a mixture of phenol and sodium (potassium) under 1 atm CO₂ (Kolbe–Schmitt reaction)⁶²:



Another CO₂ conversion and utilization that should be mentioned is the synthesis of urea with ammonia and CO₂, including two steps:



The overall process ($\text{CO}_2 + 2\text{NH}_3 \rightarrow \text{H}_2\text{NCONH}_2 + \text{H}_2\text{O}$) is exothermic.

Centi and Perathoner concluded that chemical recycling of CO₂ to fuels, as a complementary technology to carbon sequestration and storage (CSS), can minimize as much as possible the consumption of hydrogen (or hydrogen sources), produce fuels that can be easily stored and transported, and use renewable energy sources.⁷

1.3.3 CO₂ UTILIZATION

The use of CO₂ for the production of chemicals ranges today around 170 Mt/y (Table 1.2).⁶

1.4 ELECTROCHEMICAL REDUCTION OF CO₂

Compared with chemical CO₂ conversion, both electrocatalytical and photocatalytical CO₂ reduction have been developed greatly in the recent decades.⁶³

Electrochemical reduction of CO₂ can proceed through two-, four-, six-, and eight-electron reduction pathways in gaseous, aqueous, and nonaqueous phases at both low and high temperatures. The major reduction products are carbon monoxide (CO), formic acid (HCOOH) or formate (HCOO⁻) in basic solution, oxalic acid (H₂C₂O₄) or oxalate (C₂O₄²⁻ in basic solution), formaldehyde (CH₂O), methanol (CH₃OH), methane (CH₄), ethylene (CH₂CH₂), ethanol (CH₃CH₂OH), as well as others. The thermodynamic electrochemical half-reactions of CO₂ reduction and their associated standard electrode potentials are listed in Table 1.3.⁶⁴

TABLE 1.2
Present and Short-Term Uses of CO₂

Compound	Actual Production	CO ₂ Used	2016 Forecast	CO ₂ Needed
Urea	155	114	180	132
Methanol	50	8	60	10
Dimethyl ether	11.4	3	>20	>5
<i>tert</i> -Butyl methyl ether	30	1.5	40	3
Formaldehyde	21	3.5	25	5
Other Fuels				
Higher alcohols				
Hydrocarbons				
Methane				
Carbonates	0.2	0.005	>2	0.5
Polycarbonates	4	0.01	5	1
Carbamates	5.3	0	>6	1
Polyurethane	>8	0	10	0.5
Acrylates	2.5	0	3	1.5
Polyacrylates				
Formic acid	0.6	0	1	0.9
Inorganic carbonates	200	ca. 50	250	70
Soda Solvay, pigments	113.9, 50			
Total		172		207
Technological		28		80
Algae for the production of biodiesel	0.005	0.01	1	2
		200		299

Source: Adapted from Aresta, M.; Dibenedetto, A., *Dalton Trans* **2007**, (28), 2975–2992.

CO₂ conversion using electrochemical catalysis approaches have attracted great attention due to their several advantages⁶⁵:

- The process is controllable by electrode potentials and reaction temperature.
- The supporting electrolytes can be fully recycled so that the overall chemical consumption can be minimized to simply water or waste water.
- The electricity used to drive the process can be obtained without generating any new CO₂—sources include solar, wind, hydroelectric, geothermal, tidal, and thermoelectric processes.
- The electrochemical reaction systems are compact, modular, on-demand, and easy for scale-up applications.

TABLE 1.3
Selected Standard Potentials of CO₂ in Aqueous Solutions (V vs. SHE)
at 1.0 atm and 25°C Calculated According to the Standard Gibbs
Energies of the Reactants in Reactions

Half-Electrochemical Thermodynamic Reactions	Electrode Potentials (V vs. SHE) at Standard Conditions
$\text{CO}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- = \text{C}(\text{s}) + 2\text{H}_2\text{O}(\text{l})$	0.210
$\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- = \text{C}(\text{s}) + 4\text{OH}^-$	-0.627
$\text{CO}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- = \text{HCOOH}(\text{l})$	-0.250
$\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- = \text{HCOO}^-(\text{aq.}) + \text{OH}^-$	-1.078
$\text{CO}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- = \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{l})$	-0.106
$\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- = \text{CO}(\text{g}) + 2\text{OH}^-$	-0.934
$\text{CO}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- = \text{CH}_2\text{O}(\text{l}) + \text{H}_2\text{O}(\text{l})$	-0.070
$\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l}) + 4\text{e}^- = \text{CH}_2\text{O}(\text{l}) + 4\text{OH}^-$	-0.898
$\text{CO}_2(\text{g}) + 6\text{H}^+ + 6\text{e}^- = \text{CH}_3\text{OH}(\text{l}) + \text{H}_2\text{O}(\text{l})$	0.016
$\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}(\text{l}) + 6\text{e}^- = \text{CH}_3\text{OH}(\text{l}) + 6\text{OH}^-$	-0.812
$\text{CO}_2(\text{g}) + 8\text{H}^+ + 8\text{e}^- = \text{CH}_4(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	0.169
$\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l}) + 8\text{e}^- = \text{CH}_4(\text{g}) + 8\text{OH}^-$	-0.659
$2\text{CO}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{C}_2\text{O}_4(\text{aq.})$	-0.500
$2\text{CO}_2(\text{g}) + 2\text{e}^- = \text{C}_2\text{O}_4^{2-}(\text{aq.})$	-0.590
$2\text{CO}_2(\text{g}) + 12\text{H}^+ + 12\text{e}^- = \text{CH}_2\text{CH}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$	0.064
$2\text{CO}_2(\text{g}) + 8\text{H}_2\text{O}(\text{l}) + 12\text{e}^- = \text{CH}_2\text{CH}_2(\text{g}) + 12\text{OH}^-$	-0.764
$2\text{CO}_2(\text{g}) + 12\text{H}^+ + 12\text{e}^- = \text{CH}_3\text{CH}_2\text{OH}(\text{l}) + 3\text{H}_2\text{O}(\text{l})$	0.084
$2\text{CO}_2(\text{g}) + 9\text{H}_2\text{O}(\text{l}) + 12\text{e}^- = \text{CH}_3\text{CH}_2\text{OH}(\text{l}) + 12\text{OH}^-$	0.744

Source: Reprinted with permission from Bard, A. J.; Parsons, R.; Jordan, J., *Standard Potentials in Aqueous Solutions*. CRC Press: 1985; Vol. 6. Copyright © 1985 CRC Press.

However, challenges remain:

- The slow kinetics of CO₂ electroreduction, even when electrocatalysts and high electrode reduction potential are applied.
- The low energy efficiency of the process, due to the parasitic or decomposition reaction of the solvent at high reduction potential.
- The high energy consumption. Researchers have recognized that the biggest challenge in CO₂ electroreduction is low performance of the electrocatalysts (i.e., low catalytic activity and insufficient stability).

1.5 FARADAIC/CURRENT EFFICIENCY OF CO₂ ELECTROREDUCTION

Both current and faradaic efficiencies (η and f) are two indexes that are being popularly used to measure the utilization efficiency of electricity within an electrochemical reaction system.

η can be either the instantaneous current efficiency ($i_{r,t}/i_{total,t}$) or the overall current efficiency ($Q_{r,T}/Q_{total,T}$). $i_{r,t}$ and $i_{total,t}$ are the currents of the r th process and all processes that occur simultaneously at an electrode at a time, t , respectively. $Q_{r,T}(= \int_0^T i_{r,t} dt)$ and $Q_{total,T}(= \int_0^T i_{total,t} dt)$ are the currents of the r th process and all ones at an electrode overall a period of time, T , respectively. η will be 100% when only one process is occurring. For a desirable electrochemical reduction of CO₂, η for the formation of target products should be as high as possible with hydrogen evolution being completely inhibited.

f of a specific product of CO₂ electroreduction describes the efficiency with which charges (electrons) are transferred in an electrochemical reaction. It was calculated from the number of electrons consumed in the electroreduction process by using the formula

$$f = \frac{mnF}{\int_0^t i_{r,t} dt} \quad (1.10)$$

where m is the number of moles of product harvested, n is the number of electrons required for the formation of the product, F is the Faraday constant (9.6485×10^4 C/mol), and $i_{r,t}$ is the circuit current. If we focus on the product selectivity, f will be given.

Experimental results show that f may be affected by

- Catalysts themselves, for example, element^{66,67} and chemical composition⁶⁸
- Morphology of catalysts, for example, thickness of the catalyst layer,^{69,70} catalyst particle size⁶⁹)
- Reaction conditions, for example, temperature,^{71,72} water content of solvents,⁷² pH value in CO₂-saturated solution,⁷³ reaction time,⁷³ etc.

