

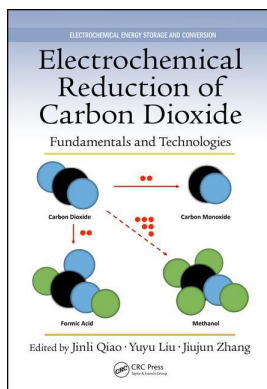
This article was downloaded by: 10.2.97.136

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Publisher: *CRC Press*

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Electrochemical Reduction of Carbon Dioxide Fundamentals and Technologies

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Challenges and Perspectives of CO Electroreduction

Publication details

<https://test.routledgehandbooks.com/doi/10.1201/b20177-11>

Jinli Qiao, Yuyu Liu, Jiujun Zhang

Published online on: 14 Jun 2016

How to cite :- Jinli Qiao, Yuyu Liu, Jiujun Zhang. 14 Jun 2016, *Challenges and Perspectives of CO Electroreduction from: Electrochemical Reduction of Carbon Dioxide, Fundamentals and Technologies* CRC Press

Accessed on: 28 Mar 2023

<https://test.routledgehandbooks.com/doi/10.1201/b20177-11>

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10 Challenges and Perspectives of CO₂ Electroreduction

Mengyang Fan and Jinli Qiao

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10.1 INTRODUCTION

The electrocatalytic reduction of CO₂ has a long history dating from the nineteenth century. However, this topic becomes more attractive from both academia and industry, because the excessive burning of fossil fuels leads to the extra emission of CO₂, which has exceeded nature's CO₂ recycle capability. To deal with the extra CO₂ recycle, the storage of renewable energy through the electrochemical reduction of CO₂ is an attractive strategy to transform the current linear utilization of carbon fuels: the process could be operated under normal condition; the electricity source used to reduce the CO₂ could be renewable green energy; the reaction system can be built up to a continuous one and scaled up to realize the industrial application.

However, to reach the final goal of CO₂ electroreduction, challenges and opportunities exist at the same time. For the CO₂ reduction reaction itself, optimal catalysts

with high catalyzed activity, selectivity, and stability should be developed, which can be used to reduce energy consumption during the CO₂ electroreduction process. For the reaction system, the electrode and electrolyte parts should be moderate to adapt the application, and the system should be designed to a more compact structure, which can be easily scaled up. Another significant part in CO₂ electroreduction process is the energy used for the CO₂ conversion. This energy source should be green electricity and will not generate additional CO₂ in the process. However, such green energy is not feasible to obtain because of the low power density and the limited power generation conditions. Therefore, all these main factors cause major challenges in CO₂ electroreduction and need to be taken into consideration and treated as the key points in future research.

10.2 INSUFFICIENT CATALYST ACTIVITY, SELECTIVITY, AND STABILITY OF CO₂ ELECTROREDUCTION

When judging the properties of catalysts, the catalyzed activity, production selectivity, and electrode stability are the main parameters to be investigated. Developing some novel kinds of effective catalysts for CO₂ electroreduction is the primary task. In current states, some of the developed catalysts may have one prominent feature of the three main aspects; however, synthesizing catalysts that function well in comprehensive performance is a big challenge.

10.2.1 HIGH OVERPOTENTIAL AND LOW CURRENT EFFICIENCY

Overpotential and current efficiency are main aspects to judge the catalyst activity. Catalysts that perform the low overpotential and high current efficiency could be considered as optimal ones within a certain range; on the contrary, those with high overpotential and low current efficiency in CO₂ electroreduction seem to be insufficiently active. Hara Kohjiro and his coworkers have compared different metal catalysts in different groups in their research, which can be seen in Table 10.1, and have classified these metals into four main groups on the basis of their electrocatalytic activities [1]. Group (1) includes Ti, Nb, Ta, Mo, Mn, and Al, which has hydrogen as the prominent product formed by water reduction. In group (2), which includes Zr, Cr, W, Fe, Co, Rh, Ir, Ni, Pd, Pt, C, and Si, there are formic acid and CO products reduced from CO₂ reduction when the pressure of CO₂ increased high up to 30 atm. However, when the CO₂ pressure was 1 atm, hydrogen was still the dominant product. In addition, the overpotentials of CO₂ reduction on these metals are higher than -1.45 V vs. Ag/AgCl. Meanwhile, the faradaic efficiencies of CO₂ reduction on these metals in group (2) are not that satisfactory. Interestingly, when the current density was 163 mA cm⁻², the faradaic efficiency of reduced formic acid on Pd was 35.4%; however, when the current density increased to 500 mA cm⁻², the faradaic efficiency of formic acid production increased to 44%. It can be seen that the production efficiency could not be improved under lower current density, which results in low current efficiency. This is one of the least known aspects of catalyst activity which needs to be investigated in the future. Metal Ag, Au, Zn, In, Sn, Pb, and Bi are classified in group (3) [1]. In this group, CO and formic acid are the major products. The faradaic

