
Electrochemical Conversion of Carbon Dioxide

-- Approaches and Challenges

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Abstract

By utilizing the renewable energy sources or waste heat generated in the fossil fuels' combustion process, electrochemical reduction of CO₂ provides a sustainable carbon-neutral pathway to recycle CO₂ from the energy system and a convenient means of storing electrical energy of high current density in chemical form. Different from the traditional review papers, this article tried to review progress related to electrocatalytic study of CO₂ in the past few years, with an emphasis on the reaction systems and approaches, and compared the liquid phase approach and gas-phase approach toward electrochemical reduction of CO₂. Finally, some challenges to further progress are also proposed and discussed.

Keywords

CO₂ reduction; Electrocatalysis; Gas-phase approach; Reaction mechanism.

1. Introduction

The increase of carbon dioxide (CO₂) in the atmosphere due to the overuse of fossil fuels, is claimed to be one of the major contributors to the greenhouse effect, which will lead to serious environmental issues such as global warming and climate change. ^[1-3] As shown by studies of Intergovernmental Panel on Climate Change, global CO₂ emissions in 2050 would have to be reduced by 50-80 % of the emission levels in the year 2000 in order to limit the global temperature and stabilize the atmospheric concentration of CO₂.^[4] Therefore, to decrease the emission of CO₂ has become one of the most urgent issues in environmental protection. Currently, there are many strategies to decrease CO₂, which can be divided into two categories: (1) Carbon capture and sequestration, such as geological burial and storage, i.e. to bury the captured CO₂ deeply underground or deposit in the sea after being dissolved, while with high energy input and consumption; (2) The chemical conversion and utilization, i.e., to convert CO₂ into useful chemicals, such as industrial chemicals (architecture materials, pharmaceutical products, etc.) and liquid fuels (HCOOH, CH₃OH, CH₃COOH, etc.). From an energy point of view, the chemical conversion of CO₂ is more favorable since it can turn waste to useful chemicals while with less energy input and consumption. ^[5] As shown in Fig. 1, currently, photosynthesis, hydrogenation, photocatalytic and electrocatalytic CO₂ conversion, although having different mechanisms, are the four most effective methods to obtain chemicals from carbon dioxide. There have been quite some research on CO₂ conversion employing the above mentioned different strategies, and different chemical products have been obtained. Although each method has its own economic and practical sense, in this study, we will focus on the CO₂ conversion and utilization by electrochemical pathway. The electrochemical method has several advantages including:

- (1) The electrochemical conversion provides a renewable electricity storage method, which can be driven by the renewable energy source including solar, wind, hydroelectric, geothermal, tidal, thermoelectric processes, etc. It converts the electrical energy to chemical energy by producing fuels from CO₂ and later the stored energy can be released by oxidation of the fuels.
- (2) The electrochemical conversion can be performed at room temperature and ambient pressure, and

the electrolyte can be recycled, all of which minimizes the energy and chemical consumption.

- (3) The electrochemical reaction system is modular and has a compact design, which makes the scale-up production feasible and simple.

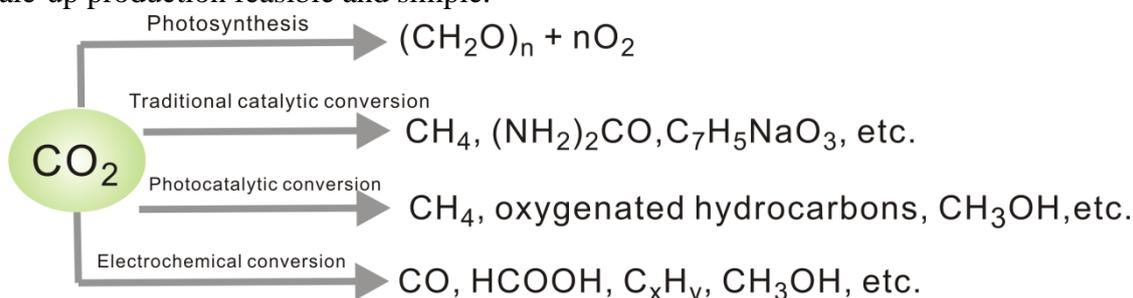


Fig. 1 Reaction pathways of CO₂ conversion to chemicals

Some excellent review papers of CO₂ conversion are already available. Jitaru reviewed the most classical methods of direct electrochemical reduction of carbon dioxide in the presence of redox mediator systems in aqueous and non-aqueous medium.^[6] J. Lee and W. Li gave two separate reviews on the studies of electrochemical CO₂ reduction to small organic molecules on metal catalysts and especially focused on the gas-phase CO₂ reduction techniques.^[7, 8] Kenis et al. analyzed the prospects of CO₂ utilization by direct heterogeneous electrochemical reduction and discussed the challenges for advancing CO₂ reduction nowadays.^[9] Lu et al. reviewed the progress related to electrochemical CO₂ reduction in the areas including electrocatalyst, reaction mechanism and process engineering.^[10] In a recent review, Gao et al. highlighted the new progress and trends in advancing the electrochemical reduction of CO₂ by nanostructured heterogeneous catalysts in recent years.^[11]

This review aims to summarize the studies of CO₂ conversion through electrochemical methods in recent years. Some basic concepts and thermodynamics of CO₂ conversion will be summarized and introduced firstly, then the research of electrochemical conversion of CO₂ by traditional liquid-phase approach and the recent gas-phase approach will be summarized and compared, the challenges to further progress will also be discussed.

2. Thermodynamic Considerations and Basic Concepts

2.1 Thermodynamic Considerations

Carbon dioxide is a kind of extremely stable linear molecule in which the oxygen atoms are weak Lewis bases and the carbon is electrophilic, reactions of CO₂ are dominated by nucleophilic attacks at the carbon, resulting in bending of the O-C-O angle to about 120°.^[12] The essential part of CO₂ conversion is to open the C=O bond, as shown in equation 1, the single electron transfer reaction of CO₂ to CO₂^{•-} is -1.9V versus the normal hydrogen electrode^[13], which has been well recognized as the first step to activate CO₂ for subsequent reduction steps and also the rate determining step (RDS) for CO₂ reduction.^[14] Due to the big geometrical difference of the linear, neutral carbon dioxide and the radical anion CO₂^{•-}, the barrier to outer-sphere electron transfer for the couple is very large, which results a significant overvoltage for the direct electroreduction. The electroreduction of CO₂ needs substantial overpotentials due to the kinetic barrier and the large difference in the HOMO and LUMO energies.