The difference in Faraday efficiencies will be found when using different metal electrodes and metal complex catalysts-loaded ones. Various reasons have been given. For example, the thickness independence of η had been concluded to be the counteractive effects caused by increasing local proton concentration and decreasing electrical field when catalyst layer thickness was increased.⁶⁹ In Figure 1.2, the effect of water contents on faradaic yield is shown during the electrochemical reduction of CO₂ to carbon CO, (COO)²⁻, HCOO⁻ (formate), and H₂.⁷²

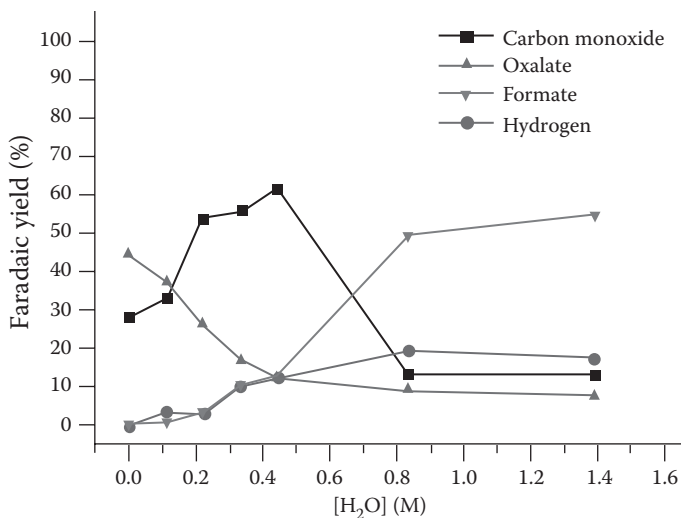


FIGURE 1.2 Faradaic yield of CO₂ reduction as a function of water content. Potentiostatic electrolysis was carried at -2.45 V (Fc/Fc⁺) at -20°C in 0.1 M (Bu)₄NPF₆/CH₃CN. (Oh, Y. et al., Electrochemical reduction of CO₂ in organic solvents catalyzed by MoO₂. *Chem Commun* **2014**, 50, (29), 3878–3881. Reproduced by permission of The Royal Society of Chemistry.)

1.6 PRODUCT SELECTIVITY OF CO₂ ELECTROREDUCTION

1.6.1 AFFECTING FACTORS

As discussed above, the catalyst selectivity to produce desired products in catalyzed CO₂ electroreduction is very important for practical applications. Normally, this selectivity is closely related to the reduction mechanism, with different reaction pathways or combinations of different pathways leading to different products. In the initial reduction step of a typical CO₂ electroreduction mechanism, CO₂ can obtain electrons either directly from the cathode surface (a bare electrode surface or a surface coated catalyst) or indirectly from a medium, such as a soluble catalyst, to produce an intermediate, such as CO₂^{•-}, which then adsorbs on the cathode for product formation. In general, which kinds of pathways and how many pathways are required for the reduction process will be strongly affected by experimental conditions, such as the catalysts and/or electrodes, electrode potential, electrolyte solution, buffer strength, pH, CO₂ concentration, and pressure, as well as temperature.^{72,74} The possible reaction pathways are summarized in Table 1.4.^{67,75–77}

1.6.1.1 Effects of Single Metal Electrode Type

Regarding product selectivity, single metal electrodes seem to be the most popular type of electrocatalysts for CO₂ reduction.^{78,79} Two groups can be roughly designated⁸⁰: (1) CO formation metals (Cu, Au, Ag, Zn, Pd, Ga, Ni, and Pt) and (2) HCOO⁻ formation metals (Pb, Hg, In, Sn, Cd, and Tl). There are other types of catalysts that

TABLE 1.4
Proposed Reaction Pathways in CO₂ Electroreduction

CO ₂ + e ⁻ → ·CO _{2(ads)} ⁻	·CO _{2(ads)} ⁻ + H ⁺ + e ⁻ → CO + OH ⁻	CO + 4H ⁺ + 4e ⁻ → ·CH _{2(ads)} + H ₂ O	·CH _{2(ads)} + 2H ⁺ + 2e ⁻ → CH ₄ 2 ·CH _{2(ads)} → C ₂ H ₄ 2 ·CH _{2(ads)} + 2H ⁺ + 2e ⁻ → C ₂ H ₆ Products: CH ₄ , C ₂ H ₄ , C ₂ H ₆
or	Product: CO		
NR ₄ ⁺ + e ⁻ → ·NR ₄	·CO _{2(ads)} ⁻ + H ₂ O → ·HCO _{2(ads)} ⁻ + OH ⁻	HCO ₂ ⁻ (ads) + e ⁻ → HCO ₂ ⁻	HCO ₂ ⁻ + CH ₃ OH → HCOOCH ₃ + OH ⁻ Product: HCOOCH ₃
CO ₂ + ·NR ₄ → ·CO ₂ ⁻ + NR ₄ ⁺	2 ·CO _{2(ads)} ⁻ → C ₂ O ₄ ²⁻	C ₂ O ₄ ²⁻ + 2H ⁺ + 2e ⁻ → HC(=O)COO ⁻ + OH ⁻	HC(=O)COO ⁻ + 2e ⁻ + 2H ⁺ → H ₂ C(OH)COO ⁻ Product: H ₂ C(OH)COO ⁻
	Product: C ₂ O ₄ ²⁻		

Source: Adapted from Ikeda, S.; Takagi, T.; Ito, K., *Bull Chem Soc Jpn* **1987**, *60*, (7), 2517–2522; Saeki, T. et al., *J Electroanal Chem*, **1995**, *390*, (1–2), 77–82; Li, J. W.; Prentice, G., *J Electrochem Soc* **1997**, *144*, (12), 4284–4288; Magdesieva, T. V. et al., *Russ Chem B+* **2002**, *51*, (5), 805–812.

also have both high selectivity and high current efficiency. In addition, some electrocatalysts have been specifically designed for and show unique catalytic activities toward CO₂ reduction to produce desired products with high current efficiencies.

1.6.1.2 Effects of Metal Complex, Metal Center, and Ligand Types

It is well known that the catalytic performance of metal complex catalysts for CO₂ reduction strongly depends on the chemical properties of the metal center and ligand. Therefore, it is expected that the distribution of the electrolysis products, the current efficiencies, and the reaction mechanism of CO₂ electroreduction will also be strongly affected by the types of central metals and ligands in macrocyclic complexes. For example, CO₂ electroreduction on a glassy carbon electrode (GCE) modified with polymeric M-tetrakis aminophthalocyanines (M = Co, Ni, Fe) indicated that different metal centers produced different products.⁸¹ When M was Co, HCOOH was the only product; when M was Fe, a mixture of CH₂O and H₂ was produced; and when M was Ni, a mixture of HCOOH and CH₂O was observed.⁸² Furuya and Matsui⁸³ investigated the electrocatalytic reduction of CO₂ on gas diffusion electrodes (GDEs) modified by 17 kinds of metal phthalocyanine (MPc) catalysts (where M = Co, Ni, Fe, Pd, Sn, Pb, In, Zn, Al, Cu, Ga, Ti, V, Mn, Mg, P) in 0.5 M KHCO₃. They found that the distribution and current efficiencies of the electrolysis products were strongly dependent on the nature of the central metal coordinated to the phthalocyanines. With transition metals of Co- and Ni-phthalocyanines, the main electrolysis product was CO, with a current efficiency of ~100%. On the other hand, HCOOH was the main product on phthalocyanines with Sn, Pb, or In metal centers. The highest current efficiency, ~70%, was observed on SnPc around -1.6 V. In the case of Cu-, Ga-, and Ti-phthalocyanines, CH₄ was the main product, with the highest current efficiencies being 30%–40%. Analogously, in the simultaneous reduction of CO₂ and NO₃⁻ with various MPc catalysts (where M = Ti, V, Cr, Mo, Fe, Ru, Co,

Ni, Pd, Cu, Zn, Cd, Ga, In, Ge, Sn, Pb), the current efficiencies of CO formation at CoPc and NiPc catalysts in the reduction of CO₂ alone were further demonstrated to be far higher than at pure metal catalysts; hence, these M/Pc catalysts were expected to have a fairly high capacity for urea formation.⁸⁴ The effects of various aza-macrocyclic ligands on the production of fuels from macrocyclic complexes were also investigated, including simple tetraazamacrocycles, porphyrin, phthalocyanine, and biphenanthroline hexaazacyclophanes.^{85,86} The mechanism for producing a particular product is normally related to the structural features of the azacyclam framework and its interaction with the central metal and CO₂ or CO molecules, whereas the replacement of a -CH₂ group in the ligand backbone by an amide residue, for example, does not disturb the catalytic process.