TABLE 10.1
Electrochemical Reduction of CO₂ under a Pressure of 30 atm on Various Electrodes at 163 mA cm⁻²

Group	Electrode	E ^a (V)	Faradaic Efficiency (%)										PCD/(CO ₂ red.) ^c (mA cm ⁻²)
			CH ₄	C ₂ H ₆	C ₂ H ₄	CO	HCOOH	H ₂	CO ₂ red ^b	Total			
4	Ti	-1.57	0.18	0.01	0.08	Trace	4.6	80.8	4.9	85.7	8		
	Zr	-1.73	0.13	0.01	0.01	32.5	7.6	44.2	40.3	84.5	65.7		
5	Nb	-1.45	0.56	0.05	0.01	n ^d	3.5	81.4	4.1	85.5	6.7		
	Ta	-1.51	0.55	0.05	Trace	Trace	7.6	74.4	8.2	82.6	13.4		
6	Cr	-1.49	0.53	0.05	0.07	11.8	8.2	68.6	20.7	89.3	33.7		
	Mo	-1.34	0.4	0.05	0.03	n	6.5	83.3	7	90.3	11.4		
7	W	-1.61	0.38	0.04	0.01	Trace	31.9	53.1	32.3	85.4	52.6		
	Mn	-1.69	0.68	0.1	0.06	2.8	2.8	78.8	6.5	85.3	10.6		
8	Fe	-1.63	2.03	0.4	0.16	4.2	28.6	51.6	35.4	87.0	57.7		
	Co	-1.54	3.09	0.17	0.38	15.8	21.9	46.9	41.5	88.4	67.6		
9	Rh	-1.41	0.26	0.03	0.01	61	19.5	13.1	80.8	93.9	131.7		
	Ir	-1.55	0.62	0.05	0.05	17.5	22.3	48.3	40.5	88.8	66		
10	Ni	-1.59	0.72	0.08	0.11	33.5	31.3	26	65.7	91.7	107.1		
	Pd	-1.56	0.13	0.01	Trace	46.1	35.6	12.8	81.8	94.6	133.3		
11	Pd ^e	-1.76	0.21	0.01	0.02	35.2	44	13.8	79.4	93.2	397		
	Pt	-1.48	0.22	0.02	Trace	6.1	50.4	33.6	56.7	90.3	92.4		
11	Cu	-1.64	9.95	0.06	3.74	20.1	53.7	2.5	87.6	90.1	142.8		
	Ag	-1.48	0.2	0.01	Trace	75.6	16.8	3.9	92.6	96.5	150.9		
	Au	-1.3	0.21	0.02	0.11	64.7	11.8	15.4	76.8	92.2	125.2		

(Continued)

TABLE 10.1 (Continued)
Electrochemical Reduction of CO₂ under a Pressure of 30 atm on Various Electrodes at 163 mA cm⁻²