(*at pH 7 in aqueous solution VS NHE, 25 °C, 1 atm for the gases and 1 M for the other solutes^[15])

The thermodynamic barriers can be reduced by protonating the reduction product. Eqns. (2) to (6) list the multi-electron reactions of CO₂ with different numbers of protons in aqueous solution. The equilibrium potentials for CO₂ reduction to different products are also shown, which are much lower than that of single-electron transfer reaction. Various products of CO₂ reduction (CO, HCOOH, HCHO, CH₃OH and CH₄) can be obtained at different equilibrium potentials. Therefore, from the thermodynamic point of view, the multi-electron reduction is more favorable than the single-electron reduction, and the major reaction products are dependent of the electrons participating in the reaction.^[16] It needs to point out that, governed by the Nernst equation, the theoretical equilibrium potentials decrease with pH increasing.^[17] Different products can be obtained with different thermodynamic energies, as some selected major reaction products with their associated free energies and standard potentials shown in Fig. 2.^[18]

However, because of the close proximity of the hydrogen potential (equation 7), reduction of H⁺/H₂O to H₂ (Hydrogen evolution reaction (HER)) may also occur as a concurrent reaction depending on the system. Since HER is prevalent in acidic solution while CO₂ does not exist in basic solution, most CO₂ reduction study was conducted in neutral or close neutral electrolyte solutions. Actually, the suppression of hydrogen formation is very important to save the energy for the reduction of CO₂.

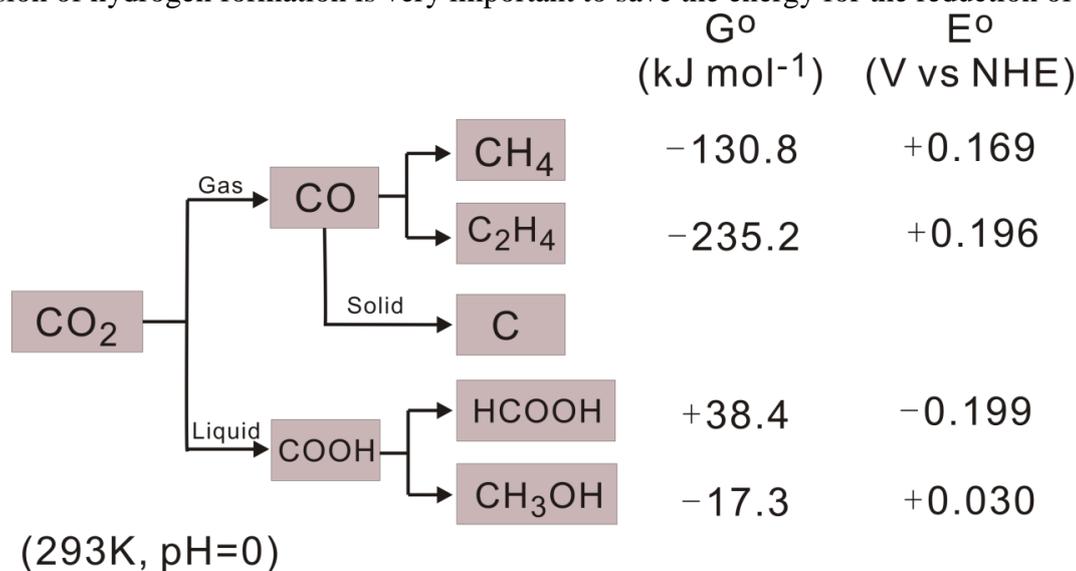


Fig. 2 Selected major reaction products and intermediates for CO₂ reduction reactions with their associated free energies and standard potential [8]

2.2 Basic Concepts

Overpotential

As the potential difference between a half-reaction's thermodynamically determined reduction potential and the potential at which the redox event is experimentally observed,^[19] overpotential is one critical parameter in the process of CO₂ reduction. In electrochemistry, this overpotential appears because of a combination of electrolyte diffusion rate limitation and the intrinsic activation barrier of transferring electrons from an electrode to the electrolyte. As shown in Fig. 3, there is a high overpotential between the intermediate radical anion CO₂⁻ and the product, while catalysts can lower the energy of the intermediate, reduce the overpotential and thus facilitate the conversion and improve the energetic efficiency.

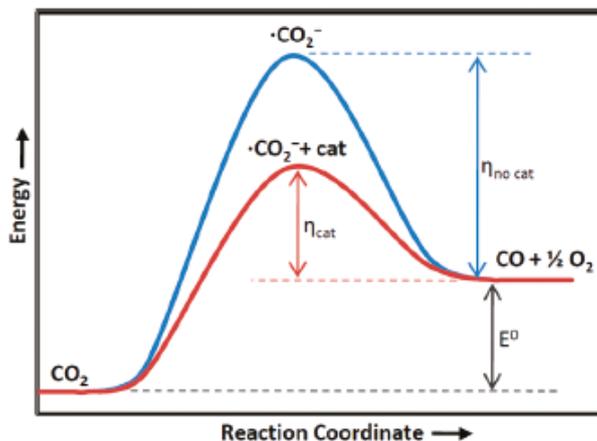


Fig. 3 Qualitative reaction scheme for CO₂ conversion. [9] where, E₀: standard potential, η: overpotential.

Faradaic efficiency and Energetic efficiency

Faradaic efficiency, or current efficiency, given by equation (8), describes the efficiency with which charge (electrons) are transferred in an electrochemical reaction. Faradaic efficiency of a cell design is usually measured through bulk electrolysis where a known quantity of reagent is stoichiometrically converted to product, then compared to the observed quantity of product measured through another analytical method.

Energetic efficiency, which is corresponding to Faradaic efficiency, demonstrates the efficiency of the ratio between the useful output of an energy conversion and the input, is given by equation.

$$\epsilon_{\text{Faradaic}} = \frac{n \cdot F \cdot n}{Q} \quad (8)$$

$$\epsilon_{\text{energetic}} = \frac{E^0}{E^0 + \eta} \times \epsilon_{\text{Faradaic}} \quad (9)$$

where, $\epsilon_{\text{Faradaic}}$ stands for the Faradaic efficiency and $\epsilon_{\text{energetic}}$ is the energetic efficiency, n = number of electrons transferred in the reaction, F = Faraday's constant, n = number of moles of product, Q = charge passed, E^0 = standard (equilibrium) potential, η = overpotential.