1.6.1.3 Effect of Cations and Anions in the Electrolyte

As described previously, alkaline metals and alkaline earth metals cannot be used as electrodes for CO₂ catalytic reduction catalysts. However, their salts have commonly been used as supporting electrolytes in electrochemical cells for CO₂ electroreduction, and they have different effects on product selectivity. For example, in the case of FeTPP catalyst, the addition of Lewis acid cations such as Mg²⁺, Ca²⁺, Ba²⁺, Li⁺, or Na⁺ decreased HCOOH formation as the acidity increased; the order of reactivity of these Lewis acid synergists was Mg²⁺ = Ca²⁺ > Ba²⁺ > Li⁺ > Na⁺.⁸⁷ Thorson et al.⁸⁸ confirmed that the presence of large cations such as cesium (Cs) and rubidium (Ru) in the electrolyte could enhance the electrochemical conversion of CO₂ to CO. This was explained by the interplay between the level of cation hydration and the extent of cation adsorption on the metal electrodes. The effects of anions in the electrolyte on the products of CO₂ electroreduction were also investigated using a copper mesh electrode in aqueous solutions containing 3 M of KCl, KBr, and KI as the respective electrolytes.⁸⁹ The results showed that the bond between adsorbed halide anion (e.g., Br⁻, Cl⁻, or I⁻) and carbon helped the electron transfer from the adsorbed halide anion to the vacant orbital of CO₂, promoting CO₂ conversion.⁸⁹ The stronger the adsorption of the halide anion to the electrode, the more strongly CO₂ was restrained, resulting in a higher CO₂ reduction current. Furthermore, the specifically adsorbed halide anions suppressed the adsorption of protons, leading to a higher hydrogen overvoltage. This reaction mechanism was also confirmed by Schizodimou and Kyriacou,⁹⁰ who showed that the rate of electrochemical reduction of CO₂ increased in the order Cl⁻ < Br⁻ < I⁻.

1.6.1.4 Effects of Supporting Electrolytes

In fact, even for the same metal electrode with the same purity, different supporting electrolytes have a great effect on the final products. For example, in the electroreduction of CO₂ at a copper electrode (99.999% purity) in CH₃OH, Saeki et al.⁷⁵ observed two different main products—CO (current efficiency, 48.1%–86.8%) and CH₃COOH (54.5% and 46.7%)—when the supporting electrolyte was either (Bu)₄N⁺ (TBA) salts (i.e., TBA · BF₄ and TBA · ClO₄) or lithium salts (LiBF₄ and LiClO₄). They proposed that the intermediate, CO₂^{*-}, was stabilized by forming a TBA⁺ - CO₂^{*-} ion pair or by being adsorbed on the electrode surface. By contrast, NH₄ClO₄ as a supporting

electrolyte in the same electrolysis only led to hydrogen evolution (84.6%). Other electrolytes have also been explored, such as $(\text{CH}_3)_4\text{N} \cdot \text{ClO}_4(\text{TEA})$.⁹¹

1.6.1.5 Effects of Solvent/ CO_2 Concentration

It should be mentioned that CO_2 utilization in aqueous solution can be limited by its low solubility in water at standard temperature and pressure.⁹² This is because there are relatively small amounts of CO_2 available for the reaction to proceed at the electrode surface. To speed up the reaction process for industrial purposes, pressurized CO_2 is normally required,^{93,94} which often causes a certain degree of change in product selectivity. Normally, in aqueous solutions, metallic catalysts (or electrodes), such as *sp* group metals (e.g., In or Pb), tend to give higher CO production at pH levels higher than 4, whereas *d* group metals (such as Pd and Cu) can promote HCOOH production.⁷⁴ It was concluded that the main products obtained in aqueous media under ambient conditions were strongly dependent on the type of cathode: Cu electrodes mainly yielded mixtures of hydrocarbons (mostly methane and ethylene) and alcohols; Au, Ag, and Zn mainly produced CO, whereas other metals, such as In, Sn, Hg, and Pb, were selective for the production of HCOOH/HCOO⁻.⁹⁵ Compared with water solutions, the application of nonaqueous solvents is relatively popular due to their high solubility for CO_2 . For example, *N,N*-dimethylformamide (DMF), PC, and CH_3OH may contain up to 20, 8, and 5 times more CO_2 , respectively, than corresponding amounts of aqueous solutions. Among them, solvents having low proton availability, such as DMF, favor the formation of oxalate and CO, whereas aqueous solution favors HCOO⁻.⁹⁶ Strategies that have been demonstrated experimentally are further described below according to the selective generation of desired products.

1.6.2 SELECTIVE PRODUCTION OF CARBON MONOXIDE

CO is one of the important products generated in CO_2 electroreduction. The electrochemical conversion of CO_2 to CO is a two-electron process. Some metal cathodes, such as Ag, Au, and Zn, are highly selective for the electrocatalytic reduction of CO_2 to CO in KHCO_3 aqueous solutions.⁶⁶ $[\text{Ni}(\text{cyclam})]^{2+}$ is a well-known catalyst for CO_2 electroreduction to CO on a mercury cathode at -0.9 V in aqueous solutions.⁹⁷ Two other electrocatalysts with a similar structure to $[\text{Ni}(\text{cyclam})]^{2+}$ were also found to be selective for CO production.⁹⁸ In addition, metal polyphosphine complexes, such as $\text{Pd}(\text{triphosphine})\text{L}^{2+}$ ($\text{L} = \text{CH}_3\text{CN}$, $\text{P}(\text{OMe})_3$, PEt_3 , $\text{P}(\text{CH}_2\text{OH})_3$, and PPh_3), exhibited high catalytic activity for the reduction of CO_2 to CO in acidic CH_3CN solutions.⁹⁹

As an enzyme-based catalyst, a Ni- and Fe-containing metalloenzyme isolated from *Moorella thermoacetica* showed highly selective activity toward the conversion of CO_2 to CO, with a current efficiency as high as $\sim 100\%$ at -0.57 V vs. normal hydrogen electrode (NHE) in a 0.1 M phosphate buffer solution (pH 6.3).¹⁰⁰

1.6.3 SELECTIVE PRODUCTION OF FORMIC ACID (AND FORMATE)

The electrochemical conversion of CO_2 to formic acid “HCOOH” (and HCOO⁻) is also a two-electron process. Electrochemical reduction of CO_2 in aqueous solution to HCOOH and HCOO⁻ was reported as early as 1870.¹⁰¹ Noda et al.⁶⁶ reported that

Zn, Cd, Hg (Group 12), In (Group 13), Sn, and Pb (Group 14) metal cathodes in 0.1 M KHCO₃ aqueous solution exhibited high production selectivity for HCOO⁻ formation. Chen et al.¹⁰² reported that HCOOH was the main product of CO₂ electroreduction by both [Ir₂(dimen)₄²⁺](PF₆⁻)₂ and [Ir₂(dimen)₄²⁺](B(C₆H₅)₄)₂ (dimen = 1,8-diisocyanomenthane) electrocatalysts. Kang et al.¹⁰³ reported selective electrocatalytic reduction of CO₂ to HCOO⁻ by a water-soluble iridium pincer catalyst. HCOO⁻ was the only reduced carbon product, formed in 93% faradaic yield with no formation of CO. As previously mentioned, to optimize the large-scale (even industrial-scale) electrocatalytic reduction of CO₂ to HCOO⁻, Li and Oloman¹⁰⁴ investigated a series of condition variables that might affect the performance of a reactor. The current efficiency of HCOO⁻ formation was reportedly as high as 91%. Recently, the engineering and economic feasibility of the large-scale electrochemical reduction of CO₂ to HCOOH and HCOO⁻ has been discussed by Agarwal et al.⁶⁵

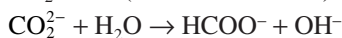
Electrocatalytic reduction of CO₂ by an enzyme catalyst, formate dehydrogenase enzyme (FDH1), which was isolated from *Syntrophobacter fumaroxidans*, was found (as either a homogeneous or a heterogeneous catalyst) to produce HCOO⁻ exclusively.¹⁰⁵ Two acetogenic bacteria, *M. thermoacetica* (Mt, formerly *Clostridium thermoaceticum*, ATCC 35,608) and *Clostridium formicoaceticum* (Cf, DSM 92), were explored as catalysts for CO₂ electroreduction in 1.0 atm CO₂-saturated 0.1 M phosphate buffer solution (pH 7.0) at -0.58 V vs. NHE; the results showed that these catalysts could efficiently convert CO₂ to HCOO⁻ with current efficiencies of 80% for Mt and 100% for Cf.¹⁰⁶

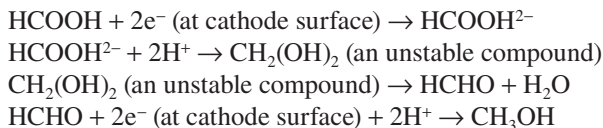
1.6.4 SELECTIVE PRODUCTION OF FORMALDEHYDE

There are very few cases of highly selective production of HCHO by the electrochemical reduction. Sende et al.⁶⁸ earlier reported that [M(4-v-tpy)₂]²⁺ and [M(6-v-tpy)₂]²⁺ (M = Cr, Ni, Co, Fe, Ru, or Os), after being electropolymerized onto GCEs to form films, exhibited electrocatalytic activity toward CO₂ reduction, with HCHO as virtually the only product. The current efficiency for films of Cr(4-v-tpy)₂²⁺ was as high as 87%. Nakata et al.¹⁰⁷ also achieved a high-yield electrochemical production of HCHO from CO₂ and seawater using a boron-doped diamond electrode under ambient conditions. The high faradaic efficiency for the production of HCHO was 74%, using either CH₃OH, aqueous NaCl, or seawater as the electrolyte, and attributed to the sp³-bonded carbon of the boron-doped diamond.

1.6.5 SELECTIVE PRODUCTION OF METHANOL

The mechanism of reaction is always a topic of interest. Ganesh¹⁰⁸ suggested a most probable reaction sequence that occurred in the electrochemical reduction of CO₂ to CH₃OH, which is as follows:





Although the mechanism requires further confirmation, the net reaction is certainly a six-electron process: $\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$, and the other compounds such as HCOOH, HCHO, and CH_4 will also form. Some electrocatalysts have been found to be fairly selective for CH_3OH production in CO_2 electroreduction, as listed in Table 1.5.