Group	Electrode	E ^a (V)	Faradaic Efficiency (%)										PCD(CO ₂ red.) ^c (mA cm ⁻²)
			CH ₄	C ₂ H ₆	C ₂ H ₄	CO	HCOOH	H ₂	CO ₂ red ^b	Total			
12	Zn	-1.7	0.31	0.03	Trace	48.7	40.5	2.8	89.5	92.3	145.9		
	Al	-1.97	0.66	0.01	n	n	1.3	86.5	2	88.5	3.3		
13	In ^f	-	0.28	Trace	0.04	3.8	90.1	5.6	90.5	99.1	147.5		
	C ^g	-1.68	0.45	0.03	0.04	44	30.2	15.6	74.7	90.3	37.4		
14	C	-2.14	0.66	0.02	0.05	3.6	6.8	75.5	11.2	86.7	18.3		
	n-Si	-2.04	0.87	0.01	0.02	2	46.3	40.6	49.2	89.8	80.2		
	Sn	-1.39	0.06	Trace	8	92.3	1.3	100.4	101.7	163			
	Pb	-1.57	0.2	Trace	Trace	95.5	1.2	95.7	96.9	156			
15	Bi ^h	-1.42	0.17	0.01	Trace	3.3	82.7	6.3	86.2	92.5	140.5		

Source: Reprinted from *Journal of Electroanalytical Chemistry*, 391(1), Hara, K., Kudo, A., and Sakata, T., Electrochemical reduction of carbon dioxide under high pressure on various electrodes in an aqueous electrolyte, 141–147, Copyright 1995, with permission from Elsevier.

Note: Reaction temperature, 25°C; electrolyte, 0.1 mol dm⁻³ KHCO₃; charge passed, 300°C.

^a Corrected with an IR compensation instrument (vs. Ag/AgCl).

^b Total faradaic efficiency for CO₂ reduction.

^c Partial current density for CO₂ reduction.

^d Not detected.

^e Current density, 500 mA cm⁻².

^f Current density, 200 mA cm⁻².

^g Current density, 50 mA cm⁻².

^h Current density, 150 mA cm⁻².

efficiency of formic acid was enhanced by the increase of CO₂ pressure. However, by observing the production of CO₂ reduction, only Au and Sn have the overpotential more positive than -1.4 V vs. Ag/AgCl, which is not that sufficient for CO₂ reduction when this technology needs to be enlarged in the future. Cu was classified in the fourth group (group [4]) [1]. The overpotential of CO₂ production is about -1.64 V vs. Ag/AgCl, not higher than Sn and Au, and the selectivity of the reduction products on Cu electrodes depends strongly on current density and CO₂ pressure. From what has been discussed above, it could not be ignored that insufficient catalyst activity, including the high overpotential and low current efficiency, especially under normal CO₂ pressure, is one of the biggest challenges in the investigation of CO₂ electroreduction.

10.2.2 INSUFFICIENT SELECTIVITY OF PRODUCTIONS

Selectivity is another key aspect to judge the properties of catalysts. The final goal of CO₂ electroreduction investigation is to find some kinds of catalysts which can catalyze the CO₂ reduction reaction to produce more target products under low energy depletion. Therefore, in most research of CO₂ reduction, the production selectivity is one of the significant points to be investigated when evaluating the properties of catalysts.

In general, formic acid (HCOOH) and methane are the most desired target products [2,3]. Further, according to the CO₂ reduction mechanism, HCOOH is a product which is much easier to obtain [4]. In Table 10.1, Sn, Cu, and Pb are the kinds of metals which could catalyze CO₂ reduction to get a relatively high HCOOH faradaic efficiency. However, in most previous work, the HCOOH selectivity of CO₂ electroreduction is not that satisfied, especially under normal temperature and pressure conditions. Table 10.2 shows the faradaic efficiency of formate on different Cu and Sn catalysts or metal electrodes. It could be seen that most of the formate faradaic efficiencies on these Cu- and Sn-based catalysts are lower than 50%. A higher faradaic efficiency can be obtained merely when the electrolysis potential is high enough or the CO₂ pressure high up to some extent [1,10,19]. In Kaneco's paper, the Cu foil could catalyze CO₂ reduction in methanol electrolyte and the HCOOH efficiency reaches about 85% when the CO₂ pressure is 10 atm [10]. In addition, Hara reported that the faradaic efficiency of HCOOH in 0.1 M KHCO₃ saturated with 30 atm CO₂ could reach high up to 92.35% [1]. However, this high-pressure condition for CO₂ catalyzed electroreduction decreases the durability of catalysts and increases the application costs. In this case, developing efficient catalysts with high selectivity for target products under normal conditions is one of the key aspects to reduce costs when the CO₂ electroreduction technique is applied to the reality.