Energy consumption

As an important metric of the reaction process, the specific energy consumption, E (MWh⁻¹), as given by Equation (10) [20], is determined by the number of electrons involved in reducing 1 molecule of CO₂ to products, cell voltage and Faradaic efficiency.

$$E = \frac{V(1+\alpha)n}{1.641\epsilon_{\text{Faradaic}}} \quad (10)$$

Here, V is the cell voltage, α is a factor representing the auxiliary energy required for the process, n is the number of electrons transferred in the reaction, and $\epsilon_{\text{Faradaic}}$ is the Faradaic efficiency.

3. Approaches to the electrochemical reduction of CO₂

3.1 The liquid-phase approach

During the last several decades there has been extensive work on electrochemical reduction of CO₂ in aqueous reaction system, and various useful products have been obtained with high selectivity, low cost and heterogeneous catalysts. [16, 21-25] Metal electrodes as cathodes have been the focus of extensive CO₂ electrochemical study [23, 26-31]. It was found that the reduction products are closely

related with the cathodic metal catalysts. Azuma et al. summarized the relations between metal catalysts and the major products:

- The *sp* metals (e.g. Zn, Cd, Hg, In, Tl, Sn, Pb and Bi), which have high hydrogen overvoltages. They mainly produce formate in aqueous solutions.
- The *d* metals (e.g. Pd, Pt, Ag and Au), which have medium hydrogen overvoltages. They mainly generate CO and hydrocarbons.
- Metals including Ti, Mo, Rh, Fe and Ni, which have low hydrogen overvoltages. They only give H₂ (no CO₂ reduction occurs).
- Cu. Cu is unique for CO₂ reduction. It is able to react with CO further to more reduced species on Cu, and it behaves sensitive to pressure.

Kohijiro et al. studied the reduction efficiency and selection of CO₂ electrochemical reduction on a series of metal electrodes under 3 MPa, showing that the current efficiency is above 80% on Rh, Pd, Cu, Ag, Zn, In, Sn, Bi and Pb etc. while much lower on other metal electrodes.^[16] Due to the simple preparation, metal electrodes have been used very broadly, while with low selectivity, stability and current efficiency. The employment of gas diffusion electrodes^[32] can greatly improve CO₂ transport and thus facilitate CO₂ reduction.^[8, 16, 33, 34] On the other hand, the employment of GDE in CO₂ reduction can also help weaken the H₂ evolution---the competing reaction of CO₂ reduction.^[35] Since the lifetime of GDE is not very long, the use of modified GDE electrodes is one effective path to increase the selectivity and efficiency of CO₂ reduction, and it can also help control the distribution of reduction products. Hori et al. prepared modified membrane electrodes by loading Ag onto ion exchange membrane and studied electrochemical CO₂ reduction, with a result of partial current density up to 600 A/m².^[36]

The traditional liquid-phase approach of CO₂ electrochemical reduction has also had a detailed study on catalysts and other influencing factors. As above mentioned, the appropriate catalyst can reduce the activation energy so to increase the reaction product selectivity and current efficiency by reducing the overpotential. The qualitative reaction scheme in Fig. 3 shows the function of catalysts in activating CO₂ molecules, both catalysts and electrolytes can act as co-catalysts to reduce the energy needed by the intermediates so to increase the conversion energy efficiency.^[9] The traditional catalyst for electrochemical CO₂ reduction refers to metal compound molecules with Nitrogen heterocyclic ligands. It was found that the ligands in metal-polypyridine such as 2,2'-bipyridine, and 1,10-Phenanthroline monohydrate can stabilize metals at oxidation states, they can also store electrons by π^* orbitals at about -0.7V ~-1.7V.^[37, 38] Due to the strong π - π interaction in conjugated system, metal complexes such as phthalocyanines showed respectable catalytic effect to CO₂ electrochemical reduction.^[39, 40] Bocarsly group has developed an interesting system for electrocatalytic CO₂ reduction using pyridinium as a catalyst.^[17, 41, 42] In the study they found that CO₂ could be reduced to methanol on Pd electrode, to HCOOH on Pt electrode, while no CO₂ reduction was observed with pH > 7, which confirms that pyridinium was the active catalyst. In recent years the novel catalysts based on carbon nanotubes have attracted researchers' great attention. Qu et al. found that the nanoparticle and nanotube catalysts modified by RuO₂/TiO₂ showed good catalytic ability to CO₂ reduction to CH₄, and the Faradaic efficiency can reach up to 60.5%.^[43] Employing carbon nanotube catalyst loaded with Fe and Pt, Centi group obtained long-chain hydrocarbon products from CO₂ reduction for the first time.^[44]

Product	# e ⁻	E	Product	# e ⁻	E
Formate 	2	-0.02	Acetaldehyde 	10	0.05
Carbon monoxide 	2	-0.10	Ethanol 	12	0.09
Methanol 	6	0.03	Ethylene 	12	0.08
Glyoxal 	6	-0.16	Hydroxyacetone 	14	0.46
Methane 	8	0.17	Acetone 	16	-0.14
Acetate 	8	-0.26	Allyl alcohol 	16	0.11
Glycolaldehyde 	8	-0.03	Propionaldehyde 	16	0.14
Ethylene glycol 	10	0.20	1-Propanol 	18	0.21

Fig. 4 Products of CO₂ reduction along with the number of electrons needed to produce each one and its standard reduction potential at pH 6.8. [45]

Cu is perhaps the most studied metal electrodes for electrochemical reduction of CO₂ so far, which behaves differently from the other metals although with d orbitals. It mainly generates hydrocarbons and alcohols under ambient pressure, while gives CO and HCOOH under high pressure. As a milestone discovery, Hori et al. reported that the direct reduction of CO₂ on a copper foil electrode would lead to hydrocarbons (mainly methane and ethylene) with reasonable current density (5-10 mA/cm²) and current efficiency up to 69 % at 0 °C in aqueous solution. [46] Later Cu-based electrocatalysts including Cu single crystals, Cu oxide and alloy electrodes have been extensively studied. [47-50] Gattrel et al. gave a review on the electrochemical reduction of CO₂ to hydrocarbons at Cu electrodes in aqueous electrolyte, in which the reaction mechanism and the influences of various reaction conditions were discussed. [22] Kuhl et al. studied the electrochemical reduction of CO₂ on a metallic Cu surface employing unprecedented sensitive gas chromatography and nuclear magnetic resonance techniques for the identification and quantification of gas and liquid products, and observed a total of 16 different CO₂ reduction products. [45] Figure 4 shows the total sixteen products of CO₂ reduction on Cu electrode along with structure, number electrons and reduction potential at pH 6.8 vs. RHE.