1.6.6 SELECTIVE PRODUCTION OF OXALIC ACID (OXALATE)

The electroreduction of CO_2 in DMF solution showed a current efficiency of 73% for oxalic acid $[(\text{COOH})_2]$, with a little HCOO^- and CO production.¹⁰⁹ The macrocyclic nickel complex Ni–Etn(Me/COOEt)–Etn was found to be one of the most active and persistent homogeneous catalysts for CO_2 electroreduction selectively to $(\text{COOH})_2$.¹¹⁰ Dinuclear copper (I) complexes electrocatalyzed CO_2 conversion selectively to $(\text{COOH})_2$ in CH_3CN with a soluble lithium salt, resulting in quantitative precipitation of lithium oxalate.¹¹¹ In addition, anion radicals of aromatic esters such as phenyl benzoate and methyl benzoate, and of nitriles such as benzonitrile, in DMF at an inert electrode (e.g., mercury) were able to reduce CO_2 exclusively to $(\text{COOH})_2$.^{112,113}

1.6.7 SELECTIVE PRODUCTION OF LACTIC ACID

Lactic acid ($\text{CH}_3\text{CH}(\text{OH})\text{COOH}$) is an organic C_3 compound that plays an important role in numerous industries, including food, medicine, and cosmetics. Ogura et al.¹¹⁴ found selective reduction of CO_2 to $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$, catalyzed by Fe(II)-4,5-dihydroxybenzene-1,3-disulfonate immobilized on a polyaniline/Prussian blue (PAN/PB)-modified Pt electrode in 0.5 M KCl solution. However, if Co-4,5-dihydroxybenzene-1,3-disulfonate was used, acetaldehyde (CH_3CHO) was also produced.

To summarize the selective generation of desired products in electrocatalytic CO_2 reduction, Table 1.5 lists typical examples for several important low-carbon fuels, together with their generation conditions.

1.7 CHALLENGES, PERSPECTIVES, AND RESEARCH DIRECTIONS IN CO_2 ELECTROREDUCTION

The challenges in CO_2 electroreduction come from various aspects. Generally, lowering the overpotential for the electrochemical conversion of CO_2 to useful products is one of the major challenges.¹⁶⁰ For this goal, highly effective catalysts are indispensable. However, it seems that so far we still cannot simultaneously realize high faradaic/current efficiency, product selectivity and yield, and catalyst durability,¹³⁶ which are quite essential for industrial-scale processes. Mao et al.¹⁶¹ also concluded the major issues and challenges associated with electrochemical CO_2 reduction to be

TABLE 1.5

A Summary of Selected Electrocatalytic Reductions of CO₂ to Selectively Produce Several Important Low-Carbon Fuels

Product(s)	Electrode/Electrocatalysts	Potential (V), Reference Electrode	Electrolyte	Temperature/ Pressure, etc.	Current Efficiency	Reference
(1) CO						
	Cu (99.98%) electrode	-2.0 to 3.5 V (Ag rod quasi-reference electrode)	0.5 M CsOH/10 atm CO ₂ -saturated CH ₃ OH, (<0.1%) H ₂ O	-25 ± 0.5°C, H-type cell (in stainless- steel vessel)	84%	[115]
	Ag (99.98%) electrode	-1.6 V vs. Ag/AgCl (saturated with KCl)	0.1 M KHCO ₃ /water	25°C	64.7%	[66]
	Au (99.95%) electrode				81.5%	
	Zn metallic electrode				39.6%	
	Cd metallic electrode				14.4%	
	(99.95%) Pd electrode	-1.8 V (Ag/AgCl/ KCl)	0.1 M KHCO ₃ /50 atm CO ₂ , saturated water	30°C	57.9%	[116]
	Nanoporous Ag electrocatalyst	-0.50 V (reversible hydrogen electrode [RHE])	0.5 M KHCO ₃ / CO ₂ -saturated water	Room temperature, ~9.0 mA/cm ²	92%	[117]
	Bi ³⁺ catalyst	-2.0 V (saturated calomel electrode [SCE])	0.3 mM [BMIM][PF ₆]	82 ± 12	31 ± 2	[118]
	<i>Ditto</i>		0.3 mM [BMIM][BF ₄]	82 ± 11	26 ± 4	
	<i>Ditto</i>		0.3 mM [BMIM][Cl]	79 ± 12	17 ± 2	
	<i>Ditto</i>		0.3 mM [BMIM][Br]	74 ± 4	20 ± 1%	
	<i>Ditto</i>		0.3 mM [BMIM][OTf]	87 ± 8	25 ± 2%	
	GCE		0.3 mM [BMIM][OTf] /CH ₃ CN (OTf = (CF ₃ SO ₃) ⁻)	None	<0.4 mA/cm ²	

(Continued)

TABLE 1.5 (Continued)
A Summary of Selected Electrocatalytic Reductions of CO₂ to Selectively Produce Several Important Low-Carbon Fuels

Product(s)	Electrode/Electrocatalysts	Potential (V), Reference Electrode	Electrolyte	Temperature/ Pressure, etc.	Current Efficiency	Reference
	CsCl		~mmol disilane (e.g., (Ph ₂ MeSi) ₂ , (PhMe ₂ Si) ₂ , (Me ₃ Si) ₃ SiH), or silylborane, or (pinacolato)BSiMe ₂ Ph/ (CH ₃) ₂ S=O	20°C		[119]
	MoO ₂ microparticle	-2.45 V (Fc/Fc ⁺)	0.1 M (Bu) ₄ N ⁺ · PF ₆ ⁻ / CH ₃ CN, 0.4 M H ₂ O	-20°C	70%	[72]
	Bulk MoS ₂	-0.764 V (RHE)	1-Ethyl-3- methylimidazolium tetrafluoroborate solution		100%	[120]
	Re ⁰ (bpy)(CO) ₃ Cl, glassy carbon electrode (bpy = 2,2'-bipyridine)	-1.25 V (NHE)	0.1 M Et ₄ N ⁺ · Cl ⁻ / CO ₂ -saturated (CH ₃) ₂ NCHO/H ₂ O (4:1-19:1) solutions	25°C	91%–98%	[121]
	<i>fac</i> -Re(5,5'-bisphenylethynyl) 2,2'-bipyridyl)(CO) ₃ Cl	-1.75 V (NHE)	0.1 M Bu ₄ N ⁺ · PF ₆ ⁻ / CO ₂ -saturated CH ₃ CN	One-compartment cell	45%	[122]
	(1 mM) <i>fac</i> -Re(L)(CO) ₃ Cl, Pt disk electrode (L = pyrrole-substituted 2,2'-bipyridine)	-1.85 V (Ag/ [0.01 M]Ag ⁺)	0.1 M Bu ₄ N ⁺ · ClO ₄ ⁻ / CO ₂ -saturated CH ₃ CN	Metrohm cell made airtight with vacuum grease (M Apiezon)	92%	[123,124]

(Continued)

TABLE 1.5 (Continued)
A Summary of Selected Electrocatalytic Reductions of CO₂ to Selectively Produce Several Important Low-Carbon Fuels

Product(s)	Electrode/Electrocatalysts	Potential (V), Reference Electrode	Electrolyte	Temperature/ Pressure, etc.	Current Efficiency	Reference
	<i>fac</i> -Re(L)(CO) ₃ Cl, carbon felt (WE)			2 h	~98.5%	[124]
	Re film electrodeposited onto a polycrystalline Au support	-1.35 V (SCE)	0.1 M LiClO ₄ /1 atm CO ₂ -saturated CH ₃ OH	Stirred conditions	87%	[125]
	poly-Re(CO) ₃ (vbpy)Cl, Pt gauze electrode (vbpy = 4-vinyl-4'-methyl-2,2'-bipyridine)	-1.55 V (sodium saturated calomel electrode [SSCE])	0.1 M Bu ₄ N ⁺ · PF ₆ ⁻ / CO ₂ -saturated CH ₃ CN	Quiescent conditions 80 min, gas-tight cell	57%	[126]
	Polymeric films formed by coelectropolymerization of <i>cis</i> -[Ru(bpy) ₂ (vpy) ₂] ²⁺ with <i>fac</i> -[Re(CO) ₃ (vbpy)Cl] or <i>fac</i> -[Re(CO) ₃ (vbpy)CH ₃ CN] ⁺	-1.55 V (SSCE)	0.1 M Bu ₄ N ⁺ · OH/ CO ₂ -saturated CH ₃ CN		90%–98%	[127]
	<i>fac</i> -Re(2,2'-bipyridine)(CO) ₃ Cl (homogeneous catalyst), working electrode: glassy carbon	-1.66 V (Fc ^{+/0})	1 atm CO ₂ -saturated 1-ethyl-3-methylimidazolium tetracyanoborate	25 ± 3°C	88 ± 10%	[128]
	[Mn(bpy)(CO) ₃] ⁺	-2.11 V (Fc ^{+/0})	0.1 M Bu ₄ N ⁺ · PF ₆ ⁻ /1 atm CO ₂ -saturated CH ₃ CN			
	[Mn(dimpy)(CO) ₃] ⁺	-1.70 V (Ag/[10 mM]Ag ⁺)	0.1 M Bu ₄ N ⁺ · ClO ₄ ⁻ / CO ₂ -saturated CH ₃ CN	Room temperature	85%	[129]
					100%	