10.2.3 POOR STABILITY OF THE ELECTRODE

Catalyst deactivation caused by the poisonous formation and deposition on the electrode surface is the foremost reason that results in the poor stability of catalysts in the CO₂ electroreduction [21–26]. The main causes of the limited stability on Cu electrode were summarized by Hori as (1) heavy metal impurities contained in electrolyte solution; (2) very small amount of organic substances contained in water; and (3)

TABLE 10.2
Faradaic Efficiency of Formate on Different Cu and Sn Catalysts or Electrode

Catalysts/ Electrode	Electrolyte	Electrolysis Potential	Faradaic Efficiency (Formate)	References
Cu foil	1.5 M KCl	-1.36 V vs. normalized hydrogen electrode (NHE)	31.6%	[5]
Cu foil	0.1 M KHCO ₃	-1.41 V vs. NHE	9.7%	[6]
Cu foil	LiClO ₄ (40 atm)	-4.1 V vs. Ag quasi- reference electrode (QRE)	46.7 %	[7]
Cu foil	0.08 M LiOH in methanol	-2.0 V vs. Ag/AgCl	~35%	[8]
Cu foil	0.08 M CsOH in methanol	-4.5 V vs. Ag/AgCl	~10%	[9]
Cu foil	0.5 M CsOH in methanol (10 atm)	-3.5 V vs. Ag QRE	~85%	[10]
Sn/Cu mesh	0.45 M KHCO ₃	3.9–5.9 V	36%	[11]
Cu ₂ O/carbon cloth	0.5 M NaOH	-1.70 V vs. SCE	–	[12]
Cu ₂ O/Zn	0.3 M KOH in methanol	-3.0 V vs. Ag QRE	~35%	[13]
CuO/Zn	0.3 M KOH in methanol	-3.0 V vs. Ag QRE	~35%	[13]
Cu ₂ O/Cu	0.5 M NaHCO ₃	-0.75 V vs. relative standard hydrogen electrode (RHE)	~33%	[14]
Sn	0.5 M KHCO ₃	-1.40 V vs. SCE	~65%	[15]
Sn granules	0.5 M KHCO ₃	-2.0 V vs. SCE	47%	[16]
Sn/GDE	0.35 M Na ₂ SO ₄	-1.80 V vs. SCE	57%	[17]
Sn powder/GDE	0.5 M NaHCO ₃	-1.6 V vs. NHE	~70%	[18]
Sn	0.5 M KHCO ₃ (high pressure)	-1.8 V vs. Ag/AgCl	99.2%	[19]
Sn	0.1 M KHCO ₃ (30 atm)	–	92.35	[1]
Sn/SnO _x	0.5 M NaHCO ₃	-0.70 V vs. RHE	~40%	[20]

some intermediate products formed during the CO₂ reduction [26]. Research shows that the Sn particles exhibited more stable operating times than the tin-coated Cu mesh cathode (formate efficiency dropped from 50% to 20% in minutes) [11]. In addition, the catalysis condition (such as catalysis potential or current density) is another factor that may affect the durability of catalysts. For instance, the pulse electrolysis method could alleviate the deactivation of the electrode [27]. The pretreatment on Cu electrode by applying a potential to change the electrode surface can significantly prolong the durability of the electrode. However, the detailed mechanism of CO₂ reduction on such changed electrode surface is still unclear and needs to be discussed.

When discussing about Sn catalysts, four main factors of the deactivation on pure Sn electrode are summarized as (1) cathodic degradation of the catalyst surface [28], (2) deposition of noncatalytic species from reaction intermediates in the reduction of the pollutant species [29], (3) organometallic complex formation on the electrode surface [30], and (4) deposition of noncatalytic metallic species from contaminants in the

electrolyte [31]. Agarwal conducted experiments on Sn and proprietary Sn alloy electrode using a flow-through reactor at a gas/solid/liquid interface. The Sn electrode performed better durability than Cu electrode. However, the reason for the color change appearing on the surface during the electrode degradation was still unclear [32].