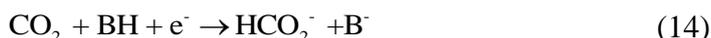
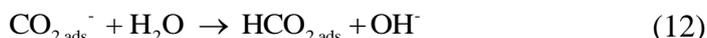
There are several trends that can be obtained from the previous studies of electrochemical reduction of CO₂ by liquid-phase approach:

- Cu and Cu-based electrodes are still the most studied metal electrodes in liquid-phase electrochemical CO₂ reduction, other metal electrodes that have been studied including Pb, Sn, Ag, Pt, Au;
- More and more new approaches of electrochemical study such as continuous flow cell, solid oxide fuel cell and biofuel cell have been tried;
- To decrease high overpotentials have become the main research challenge, other research topics include: to increase the product selectivity, to study the reaction mechanism, and to inhibit H evolution.

7.1.1 Electrochemical conversion in aqueous system

Basic reaction mechanism

As the most economical proton source, the aqueous solution has been the most studied system for electrochemical reduction of CO₂. It is generally believed that the mechanism of the electrochemical reduction of CO₂ in aqueous solution follows the reactions shown in eqns. 11-14.



(where, BH is the proton donor.)

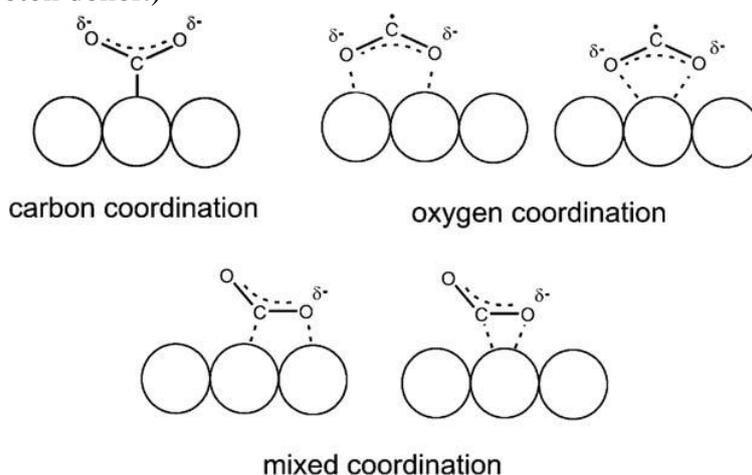


Fig. 5 Possible structure for adsorbed CO₂^{δ-} on metals [22]

It is widely accepted that the formation of CO₂^{δ-} is the rate-determining step at medium and high overpotential regions. CO₂ can be firstly chemisorbed as a bent CO₂^{δ-} molecule and its geometry is unclear, as the possible structures for adsorbed CO₂^{δ-} shown in Fig. 5. Since CO₂ is a kind of “amphoteric” molecule possessing both acid and basic properties, the adsorption and stabilization of CO₂^{δ-} are dominantly governed by the electrode metals and promoted by the surface defects, alkali metal promoted surfaces. The electrode metals can interact with carbon or oxygen or both in CO₂ to form carbon coordination, oxygen coordination or mixed coordination adsorption mode. Jordan and Smith firstly proposed that the formation of CO₂^{δ-} anion radical by one electron-transfer to CO₂ is the initial step for subsequent reactions of CO₂ reduction (eqn.11).^[51] Later Pacansky et al. studied *scf ab initio* molecular orbital energies and atomic population analysis of CO₂^{δ-} at the minimum energy geometry and suggests that CO₂^{δ-} is ready to react as a nucleophilic reactant at the carbon atom.^[52] The standard potential of CO₂^{δ-} formation is -1.90 V vs. NHE in aqueous media.^[53-55] The CO₂^{δ-} anions can be present freely in both aqueous and non-aqueous electrolyte solutions, which has been confirmed by ultraviolet spectroscopic study.^[56]

A schematic overview of the reaction pathways is shown in Fig. 6. After the formation of CO₂^{δ-}, there are two pathways, one leading to formate and the other to CO and hydrocarbon products. Both CO₂ reduction and hydrogen evolution occur on unblocked areas of the electrode surface, with CO being the primary cause of surface inhibition. The adsorbed hydrogen is also indicated as the possible involvement, that is, the hydrogen evolution will happen if the reaction pathways involve hydrogenation. The main product of electrochemical reduction of CO₂ on metals of high hydrogen overvoltage is HCOOH (Fig. 6B), on metals of medium hydrogen overvoltages is CO (Fig. 6C), while there are only H₂ produced on metal electrodes of low hydrogen overvoltages (Fig. 6D).

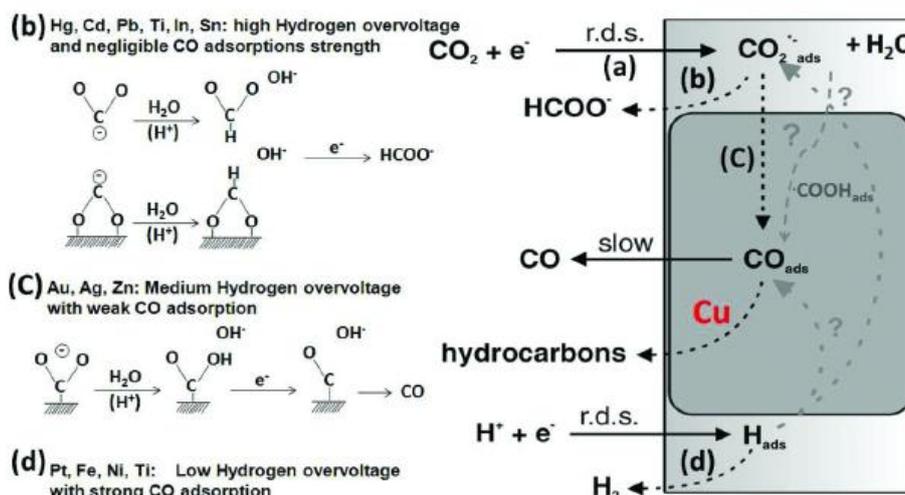
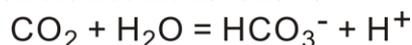