(Continued)

TABLE 1.5 (Continued)
A Summary of Selected Electrocatalytic Reductions of CO₂ to Selectively Produce Several Important Low-Carbon Fuels

Product(s)	Electrode/Electrocatalysts	Potential (V), Reference Electrode	Electrolyte	Temperature/ Pressure, etc.	Current Efficiency	Reference
	[Mn(bpy) ₄ -t-Bu](CO) ₃ ⁺	-2.2 V (SCE)	0.1 M Bu ₄ N ⁺ · BF ₄ ⁻ CO ₂ -saturated CH ₃ CN		100%	[130]
	Mn(mesbpy)(CO) ₃ Br, [Mn(mesbpy)(CO) ₃ (CH ₃ CN)] (OTf)		0.1 M Bu ₄ N ⁺ · PF ₆ ⁻ CH ₃ CN			[131]
	mesbpy = 6,6'-dimesityl]-2,2'- bipyridine OTf = CF ₃ SO ₃ ⁻					
	(1) Iron 5,10,15,20-tetrakis (2',6'-dihydroxyphenyl)- porphyrin	-1.333 V (SCE)	(0.23 M) CO ₂ , (CH ₃) ₂ NCHO, 0.1 M Bu ₄ N ⁺ · PF ₆ ⁻ /2 M H ₂ O	A single- compartment cell	41%–56%	[132]
	(2) Iron 5,10,15,20-tetrakis (2',6'-dimethoxyphenyl)- porphyrin Working electrode: glassy carbon	-1.69 V (SCE)			89%–104%	
	Carbon monoxide dehydrogenase (CODH) from <i>M. thermoacetica</i> Working electrode: glassy carbon disk	-0.57 V (NHE)	1 atm CO ₂ -saturated 0.1 M phosphate buffer solution (pH 6.3)	50°C	~100%	[100]

(Continued)

TABLE 1.5 (Continued)
A Summary of Selected Electrocatalytic Reductions of CO₂ to Selectively Produce Several Important Low-Carbon Fuels

Product(s)	Electrode/Electrocatalysts	Potential (V), Reference Electrode	Electrolyte	Temperature/ Pressure, etc.	Current Efficiency	Reference
	Ni(cyclam) ²⁺ , Ni ₂ (biscyclam) ⁴⁺ (cyclam = 1,4,8,11-tetraazaacyclotetradecane)	-1.25 V (SCE)	Water	Room temperature	>93%	[133]
	[Ru(bpy)(CO) ₂ Cl] ₂ , [Ru(bpy) Cl(CO) ₂ Cl(COOCH ₃) ₂], Cl(CO) ₂ (bpy)Ru-Ru(bpy) (CO) ₂ Cl, CH ₃ OO(CO) ₂ (bpy) Ru-Ru(bpy)(CO) ₂ COOCH ₃	-1.5 V (Ag/[0.01 M] Ag ⁺)	0.1 M (Bu) ₄ N ⁺ · ClO ₄ ⁻ CO ₂ -saturated CH ₃ CN		95%–97%	[134]
(2) HCOOH/HCOO ⁻	In electrode Pb electrode Zn electrode Sn electrode Zn electrode Cd electrode Hg electrode In electrode Sn electrode Pb electrode	-2.0/2.4 V (Ag/ AgCl) -1.6 V (Ag/AgCl saturated with KCl) ~-1.9 V, ~-1.9 V, -2.17 V, Ag/AgCl (3 M NaCl)	0.1 M (CH ₃ CH ₂) ₃ N ⁺ · H ₃ PO ₄ ⁻ / water 0.1 M KHCO ₃ /water CO ₂ -saturated 1-ethyl-3- methylimidazolium trifluoroacetate with 33% water 2 M KCl/CO ₂ -saturated water	100°C, normal pressure 25°C	87.6%/83.2% 72.9%/78.9% 46.6%/53.4% 67.5%/37.1% 20% 39% 94% ~100% ~100% ~100%	[67] [66] [135]
	Sn (99.9985%) electrode	-1.8 V (SCE)			60%	[136]

(Continued)

TABLE 1.5 (Continued)
A Summary of Selected Electrocatalytic Reductions of CO₂ to Selectively Produce Several Important Low-Carbon Fuels

Product(s)	Electrode/Electrocatalysts	Potential (V), Reference Electrode	Electrolyte	Temperature/ Pressure, etc.	Current Efficiency	Reference
	Sn (99.998%) electrode	-1.7 V (SCE)	0.1 M Na ₂ SO ₄ / CO ₂ -saturated water	A conventional three-electrode electrochemical cell	~95%	[137]
		-2.0 V (SCE)	0.5 M KHCO ₃ / CO ₂ -saturated water		~63%	
	Sn powder-decorated gas diffusion layer electrode	-1.6 V (SCE)	0.5 M NaHCO ₃ /ambient CO ₂ pressure, water	27.3 mA/cm ²	70%	[138]
	Nanostructured Sn/graphene	-0.76 V (SCE)	NaHCO ₃ /water	18 h, >10 mA/cm ²	>93%	[139]
	Pb granule electrodes	-1.8 V (SCE)	0.2 M K ₂ CO ₃ (50 bar) CO ₂ -saturated water	0.5 h, 80°C, 0.41 mA/cm ²	94%	[140]
	Tinned-copper sheet		0.45 M KHCO ₃	0.22 kA/m ² , ambient conditions	86%	[141]
	Fe (99.5%) electrode	-1.53 to 1.61 V (Ag/ AgCl) saturated KCl	0.1 M KClO ₄ /30 atm CO ₂ -saturated water	25°C, 120 mA/cm ² ;	59.5%– 59.6%	[93]
	Cu ₂ O dispersed polyamine (PANI) electrodes	-0.3 V (SCE [sat. KCl])	0.1 M (Bu) ₄ NClO ₄ / CO ₂ -saturated CH ₃ OH	three-compartment glass cell in a stainless autoclave	30.4%	[142]
	MoO ₃ microparticle	-2.45 V (Fe/Fe ⁺)	0.1 M (Bu) ₄ N ⁺ · PF ₆ ⁻ / CH ₃ CN, 1.4 M H ₂ O	-20°C	55%	[72]

(Continued)

TABLE 1.5 (Continued)
A Summary of Selected Electrocatalytic Reductions of CO₂ to Selectively Produce Several Important Low-Carbon Fuels

Product(s)	Electrode/Electrocatalysts (2.00×10^{-4} M Ni(cyclam) ²⁺ / Ni ₂ (biscyclam) ⁴⁺)	Potential (V),		Electrolyte	Temperature/ Pressure, etc.	Current Efficiency	Reference
		Reference Electrode	Electrode				
[Ru(bpy) ₂ (CO) ₂] ²⁺ Working electrode: Hg pool		-1.3 V (SCE)	0.1 M NaClO ₄ /1 atm CO ₂ -saturated, (CH ₃) ₂ NCHO	20°C	75%	[133]	
			In the presence of (1) CH ₃ NH ₂ · HCl (2) (CH ₃) ₂ NH · HCl (3) C ₆ H ₅ OH CO ₂ -saturated H ₂ O/ (CH ₃) ₂ NCHO (9:1, v/v) solution	1.6 mA/cm ² 3.3 mA/cm ² 2.3 mA/cm ²	64.1% 84.3% 81.0%	[143]	
[(bpy) ₂ Ru(dimbbpy)](PF ₆) ₂ [(bpy) ₂ Ru(dimbbpy)]- Ru(bpy) ₂ (PF ₆) ₄ (dimbbpy = 2,2'-bis(1- methylbenzimidazol-2-yl)- 4,4'-bipyridine)		-1.65 V -1.55 V (Ag/AgCl)	(2.5%) H ₂ O/CO ₂ - saturated CH ₃ CN		89% 90%	[144]	
1. Carbon nanotube 2. Nitrogen-doped carbon nanotube 3. Nitrogen-doped graphenated carbon nanotube/glassy carbon (GC) electrode, polyethylenimine (cocatalyst)		-1.8 V (SCE)	0.1 M KHCO ₃ / CO ₂ -saturated water		59% 85% 87%	[145]	

(Continued)

TABLE 1.5 (Continued)
A Summary of Selected Electrocatalytic Reductions of CO₂ to Selectively Produce Several Important Low-Carbon Fuels