Therefore, considering the enhancement of catalyst stability, the catalyst category, surface morphology, and the electrocatalysis condition are the factors that should be taken into account.

10.3 HIGH COST DURING THE CO₂ ELECTROREDUCTION PROCESS

It is well known that the conversion of CO₂ requires energy because of the molecule stability of CO₂. During the CO₂ electroreduction process, the electricity cost is a main input and the electric power is a main consumption, so the energy cost should be minimized in the development of CO₂ reduction. In addition, during the electroreduction process, green energy is required to prevent extra CO₂ emission, which will also increase the operation expense. Moreover, chemical costs such as the electrolyte and the waste disposal is another major spending that cannot be ignored.

10.3.1 ELECTRICAL ENERGY COSTS

One big challenge facing CO₂ electroreduction could be obviously seen as the low cathode reaction kinetic which is not favorable to production selectivity and current efficiency [33–36]. The geometric current density should be high enough to support an industrial electroreduction of CO₂ for two main causes. For one aspect, there is a current loss according to Faraday's law. For another aspect, in Oloman's research, the cost of capital reactors for CO₂ electroreduction is about US\$ 30 × 10³ m⁻² of the electrode area [33]. Therefore, the geometric current density should be at least 1 kA m⁻² with 50% current efficiency to meet the need of the capital costs. The total installed capital cost of Oloman's system is about 170 million US\$, the product value could reach \$ 1000 t⁻¹ HCOOH, and the output of HCOOH is about 350 t day⁻¹. When using renewable electricity, the energy cost is about \$ 0.01–0.10 kW h⁻¹, and there is a little return on investment. However, the electricity price for the renewable sources should be higher in practice. Therefore, the electricity cost is a huge input, and it is a big challenge that CO₂ electroreduction technology is facing.

10.3.2 CHEMICAL CONSUMPTIONS

Chemical consumption is another huge investment of CO₂ reduction apart from the electrical energy cost. Sridhar developed a systematic modeling of the entire value chain of CO₂ reduction and utilization [32]. In his investigation, Sridhar added supporting systems analysis for CO₂ conversion, including CO₂ capture and separation, of which the price is higher than previous analysis to some extent. As a result, the chemical consumptions are main parts that cannot be ignored. In Sridhar's work, his group compared two process scenarios: (1) using a consumable chemical to reduce the total energy costs and (2) using a portion of waste water instead of the consumable

TABLE 10.3
General Inputs for Scenarios 1 and 2, Not Specific to the Product or Electrochemical Reaction

Parameter ^a	Minimum	Most Likely	Maximum
Emissions source output (tpd)	0.8	1	1.2
Electricity price (\$ [kW h] ⁻¹)	0.06	0.07	0.08
CAPEX MEA plant (10%\$ [tpd] ⁻¹)	0.6	0.7	1.4
CAPEX diversion and delivery equipment (10%\$ [tpd] ⁻¹)	0.10	0.15	0.20
CAPEX product purification and storage (10%\$ [tpd] ⁻¹)	0.75	1.00	1.20
CO ₂ price (\$ t ⁻¹)	0	0	0
NaOH price (\$ t ⁻¹)	150	165	180
NaCl price (\$ t ⁻¹)	75	101	130
NaCl price (\$ t ⁻¹)	72	95	140
O ₂ price (\$ t ⁻¹)	50	150	300
HCl price (\$ t ⁻¹)	72	150	300
H ₂ SO ₄ price (\$ t ⁻¹)	72	150	300
H ₂ price (\$ t ⁻¹)	2300	2700	5000
H ₂ O price (\$ t ⁻¹)	1	2	3
Nominal discount factor	0.03	0.04	0.05
Financing interest rate	0.04	0.05	0.06
Electrode lifetime (year)	0.4	0.5	0.8
Plant lifetime (year)	25		

Source: Agarwal, A. S., Zhai, Y., Hill, D., and Sridhar, N.: The electrochemical reduction of carbon dioxide to formate/formic acid: Engineering and economic feasibility. *ChemSusChem*. 2011. 4(9). 1301–1310. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

^a tpd: ton per day, \$ (kWh)⁻¹: US\$ per kWh of electricity, \$ t⁻¹: US\$ per ton.

chemicals, which increases the energy consumption. The detailed inputs of these two scenarios are listed in Table 10.3 [32]. Sridhar concluded that both the scenarios are profitable after 25 years of operation, which is comparatively long.