Fig. 6 The main reaction pathways at the electrode surface, with adsorbed CO blocking the majority of the surface and hydrocarbon products being formed by the further reduction of adsorbed CO [7, 22]

Active species during CO₂ reduction

When carbon dioxide dissolves in aqueous solution, both carbonate and bicarbonate ions are formed, and the reaction equations of carbon dioxide are as follows:



There is a debate whether HCO_3^- or CO_3^{2-} can be electrochemically reduced for a long time. Teeter et al. studied CO₂ reduction on Hg electrode and found that the polarographic wave height depends on the CO₂ concentration in the solution.^[57] The result reveals that the electroactive species of CO₂ reduction is the CO₂ molecule while not HCO_3^- or CO_3^{2-} . It was later argued that HCO_3^- can be reduced at different metal electrodes^[58, 59] but the current density was very weak ($<0.1 \text{ mA/cm}^2$),^[60] thus it was concluded that CO₂ molecules rather than HCO_3^- are the active species and HCO_3^- is decomposed to CO₂ primarily near the electrode.^[61] However, since the reduction potential of CO₂ is much more negative than the values estimated from the thermodynamic data, as a result, CO₂⁻ anion radical, is proposed to be an intermediate species since it requires highly negative potential for formation. Jordan and Smith firstly proposed that the formation of CO₂⁻ anion radical occurs by one electron transfer to CO₂ molecule as an initial step in CO₂ reduction process,^[51] which was later verified by Hori et al.^[62]

Hydrogen evolution

However, due to water's presence, the hydrogen evolution reaction easily takes place by cathodic polarization, which is strongly competing with CO₂ reduction. Therefore, the inhibition of H evolution is very important for the reduction of CO₂, so as to save the energy and to increase the product selectivity. There are many studies carried out in aqueous solutions with metal electrodes of high overvoltages (such as Hg and Pb) in order to suppress the HER during the electrochemical CO₂ reduction process. Hori et al. studied the electrochemical reduction of CO₂ on Hg electrode and found that the partial current of HCOO⁻ formation is not pH dependable, but the HER is proportional to proton activity.^[62]

It needs to point out that the aqueous system suffers several problems including:

- (1) sluggish reaction kinetics;
- (2) low selectivity, CO₂ reduction and Hydrogen evolution are two competitive reactions;
- (3) formation of various by-products;
- (4) low solubility of CO₂ in aqueous electrolyte;

(5) deactivation of the electrode catalysts after a short period of operation.

7. 1. 2 Electrochemical conversion in non-aqueous system

Compared with the reduction in aqueous solution, there are a lot of advantages in non-aqueous medium. [63] Firstly, the solubility of CO₂ in organic solvents is much higher than that in water, for example, the solubility of CO₂ in methanol is approximately five times compared to that in water at ambient temperature and 8 to 15 times at temperatures less than 273 K. [64] Secondly, due to the absence of water or presence of only a little amount of water, the hydrogen evolution reaction competing with CO₂ reduction reaction can be suppressed significantly. Different non-aqueous solutions are studied for CO₂ reduction, such as propylene carbonate (PC), dimethyl sulfoxide (DMSO), DMF, acetonitrile (AN), and Methanol. Carbon monoxide, oxalic acid and formic acid were found to be the main reduction products in PC and DMSO.

Basic reaction mechanism

Tyssee et al. studied CO₂ reduction at an Hg electrode in DMF and showed that oxalic acid formed. [65] Sav éant and his coworkers found that the electrochemical CO₂ reduction at Pb and Hg in H₂O-DMF solutions give CO, HCOOH and oxalic acid, [19] with the assumption that intermediate CO₂⁻ is not adsorbed on Pb or Hg and no specific interaction exists between intermediates or products and the electrodes. [47] With Au and Hg as electrodes, Haynes and Sawyer studied CO₂ reduction in DMSO and discovered that CO and carbonate ions are the main products on both electrodes. [59] Some formate and bicarbonate ions were formed if water is added. Ito et al. studied CO₂ electroreduction with tetraethylammonium perchlorate (TEAP) as the electrolyte with different small amount of water content. [66] They employed various electrode metals for constant potential electrolysis of CO₂ reduction at -2.8 V vs. Ag/AgCl in PC. They found that in aqueous solution, In, Pb and Hg mainly yield formic acid; while in non-aqueous solution, Pb, Hg and Tl give oxalic acid and In, Zn, Au and Sn electrodes are preferable for CO generation. The reaction mechanism was demonstrated in Fig. 7.

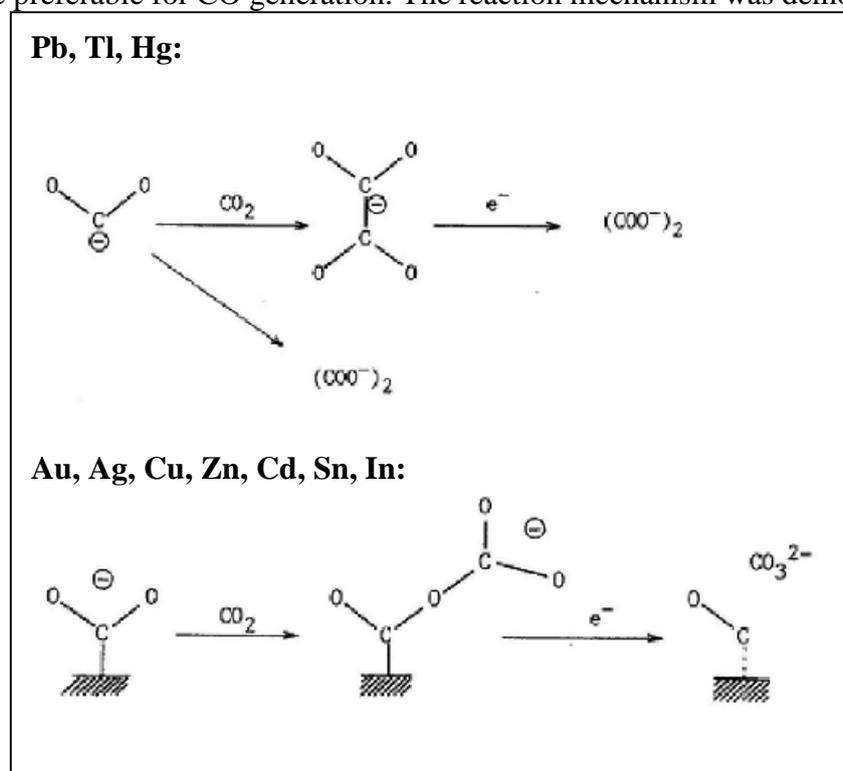


Fig. 7 The main reaction pathways at metal electrodes in non-aqueous solution[67]