Product(s)	Electrode/Electrocatalysts	Potential (V), Reference Electrode	Electrolyte	Temperature/ Pressure, etc.	Current Efficiency	Reference
	Tungsten-containing formate dehydrogenase enzyme (FDHI) from <i>S. fumaroxidans</i> Working electrode: rotating disk pyrolytic graphite edge electrode	-0.41 to 0.81 V (Ag/AgCl)	0.02 M Na ₂ CO ₃ /water (pH 6.5)	37°C	97.3%–102.1%	[105]
(3) CH ₃ COOH	Cu ₂ O dispersed polyamine (PANI) electrodes	-0.3 V (SCE [sat. KCl])	0.1 M (Bu) ₄ NClO ₄ / CO ₂ -saturated CH ₃ OH	25 ± 5°C	63.0%	[142]
(4) CH ₃ OH CO _{2(g)} + 6H ⁺ + 6e ⁻ = CH ₃ OH _(l) + H ₂ O _(l) , (0.016) CO _{2(g)} + 5H ₂ O _(l) + 6e ⁻ = CH ₃ OH _(l) + 6OH ⁻ , (-0.812)	Cu	-1.1 V (Ag/AgCl)	0.1 M LiCl/(34/68 atm) CO ₂ -saturated C ₂ H ₅ O-H ₂ O with 20 ml/o H ₂ O	80°C, 8 h, 9.0 mA/ cm ²	36%/40%	[76]
	Preoxidized Cu foil electrode	-0.4 V (SCE)	0.5 M KHCO ₃ / CO ₂ -saturated water (pH = 7.6)	pH 7.5–7.6 at 25°C 33 mA/cm ²	100%	[146]
	Preoxidized Cu foil electrode: electrodeposited cuprous oxide film	-1.1 V (SCE)	0.5 M KHCO ₃ / CO ₂ -saturated water	A typical three-electrode cell (30 mL)	38%	[147]

(Continued)

TABLE 1.5 (Continued)
A Summary of Selected Electrocatalytic Reductions of CO₂ to Selectively Produce Several Important Low-Carbon Fuels

Product(s)	Electrode/Electrocatalysts	Potential (V), Reference Electrode	Electrolyte	Temperature/ Pressure, etc.	Current Efficiency	Reference
	Hydrogenated Cu-modified Pd electrode	-1.6 V (SCE)	0.1 M KHCO ₃ / CO ₂ -saturated water		15%	[148]
	Hydrogenated Pd electrode, (0.01 M) pyridine		0.5 M NaClO ₄ / CO ₂ -saturated water	pH 5	30%	[149]
	Ru	-0.54 V (SCE)	0.2 M Na ₂ SO ₄ / CO ₂ -saturated water (pH 3.5–5.5)	60°C, 0.387 mA	42%	[150]
	Ru	-0.8 V (SCE)	0.5 M NaHCO ₃ / CO ₂ -saturated water	2 h 4 h 6 h 8 h	30.5% 23.6% 15.3% 17.2%	[151]
	Ru/Cu			2 h 4 h 6 h 8 h	18.2% 28.3% 32.4% 41.3%	
	Ru/Cd			2 h 4 h 6 h 8 h	20.4% 21.3% 28.4% 38.2%	
	Hydrochloric acid-pretreated Mo electrode (KOH/HF-pretreated) Mo electrode	-0.8 V (SCE)	0.2 M Na ₂ SO ₄ / CO ₂ -saturated water	22°C/pH 4.2	55%	[152]
					84%	

(Continued)

TABLE 1.5 (Continued)
A Summary of Selected Electrocatalytic Reductions of CO₂ to Selectively Produce Several Important Low-Carbon Fuels

Product(s)	Electrode/Electrocatalysts	Potential (V), Reference Electrode	Electrolyte	Temperature/ Pressure, etc.	Current Efficiency	Reference
	RuO ₂ /TiO ₂ (i.e., Ru ₃ TiO ₈)	-0.035 V (Ag/ AgCl/3 M KCl)	0.2 M Na ₂ SO ₄	20°C	30%	[153]
	RuO ₂ /TiO ₂ nanoparticles composite-modified Pt electrodes	-0.8 V (SCE)	0.5 M NaHCO ₃ / CO ₂ -saturated water		40.2%	[154]
	RuO ₂ /TiO ₂ nanotubes composite-modified Pt electrodes				60.5%	
	K ₃ Fe ^{II} [Fe ^{III} (CN) ₆] film coated on Pt plate electrode	-0.337 to 0.394 V (SCE)	0.015 M Na ₃ [Fe(CN) ₅ (H ₂ O)]/ CO ₂ -saturated water (pH 3.5)/20 mM CH ₃ OH		>80%	[155]
(5) H ₂ C ₂ O ₄ /C ₂ O ₄ ²⁻ 2CO ₂ (g) + 2H ⁺ + 2e ⁻ = H ₂ C ₂ O ₄ (aq.), (-0.500) 2CO ₂ (g) + 2e ⁻ = C ₂ O ₄ ²⁻ (aq.), (-0.590)	Ni-ET _n (Me/COOET)Et _n		0.25 M Bu ₄ N ⁺ · ClO ₄ ⁻ / CO ₂ -saturated CH ₃ CN		98%	[110]
	[(bpy) ₂ Ru(dimbbpy)](PF ₆) ₂ ; [(bpy) ₂ Ru(dimbbpy)]- Ru(bpy) ₃ (PF ₆) ₄ Pb electrode	-1.65 V, -1.55 V vs. Ag/AgCl -2.6 V Ag/AgCl	CO ₂ -saturated CH ₃ CN		64% 70%	[144]
			0.1 M tetraethylammonium (TEAP)/propylene carbonate	100°C under normal pressure	73.3%	[67]

(Continued)

TABLE 1.5 (Continued)
A Summary of Selected Electrocatalytic Reductions of CO₂ to Selectively Produce Several Important Low-Carbon Fuels

Product(s)	Electrode/Electrocatalysts	Potential (V), Reference Electrode	Electrolyte	Temperature/ Pressure, etc.	Current Efficiency	Reference
(6) CH ₄ CO ₂ (g) + 8H ⁺ + 8e ⁻ = CH ₄ (g) + 2H ₂ O(l), (0.169) CO ₂ (g) + 6H ₂ O(l) + 8e ⁻ = CH ₄ (g) + 8OH ⁻ , (-0.659)	MoO ₂ microparticle Ppy Re microalloy polypyrrole/ Ppy Cu-Re microalloy polypyrrole Au electrodes	-2.45 V (Fc/Fc ⁺) -1.35 V	0.1 M (Bu) ₄ N ⁺ PF ₆ ⁻ / CH ₃ CN, without H ₂ O 0.1 M LiClO ₄ /CH ₃ OH	-20°C 1 atm CO ₂	45% 34% 31%	[72] [125]
(7) C ₂ H ₄	99.999% Cu sheet cathode Polycrystal Cu Cu(100) Cu(110) Cu(111) Single-crystal electrodes Cu (99.999%) electrode	-1.44 V -1.42 V -1.55 V -1.56 V (NHE)	0.5 M KHCO ₃ / CO ₂ -saturated water 0.1 M KClO ₄ /water	0°C 18°C/pH 6.8	65% 33.3% 25.0% 49.5% 38.9%	[156] [157]
	Cu (99.999%) electrode Cu (99.98%) electrode	-1.40 V (NHE) -3.5 V (Ag/AgCl)	0.5 M KHCO ₃ / CO ₂ -saturated water 0.1 M KClO ₄ / CO ₂ -saturated water 0.080 M CsOH/CH ₃ OH	40°C 19°C/pH 5.9, 5 mA cm ⁻² -30°C	20% 48.1% 32.3%	[156] [158] [159] (Continued)

TABLE 1.5 (Continued)
A Summary of Selected Electrocatalytic Reductions of CO₂ to Selectively Produce Several Important Low-Carbon Fuels

Product(s)	Electrode/Electrocatalysts	Potential (V),		Electrolyte	Temperature/ Pressure, etc.	Current Efficiency	Reference
		Reference Electrode					
	1. Polycrystal Cu	-1.44 V		0.1 M KClO ₄ /water	18°C/pH 6.8	25.5%	[157]
	2. Cu(100)	-1.42 V				31.7%	
	3. Cu(110)	-1.55 V				15.1%	
	4. Cu(111)	-1.56 V (NHE)				4.7%	
(8) HCHO	Single-crystal electrodes			0.1 M NaClO ₄ / CO ₂ -saturated water		39%	[68]
	[Co(4-v-tpy) ₂] ²⁺	-1.100 V					
	[Fe(4-v-tpy) ₂] ²⁺	-1.057 V			28%		
	[Cr(4-v-tpy) ₂] ²⁺ electropolymerized on glass carbon electrodes	-1.100 V (Ag/AgCl)			87%		

an inability to control product distribution, high operation cost, low catalyst activity, insufficient catalyst durability, and a lack of mechanistic understanding. Thus, in the following aspects, we should make more efforts:

- Develop inexpensive and efficient catalysts

To achieve the desirable product selectivity, more metal complexes with complex structures (of ligands) are being increasingly developed, such as that for CO (Figure 1.3)¹⁶² and CH₃OH (Figure 1.4).¹⁶³

The drawback is the high cost of catalysts due to the complexity of manufacturing techniques. It has also been considered to reduce the cost of catalysts by using inexpensive metals instead of Pt,^{80,164,165} Ru,^{144,151,163} Pd,^{79,116,166} etc. Besides Fe (complex catalysts),^{93,162} Cu,^{157–159} Pb,^{67,135,140} and Sn^{135–137} (single and oxide metal electrodes), Mn is attracting more and more attention as the metal center of complex catalysts.^{129,130,167–169} Medina-Ramos et al.¹¹⁸ developed a bismuth (Bi) – carbon monoxide-evolving catalyst and realized an efficient reduction of CO₂ to CO with high current density (Figure 1.5). This novel catalyst was electrodeposited on inexpensive glassy carbon under either aqueous or nonaqueous conditions.