Thus, we need to find a way to reduce the inputs of CO₂ electroreduction to shrink the process time to gain economic profits to realize the practical utilization of CO₂ electroreduction in three main parts: (1) to reduce the electrical energy consumption, (2) to improve the stability of catalysts, and (3) to study the pathways of CO₂ reduction [32].

10.4 HIGH ENERGY CONSUMPTION AND LIMITED AVAILABILITY OF GREEN ELECTRICITY SOURCES

The energy consumption during CO₂ electroreduction process is high because of the insufficient catalyzed activity of catalysts or electrodes. Meanwhile, the energy used in CO₂ conversion should be nonfossil energy or CO₂-free electricity. However, the

green energy resources are not that popular as the fossil fuels, so that the utilization of renewable electricity is limited and the price is not economical.

10.4.1 HIGH ENERGY CONSUMPTION

As discussed above, the energy consumption of CO₂ electroreduction is high mainly resulting from the low faradaic efficiency of catalyzed reduction process. Therefore, the electricity cost is a major factor to reduce the production cost of formic acid during the electrolysis of CO₂. Table 10.4 lists the cost of different energy sources [37]. It could be seen that the construction costs of the fossil fuels are comparably cheap, and the electricity generation cost of coal is not high. But the utilization of fossil fuels may lead to a new round of extra CO₂ emission, which is in contradiction with our intention. Nuclear energy seems to be more competitive considering both the construction and production costs. Other sustainable energy such as wind and solar energy may cost higher during the generation process. The production cost of wind energy is expected to decline in the future. The market price of HCOOH is about \$ 1200 t⁻¹. Therefore, if the wind energy price decreases to \$ 0.04 kW h⁻¹, the maximum energy consumption in CO₂ process should be high as about 30,000 kW h t⁻¹ when we ignore the other capital investments [37]. However, the electricity consumption is higher than the ideal value and we cannot neglect the installed fees and chemical costs. So even if the wind energy price goes down, the HCOOH production cost is still much higher than the commercial price of formic acid sold in market. This means that the electroreduction of CO₂ technology is still immature and cannot be realized for commercial utilization at the present stage.

10.4.2 LIMITED GREEN ELECTRICITY SOURCES

Green electricity technologies include solar thermal, wind energy, biomass, geothermal, tidal, and nuclear energy [38,39]. For the most competitive wind energy, electricity is the dispersed source and needs to be transmitted, stored, and regulated before utilization. For biomass and solar energy, they need more land for the system

TABLE 10.4
Construction Costs and Electricity Generation Costs of Different Energy Sources

	Construction Cost (US\$/kWe)	Electricity Generation Costs (US¢/kWh)
Coal	1000–1500	2.5–5
Natural gas	400–800	3.7–6
Nuclear	1000–2000	2.1–3.1
Wind	1000–2000	3.5–9.5 (mostly under 6.0)
Solar	3000–10,000	15–40

Source: Reprinted with permission from Olah, G. A., Prakash, G. S., and Goeppert, A. Anthropogenic chemical carbon cycle for a sustainable future. *Journal of the American Chemical Society* 2011; 133(33): 12881–12898. Copyright 2011 American Chemical Society.

and plantations so that the power densities of these two green energy sources are low [38,40]. Besides, the existing grids could not manage the unstable loads of such renewable energy, the electricity grids should build advanced system with loads of conditioner to adapt to the new energy resources, which is another major input for the green electricity. Nuclear energy, which is most commonly used, is produced by ^{235}U . There are about 500 plants that produce nuclear energy in the world [38,41]. However, waste disposal and nuclear leakage are dangerous, and they are big hazards in nuclear energy operation.