Methanol based electrolytes

Being inexpensive, having low toxicity, and can be produced at a large industrial scale, methanol is an attractive solvent for non-aqueous electrolyte solutions. [66] As a non-aqueous electrolyte solution, it also offers a relatively easy-to-study mechanism since it has many similarities to water, therefore it

is normally classified as a protic solvent. The product selectivity of CO₂ reduction depends on the electrode metal in methanol based electrolytes as well. Formate is favorably produced instead of oxalate in methanol based electrolytes. However, if some other additives are added into methanol electrolyte, there will be formation of other products. There are many CO₂ reduction studies at metal electrodes in methanol-based electrolytes. Ohta et al. demonstrated that CO₂ could be reduced to CO, CH₄, C₂H₆ etc. in methanol based supporting electrolytes with benzalkonium chloride as the ionophore on Ti, Fe, Co, Ni, Pt, Ag, Au, Zn and Sn metals electrode.^[63] Ag, Au, Zn and Sn cathodes allows for the best Faradaic yields of CO, the maximum amount of which was formed on the Ag electrode. CH₄ were produced on all of the nine tested electrodes with current yields from 0.2 to 3.0 %, C₂H₆ and C₂H₄ were obtained on Ni electrodes with low Faradaic efficiency of 0.5 and 0.3 % respectively. Kaneco et al. studied CO₂ electrochemical study in a KOH/methanol based electrolyte on metal electrodes including In^[68], Ag^[64], Pb^[69] and Cu^[70], respectively, demonstrating that on In: a high Faradaic efficiency of 76.0 % of formic acid could be obtained and only 0.2% Faradaic efficiency of Hydrogen evolution was observed; Ag: the formation efficiency of CO increased at relatively negative potential as temperature decreased, whereas hydrogen formation decreased; Pb: the major products of electrochemical reduction of CO₂ were formic acid, CO and methane, the formation of formic acid from CO₂ predominated in a wide potential range; Cu: the main products obtained were methane, ethylene, ethane, carbon monoxide and formic acid, and the product selectivity of the electrochemical reduction of CO₂ in methanol was greatly affected by the anionic species. All the study demonstrated that Hydrogen evolution was significantly inhibited in the methanol based solutions.

Ammonium salts and aniline

Ammonium salts were utilized as a nucleophilic attack reagent in CO₂ conversion in order to facilitate the reduction process. Fujishima et al. employed tetraalkyl ammonium salts in methanol-CO₂ mixture, yielding major products of HCOCH₃ and CO.^[71, 72] It was assumed that CO₂ first reduced to HCOOH and later transferred to HCOCH₃. They also reported that CH₄ and C₂H₄ were the major products instead of CO and HCOCH₃ in TEAP solution.^[73] In addition to metal electrodes, polyaniline (PAn) and polypyrrole were also investigated as electrode materials. Koeleli et al. found that CO₂ can be electrochemically reduced at a very low overpotential of -0.4 V (SCE) on PAn electrode in the methanol + LiClO₄ electrolyte system, with the main products of formaldehyde, formic acid and acetic acid with reasonable efficiency.^[74]

Ionic liquids

Due to the unique physical and chemical properties, electrochemical fixation and reduction of CO₂ in ionic liquids has drawn certain attention in recent years.^[75-77] Ionic liquids are organic salts that exist in the liquid state at near room temperature, which are considered as green reaction media, having properties including high thermal and chemical stability, high viscosity, extremely low vapor pressure, good solvating abilities, high intrinsic conductivity and wide electrochemical potential windows.^[77-80] Functionalized ionic liquids are specially designed based on the acidity of CO₂, through which CO₂ can not only be fixed but also can be converted from industry waste gas to useful chemicals directly.^[75, 81] Feroci abd Inesi et al. reported that carbamate could be obtained by an electrochemical method from amines and carbon dioxide in CO₂⁻ saturated solution of ionic-liquid C₄MIM-BF₄.^[82] The CO₂⁻ anion was proposed to react with amine to give carbamate anions, which further reacted with Et-I and gave ethyl carbamate as the final product. Yu and coworkers synthesized an ionic liquid C₂MIM-BF₃Cl which can be used for electrochemical reduction of CO₂, while as electrolyte and catalyst at the same time.^[83] Masel and coworkers reported an important progress in the electrochemical CO₂ reduction in ionic liquids C₂MIM-BF₄.^[84] The ionic liquid was believed to complex CO₂ in a way that the formation of CO₂⁻ was facilitated, resulting the overpotential of CO₂ to CO reduced.

3.2 Gas-phase reduction approach

As the fundamental research approach, liquid-phase CO₂ reduction suffers from the problems such as low catalytic activity, stability and product selectivity, especially, the low reaction rate being limited by mass transfer. The employment of gas-phase CO₂ reduction with the use of zero-gap cell could enable a considerable enhancement of mass transfer and realize the continuous production. Different from the traditional one-pot or H type electrochemical cell for CO₂ reduction, the essential part of gas-phase electrochemical CO₂ reduction is the employment of gas diffusion electrodes and continuous zero-gap reactors, which liberates the use of large amount of solvents and thus increase the CO₂ solubility greatly.^[85] Due to the close overlapping configuration of electrodes, catalyst layer and transport layer of zero-gap cell, the mass transport of CO₂ is increased greatly. Different configurations of gas-phase electrochemical CO₂ reduction have been studied in several groups^[84, 86, 87], all of which has the similar zero-gap cell structure resembling to that of the PEMFCs, consisting of two electrodes, the cathode and the anode, and a separator (Fig. 8). Either or both of the two electrodes must be gas diffusion electrodes (e.g. Nafion membrane) modified/coated with various catalysts. In the process, a substantially gas phase fuel (e.g. water) is introduced into the anode flow field and a substantially gas phase CO₂ is introduced into the cathode flow field, after reacting with the proton at least a portion of the gas phase CO₂ will be reduced on the cathode side and organic products will be released.