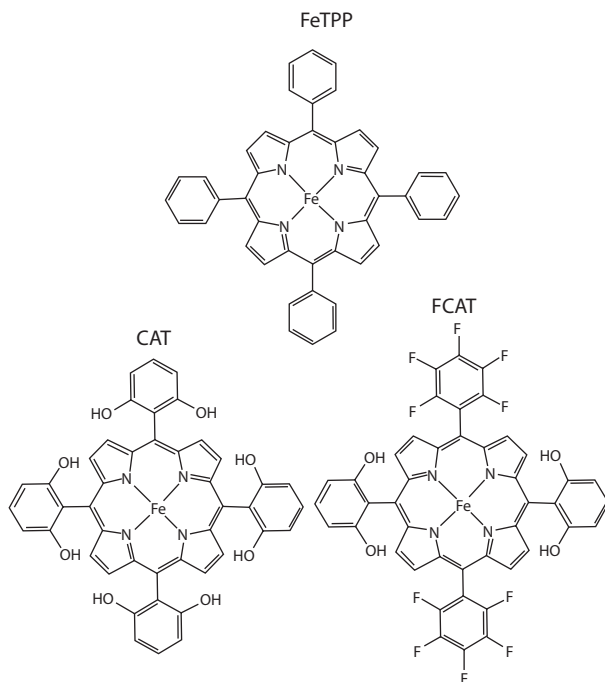


FIGURE 1.3 Iron-based catalysts for CO₂-to-CO reduction. (Reprinted with permission from Costentin, C. et al., Ultraefficient homogeneous catalyst for the CO₂-to-CO electrochemical conversion. *Proc Natl Acad Sci USA*, 111, (42), 14990–14994. Copyright 2014 American Chemical Society.)

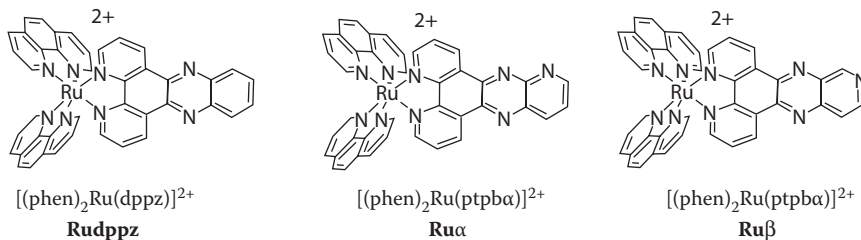


FIGURE 1.4 Structures of $[(\text{phen})_2\text{Ru}(\text{ptpb}\alpha)]^{2+}$ and $[(\text{phen})_2\text{Ru}(\text{ptpb}\beta)]^{2+}$ complexes and $[(\text{phen})_2\text{Ru}(\text{dppz})]^{2+}$ complex. (Reprinted with permission from Boston, D. J. et al., Electrochemical and photocatalytic conversion of CO_2 to methanol using ruthenium complexes with internal pyridyl cocatalysts. *Inorg Chem*, 53, (13), 6544–6553. Copyright 2014 American Chemical Society.)

- Nanotechnology applications

It seems that more attention is being focused on nanotechnology for improved electrochemical performance of catalysts and modified electrodes such as the selectivity toward desired products. Some metal elements (e.g., Ti,¹⁷⁰ Ni,¹⁷¹ Pt,¹⁷² Cu,^{142,173–177} Ag,^{178,179} and Au,^{176,179} in the state of single metals,^{172,173,175,177–179} oxides,^{142,170,174} or alloys^{176,179}) were directly used as catalysts in the form of nanoparticles, or some others (e.g., Pt,¹⁸⁰ Fe,^{180,181} Co,¹⁸² and Ru¹⁵⁴) were loaded on carbon nanotube,^{180,181} nanoporous activated carbon fiber,¹⁸² and TiO_2 nanotubes or nanoparticles.¹⁵⁴ Improved performance such as more positive reduction potentials, higher catalytic current density, faradaic efficiency, and catalyst durability have also been observed, all being undoubtedly attributed to the increase in (specific) surface area and active sites. The nanostructure of metal electrode surface can be created by two steps: high-temperature annealing to produce metal

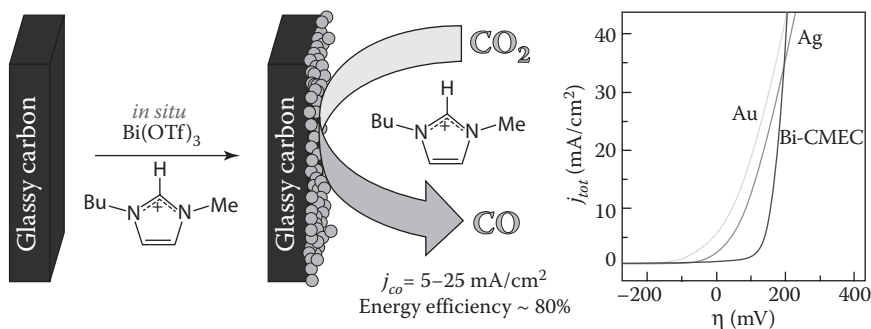


FIGURE 1.5 Efficient reduction of CO_2 to CO with high current density using *in situ* or *ex situ* prepared Bi-based materials. (Reprinted with permission from Medina-Ramos, J.; DiMeglio, J. L.; Rosenthal, J., Efficient reduction of CO_2 to CO with high current density using *in situ* or *ex situ* prepared Bi-based materials. *J Am Chem Soc*, 136, (23), 8361–8367. Copyright 2014 American Chemical Society.)

oxides, and reducing electrochemically in aqueous solutions or with H₂. It was found that controlled preparation conditions (e.g., temperature) are critical.^{173,183}

- Develop novel electrocatalytic technologies

Those so-called novel techniques often seem to be unexpected. For example, Lescot et al.¹¹⁹ reported an efficient (2 h) fluoride-catalyzed conversion of CO₂ to CO at room temperature, in which the oxygen abstraction step was performed with only the presence of catalytic cesium fluoride and a stoichiometric amount of a disilane in dimethyl sulfoxide (DMSO) (Figure 1.6). The nonaqueous solvent was used. Organic molecules such as tetraalkylammonium salts, aromatic nitriles and esters, and especially ionic liquids^{118,135,170,184} are popularly used as mediators and catalysts.¹⁸⁵ However, the drawback of using organic molecules is not cheap. The metal-free catalysts such as conducting polymers, pyridinium derivatives, aromatic anion radicals, and heteroatom-doped carbon materials^{63,161} are also considered to be the next-generation, renewable materials that promise to be cost-effective, relative to their metal-containing counterparts, particularly relative to noble-metal-based catalysts.^{63,185}

- Application of theoretical modeling techniques

Efficient catalysts for CO₂ electrochemical reduction should be developed not only by experiments but also by theoretical calculations. The use of first-principles computational techniques,^{177,186} such as density functional theory (DFT), to understand electrochemical reactions is witnessing an ever-increasing popularity within the physical electrochemistry community.¹⁸⁷ DFT calculations are thought to be an effective tool,^{188–194} which can, for example, (1) determine the potential-dependent reaction free energies and activation barriers for several reaction paths of CO₂ electrochemical

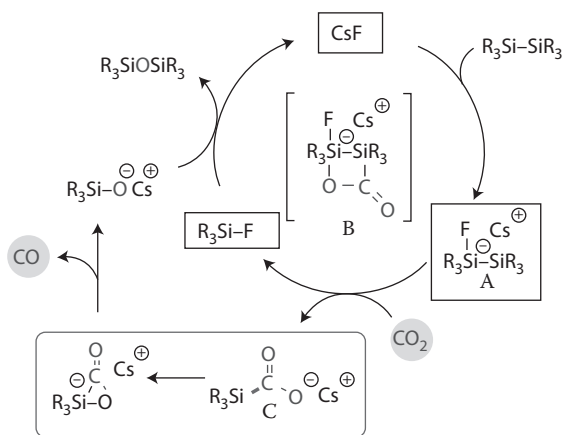


FIGURE 1.6 Proposed mechanism for CO₂ reduction with CsF and disilane. (Reprinted with permission from Lescot, C. et al., Efficient fluoride-catalyzed conversion of CO₂ to CO at room temperature. *J Am Chem Soc*, 136, (16), 6142–6147. Copyright 2014 American Chemical Society.)

reduction^{193,194}; (2) examine adsorption stabilities of H*, OH*, O*, and H₂O* species by calculating the free energy of formation of the adsorbate as a function of electrode potential¹⁹¹; and (3) determine new intermediates, searching for new catalysts, and identifying reaction pathways.¹⁸⁸ Challenges and perspectives as to DFT calculations have been outlined in several review papers.^{187,188,195} The accuracy of calculation results is to be improved.