Apart from green energy sources, many other factors will also affect the development of green electricity, such as the public policies and regulations, the technology levels, and the consumer of green energy product. For the government policies and regulations, if the government supports the renewable energy and makes some policies to encourage the green energy utilization and provides some bonus for those who uses the green electricity, the awareness of renewable power would be increased among people. The improvement of technology level is important for the decline of green energy costs because the promotion of technology could have a positive effect on the storage and transmission of green electricity and makes it less expensive and more convenient.

10.5 PROPOSED RESEARCH DIRECTIONS

To develop the CO_2 electroreduction technology, the optimization of catalysts and reaction system is the main direction. We are aiming to investigate catalysts with high activity, selectivity, and stability of CO_2 electroreduction, and at the same time, we need to optimize the working electrode and the electrolyte.

10.5.1 OPTIMIZING THE ACTIVITY, SELECTIVITY, AND STABILITY OF CATALYSTS

The catalyst property is the key factor in CO_2 electroreduction technology. Future research should be focused on the three main aspects of catalyst property: the catalyzed activity, production selectivity, and catalyst stability. To realize the commercial application of CO_2 electroreduction, the catalysts at the present stage do not meet the need of the utilization, and inventions are desirable. Keeping this in mind, developing new catalysts with high activity, selectivity, and stability is a significant target. Two principles should be mentioned: (1) the catalysts should have high production faradaic efficiency and low hydrogen evolution reaction, and (2) the catalysts should have high active surface area which may provide more active sites. With respect to these principles, the composite catalysts synthesized by materials with different advantages and the nanoscale catalysts with special three-dimensional structures could be developed and investigated in the future.

Moreover, CO_2 electroreduction is a complicated process, and the theory of the reaction is still not clear. For a target research about CO_2 reduction reaction, better understanding of this reaction process could provide us more detailed information about the decided step of reaction and lead us to do more targeting and effective research to improve catalysts.

10.5.2 SCALING UP THE REACTORS AND REACTION SYSTEMS

To realize the commercial application of CO₂ electroreduction, a continuous system on a large scale should be designed and optimized. The system partially includes the electrode design and the electrolyte choice. For electrode, the gas diffusion electrodes (GDEs) used in full cells are relatively good choice which could improve the mass transfer process. Some researchers used GDE for CO₂ reduction which is promising but also with several defects, including lacking electrode stability and the deficiency of the potential for electrochemical reactions in the pores of GDE [33,42,43]. In the future, different supporting materials such as graphene, carbon nanotubes, and other materials which could improve the conductivity and electrode surface area need to be investigated. For the electrolyte, the most commonly used type in the current state is KHCO₃ solution; however, some waste waters from factories could be used as the electrolyte of CO₂ electroreduction. If this comes into existence, the chemical costs of CO₂ electroreduction could be greatly reduced and the waste disposal of some plants could be solved at the same time.

In short, research on the electrochemical reduction of CO₂ powered by renewable electricity is justified by robust economic and environmental reasons. It shows potential for implementation on a large scale, with the predicted feasibility of the products decreasing according to the series CO \approx HCOOH $>$ CH₃OH \gg C₂H₄ $>$ CH [44]. Although these reactions require higher energy exchanges provided by strong reducing reagents (H₂, metals) and/or electricity, auxiliary processes such as CO₂ capture or distillation may be equally or more limiting than the energy consumption by electrolyzers currently [32]. From the environment point of view, using emission-free energy sources is the only sensible approach to CO₂ recycling. However, the main limiting phenomena affecting CO₂ electrolyzers in terms of durability, current efficiency, energy efficiency, faradaic efficiency, and overvoltage must be achieved, for example, to reach a similar energy storage capability as the electrochemical production of H₂ from water splitting which has been studied for decades and commercially available up to the megawatt range [45]. It is interesting to note that the conversion of CO₂ to CO and HCOOH has led the race toward practical use, although both still exhibit major performance gaps. Present energy efficiencies are low, mainly due to high overvoltages, and durability is not yet a developed research area. Besides the development of more efficient electrocatalysts, research advances on the fronts of electrode and electrolyzer design, coupled with the optimization of methods for the preparation of electrodes, are expected to push forward the electrochemical reduction of CO₂ on its way to viability.

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