PEMFC-like zero-gap cell

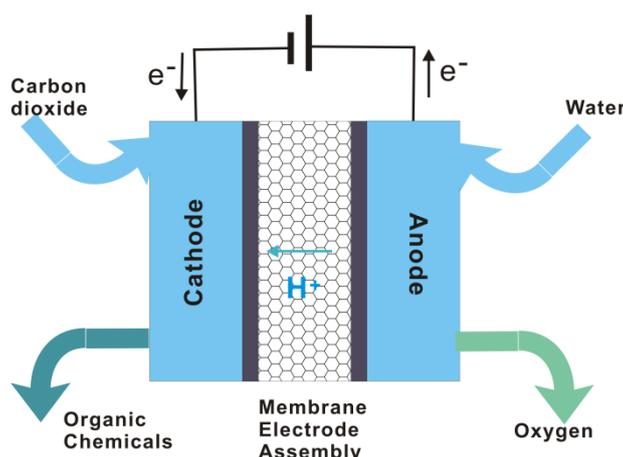


Fig. 8 The PEMFC-like zero-gap cell configuration scheme for gas-phase electrochemical CO₂ reduction

The PEMFC-like configuration to CO₂ reduction was firstly introduced by LaConti et al, who used In/ZITEX/Solid polymer electrolyte in CO₂ reduction.^[88] In recent years, a series of C_n chemicals have been obtained by gas-phase CO₂ reduction. Using Ru-Pd catalysts, Furuya et al. reduced CO₂ to HCOOH with 90% current efficiency at a current density of 80 mA/cm².^[34] Sanchez-Sanchez et al. found that CO₂ could be converted directly in a flow cell with GDE electrode with reasonably good energy efficiencies.^[89] Hara et al. obtained methane on the Pt electrocatalysts modified GDE electrode with high current density up to 900 mA/cm² and 46% faradaic efficiency during the reduction of CO₂.^[24] By employing GDEs embedded with an aqueous KHCO₃ (pH buffer) layer between the Ag based cathode catalyst layer and the Nafion membrane, Delacurt et al. presented a method for CO₂ and water reduction for making syngas (CO+H₂) operated at room temperature.^[90] The type of configuration was reported to allow for greater selectivity of CO₂ reduction to CO (~ 30 mA/cm²) at a potential of -1.7 V to -1.75 V vs SCE. Oloman and Li could obtain a continuous yield of 100 ton/day of CO₂ conversion with optimized zero-gap gas-phase reactor and they even examined the trickle-bed continuous electrochemical reactor under industrially viable conditions.^[86, 91, 92] Fig. 9A shows the schematics of the gas-phase electrochemical reactor used by Oloman, who added more membrane and modules which are more suitable for CO₂ transport and reduction. In recent years,

based on the classic structure of H₂/O₂ fuel cell, Kenis group designed several new types of reactor for CO₂ electrochemical reduction by introducing one thin layer of electrolyte chamber between the anode and the gas-phase diffusion layer, with this design they realized the electrochemical conversion from CO₂ to CH₄ with considerable efficiency. [93] Recently they made a further important progress to realize the conversion from CO₂ to CO with a much reduced overpotential of only 0.17 V and Faradaic efficiency over 96 % by employing an ionic liquid catalyst on Ag electrode. [84] Lee et al. reported that CO₂ can be reduced to formate directly by PEMFC-like zero-gap cell with catalysts on electrodeposited Sn and Pb without introducing any liquid electrolyte, although with much lower Faradaic efficiency. [94, 95] Kuhl et al. studied the electrochemical reduction of CO₂ on a metallic Cu surface employing with custom-made zero-gap cell coupling with sensitive gas chromatography and nuclear magnetic resonance techniques (Fig. 9B), by which many new undiscovered products were identified and quantified. [45] Bao's group developed a kind of gas-phase approach of CO₂ electrochemical reduction with a PEMFC-like configuration [96], they reported that there is a prominent size-dependent activity for CO₂ reduction on Pd nanoparticles and the faradaic efficiency for CO can be as high as 91.2% over 3.7 nm Pd nanoparticles. [97, 98]

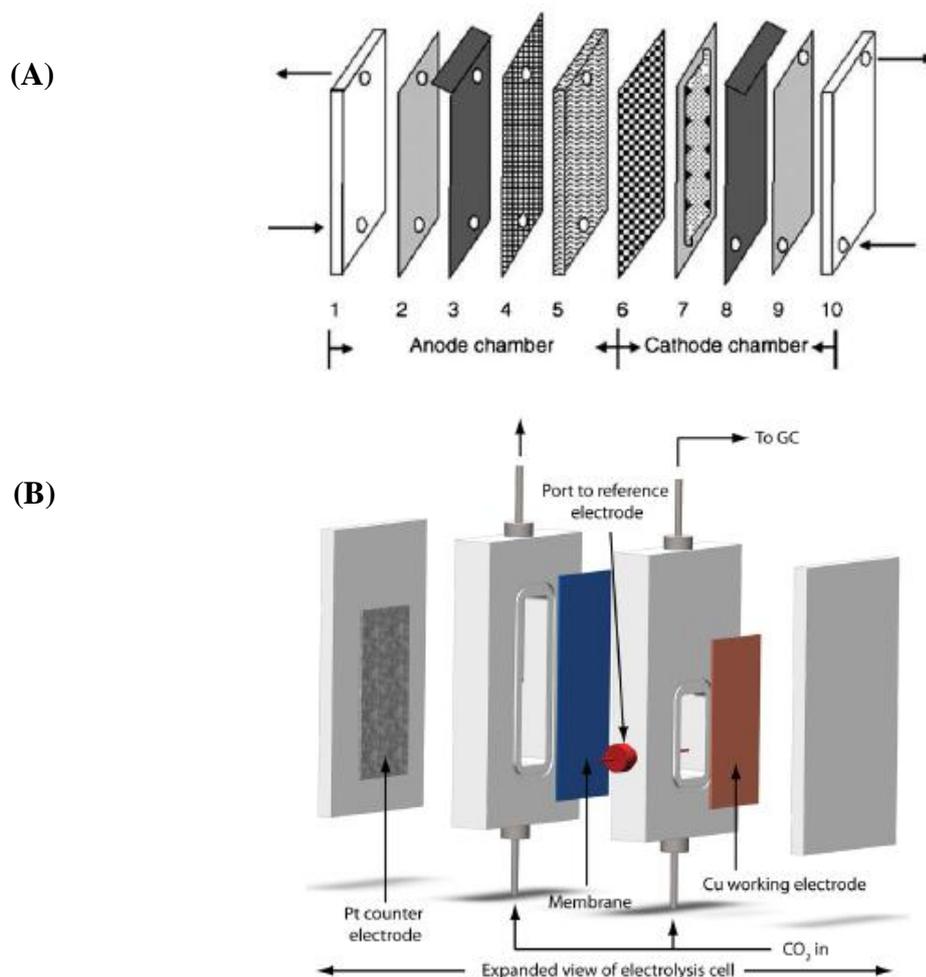


Fig. 9 (A) The zero-gap reactor scheme for electrochemical CO₂ reduction in Oloman's group [92]; (B) Schematic of the electrochemical cell and experimental setup used in electrolysis experiments [45]