1.8 APPLICATIONS OF CO₂ ELECTROREDUCTION

CO₂ electroreduction is applied for the production of low-carbon fuels,^{14,63} which may be solar fuel¹⁹⁶ or intermediate materials for the petrochemical industry.¹⁹⁷ However, large-scale processes are quite different with lab-scale ones.

It may be found that most studies toward large-scale CO₂ electrochemical reduction have used Sn as catalysts to produce HCOO⁻.^{65,104,141,195,198} Agarwal et al. discussed the engineering and economic feasibility of large-scale electrochemical reduction of CO₂ to HCOO⁻ salts and HCOOH at a gas/solid/ liquid interface, using a flow-through reactor.⁶⁵ They concluded that faradaic efficiency, current density, and voltage determine the energy and electrode costs for the large-scale process, and that further work will be needed in the areas of reducing consumable costs, increasing catalyst lifetime, and improved reactor designs to enhance the overall attractiveness of the process.⁶⁵

1.9 FURTHER READING AND HOMEWORK

1.9.1 MEASUREMENT AND COMPUTATIONAL METHODS

Cyclic voltammetry (CV) is a reversal technique and is the potential-scan equivalent of double potential step chronoamperometry. It has become a very popular technique for initial electrochemical studies of new systems and has proven very useful in obtaining information about fairly complicated electrode reactions.¹⁹⁹ An example is given in Figure 1.7,¹³¹ in which CV spectra of CO₂ electrochemical reductions which are catalyzed by Mn(mesbpy)(CO)₃Br and Mn(bpy)(CO)₃Br indicate that the potential when the electron is transferred varies with ligand. Another is that Sanchez-Sanchez et al.²⁰⁰ used CV to study the electrocatalytic reduction of CO₂ on Pt single-crystal electrodes modified with adsorbed adatoms. To our knowledge, *Cyclic Voltammetry: Simulation and Analysis of Reaction Mechanisms*,²⁰¹ is one of the early published CV monographs that can still be found, and now the related content is always more or less described in electrochemical textbooks.^{202–204} CO₂ electroreduction is also sometimes studied at catalysts using linear sweep voltammetry (LSV),¹⁷⁴ rotating ring-disk electrode (RRDE),^{179,205,206} and electrochemical impedance spectroscopy (EIS).¹⁷⁹

Gas chromatograph (GC) is used for quantitative analyses of products such as H₂, CO, CO₂, hydrocarbons (C₁–C₆), alcohols and aldehydes (C₁–C₄), and the common carboxylic acids. Gaseous products^{207,208} and reaction intermediates¹⁹⁰ are detected using online mass spectroscopy (MS). Nuclear magnetic resonance (NMR) spectroscopy is sometimes used for detecting trace levels (micromole level) of aqueous

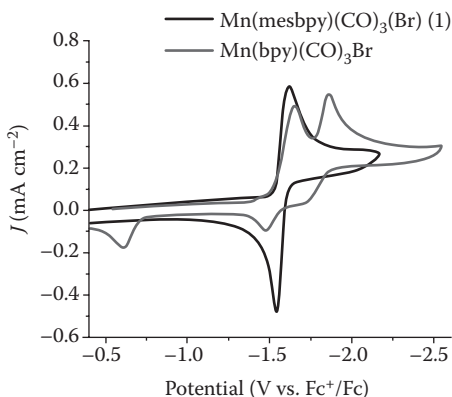


FIGURE 1.7 Comparison of the cyclic voltammograms of Mn(mesbpy)(CO)₃(Br)(1) and Mn(bpy)(CO)₃Br under identical conditions (1 mM complex). Each experiment is performed in MeCN with 0.1 M (Bu)₄N⁺PF₆⁻ as the supporting electrolyte, under an atmosphere of N₂, at a scan rate of 100 mV/s, with a glassy carbon working electrode (3 mm diameter), a platinum wire counter electrode, a Ag/AgCl wire pseudo-reference, and Fc added as an internal reference. (Reprinted with permission from Sampson, M. D. et al., Manganese catalysts with bulky bipyridine ligands for the electrocatalytic reduction of carbon dioxide: Eliminating dimerization and altering catalysis. *J Am Chem Soc*, 136, (14), 5460–5471. Copyright 2014 American Chemical Society.)

electrolysis organic products.^{209,210} HCOOH is often measured with NMR^{135,211} and ion chromatograph (IC).^{90,136} Metal ions in electrolytes are quantified with an inductively coupled plasma–mass spectrometry (ICP–MS). Chemical analysis of electrode surface was performed by x-ray photoelectron spectroscopy (XPS).^{136,212} Scanning electron microscopy (SEM),²¹² XPS,¹³⁶ and x-ray diffraction (XRD)²¹² are employed in *ex situ* analyses. More information can be easily found in textbooks.²⁰⁴

Theoretical modeling, in particular DFT simulations, provides a powerful and effective tool to discover chemical reaction mechanisms and design new catalysts for the chemical conversion of CO₂, overcoming the repetitious and time/labor-consuming trial-and-error experimental processes.^{188,213} DFT calculations have been widely used to characterize the reduced species from the reduction of CO₂.¹⁹⁴ As described before, many related research has recently been published.^{188–194} There have already been a lot of monographs on the theory and application of DFT, such as *Density Functional Theory: A Practical Introduction* by David Sholl,²¹⁴ *The Fundamentals of Density Functional Theory*,²¹⁵ and *A Chemist's Guide to Density Functional Theory* by Koch et al.,²¹⁶ all being suitable for researchers at different levels.

1.9.2 PUBLICATIONS

Until now, there is barely a monograph on electrochemical reduction of CO₂, although it is already not a new topic. Most of the studies associated with the electrochemical reduction of CO₂, especially the early ones, were published in

TABLE 1.6

Magazine Abbreviation/PUBLISHER/Association

<i>J Electroanal Chem</i> /ELSEVIER SCIENCE SA/International Society of Electrochemistry
<i>Electrochim Acta</i> /ELSEVIER SCIENCE SA/International Society of Electrochemistry
<i>Electrochem Commun</i> /ELSEVIER SCIENCE SA/International Society of Electrochemistry
<i>J Solid State Electr</i> /SPRINGER/International Society of Electrochemistry
<i>J Appl Electrochem</i> /SPRINGER/International Society of Electrochemistry
<i>Chem Rev</i> /AMERICAN CHEMICAL SOCIETY/American Chemical Society
<i>J Am Chem Soc</i> /AMERICAN CHEMICAL SOCIETY/American Chemical Society
<i>J Phys Chem A</i> /AMERICAN CHEMICAL SOCIETY/American Chemical Society
<i>J Phys Chem B</i> /AMERICAN CHEMICAL SOCIETY/American Chemical Society
<i>J Phys Chem C</i> /AMERICAN CHEMICAL SOCIETY/American Chemical Society
<i>Inorg Chem</i> /AMERICAN CHEMICAL SOCIETY/American Chemical Society
<i>Organometallics</i> /AMERICAN CHEMICAL SOCIETY/American Chemical Society
<i>Proc Natl Acad Sci USA</i> /NATIONAL ACADEMY OF SCIENCES/National Academy of Sciences of United States of America
<i>Energ Environ Sci</i> /ROYAL SOCIETY OF CHEMISTRY/The Royal Society of Chemistry
<i>Chem Commun</i> and the former journal <i>J Chem Soc Chem Commun</i> /ROYAL SOCIETY OF CHEMISTRY/The Royal Society of Chemistry
<i>Phys Chem Chem Phys</i> and the former journal <i>J Chem Soc Faraday Trans</i> /ROYAL SOCIETY OF CHEMISTRY/The Royal Society of Chemistry
<i>Angew Chem Int Ed</i> /WILEY-VCH VERLAG GMBH/German Chemical Society
<i>Bull Chem Soc Jpn</i> /CHEMICAL SOCIETY OF JAPAN/Chemical Society of Japan
<i>Chem Lett</i> /CHEMICAL SOCIETY OF JAPAN/Chemical Society of Japan
<i>Coord Chem Rev</i> /ELSEVIER SCIENCE SA
<i>Appl Catal A-Gen</i> /ELSEVIER SCIENCE SA
<i>Catal Today</i> /ELSEVIER SCIENCE SA
<i>J Power Sources</i> /ELSEVIER SCIENCE SA

veteran magazines such as *Journal of the American Chemical Society*,^{100,217,218} *Inorganic Chemistry*,^{219–221} *Journal of the Electrochemical Society*,^{146,164} *Journal of Electroanalytical Chemistry*,^{222–224} *Electrochimica Acta*,^{80,225,226} and *Chemical Letters*.^{156,227,228} Some interesting research and high-quality review papers are also published in *Nature*,²²⁹ *Science*,¹³² *Chemical Reviews*,²³⁰ *Chemical Society Reviews*,^{63,231} *Energy & Environmental Science*,²³² and *Proceedings of the National Academy of Sciences of the United States of America*.^{105,162} The typical journals that are noteworthy are recommended in Table 1.6.

Up to now, there still is not a monograph that focuses on electrochemical reduction of CO₂. Researchers can only find little incomplete description in several books on CO₂ conversion and utilization.^{233–235} This book aims to address this issue.

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