Solid oxide electrolysis cell

Like water electrolysis in solid oxide electrolysis cells (SOECs) can be used for production of hydrogen ($\text{H}_2\text{O} \rightarrow \text{H}_2 + 1/2\text{O}_2$), SOECs are also capable of electrolyzing carbon dioxide to carbon monoxide and oxygen ($\text{CO}_2 \rightarrow \text{CO} + 1/2\text{O}_2$). So far only limited studies have been reported for electrolysis of gas-phase CO₂, the majority of which employed with palladium, platinum and nickel as electrodes [13, 52, 68, 99-101], and only recently was performed on ceramic cells with gadolinia-doped

ceria cathodes [85]. SOECs can reduce CO₂ to CO efficiently at high current densities but require operating temperatures of 750–900 °C but cannot access other products with CO₂ as the only feeding gas. Co-electrolysis of steam and CO₂ in a SOEC produce synthesis gas (CO + H₂), and then which can be catalyzed to various types of synthesis fuels. [102] Therefore, using SOECs for recycling CO₂ would be an attractive pathway to provide CO₂ neutral synthetic hydrocarbon fuels. Fig. 10 shows the basic principle for a SOEC and SOFC operating on H₂O/H₂ and CO₂/CO. As endothermic reactions, it is advantageous for water and CO₂ electrolysis to be operated at high temperatures since a larger part of the energy can then be obtained in the form of heat. Moreover, operation at high temperatures can also facilitate reaction kinetics which leads to a decreased internal resistance of the cell and increased efficiency. Therefore, from a thermodynamic and electrode kinetic point of view, it is advantageous to operate SOECs at high temperatures, with the upper limit provided by the material stability.

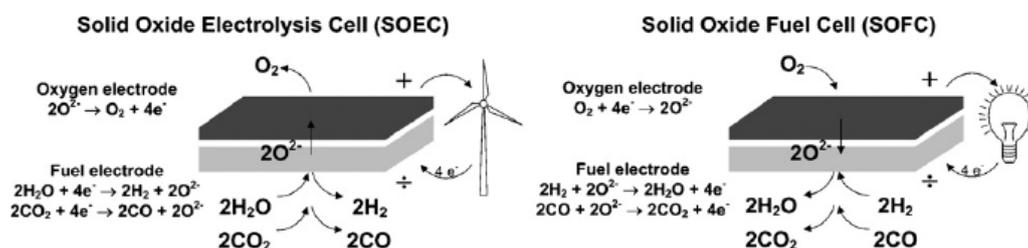


Fig. 10 Schematic presentation of the operational principle for a Solid Oxide Electrolysis Cell and Solid Oxide Fuel Cell. [100]

4. Summary and future challenges

The electrochemical reduction of CO₂ using renewable electricity has several key benefits that can help address many of the intertwined problems in energy and climate change, as it provides a carbon-neutral pathway to recycle CO₂ from the energy cycle system and a convenient means of storing electrical energy of high current density in chemical form, and it still can utilize the renewable energy sources or waste heat generated in the fossil fuels' combustion process.

This paper has shortly reviewed the recent developments of CO₂ conversion into useful chemicals through electrochemical methods. Starting from the basic concepts and thermodynamic considerations of CO₂ conversion, we discussed the electrochemical CO₂ reduction via the traditional liquid-phase approach (including both aqueous and non-aqueous electrolyte) and the most recent gas-phase approach (including PEMFC-like zero gap cell and solid oxide electrolysis cell) in details, respectively. Most of the early work focused on the liquid-phase approach method especially the reduction reactions in aqueous electrolyte. It has been shown that the products and energy efficiency of the electrochemical CO₂ reduction primarily depend on electrodes, electrolytes and catalysts, while the other experimental parameters (such as electrode potential, current density, temperature, pressure, et al.) are also of great importance. The introduction of the gas-diffusion-electrodes based gas-phase reduction approach, enables a considerable enhancement of reaction rate limited by mass transfer and builds the footstone for the potential large-scale continuous industrialization of electrochemical CO₂ conversion, which is still being improved.

The current efforts of electrochemical CO₂ reduction have focused on increasing the energy efficiency and reduce the high overpotentials of CO₂ reduction. There are many areas in which ongoing and future research can lead to new developments of carbon dioxide utilization, the main challenges include the following:

1. New catalysts, methods, approaches are required to activate the CO₂ molecule
2. New conversion setups and configurations are needed to increase CO₂ efficiency

Advanced in-situ characterization techniques are demanded to identify the key reaction intermediates and elucidate the reaction pathways

Currently, the various utilization technologies together have the potential to reduce CO₂ emissions by about 3.7 gigatons/year, which is only ~10% of total current annual CO₂ emissions. The combination of different utilization pathways such as photoelectrochemical CO₂ conversion helps realize the conversion of CO₂ most efficiently. An economically viable electrochemical technology requires the optimization of the following key parameters: high current density (> 1kA/cm²), higher Faradaic efficiency (> 50%), low energy consumption (<500 kWh/kmol), long electrode lifetime (> 4000 hr), high one-pass conversion rate and continuous operation. Among the various products obtained by electrochemical reduction of CO₂, formic acid is one of those to be considered to be commercialized earliest and most likely to be profitable. In the future, research efforts should also be focused on addressing the engineering issues such as the design and construction of reactors, the fabrication of electrodes, the assembly of the membranes, etc., so as to make the industrialization of electrochemical CO₂ conversion come to the fore more earlier.

Acknowledgments

The author is grateful for financial support from the Doctoral Research Foundation of Guizhou University (Natural Science No. 201532) and the Science and Technology Cooperation Program of Guizhou Province (Qiankehe No. [2015]7654 LH).

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