Chapter 5

Electrocatalytic Reduction of CO₂ to Small Organic Molecule Fuels on Metal Catalysts

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The electrocatalytic reduction of carbon dioxide (CO₂) to liquid fuels has tremendous positive impacts on atmospheric carbon balance and help to reduce global warming issues. This paper reviewed current knowledge of electrochemical CO₂ reduction to small organic molecule fuels on metal catalysts and gas-phase CO₂ reduction techniques based on gas diffusion electrode and solid polymer electrolyte. Future research and development needs in this area were also discussed.

Keywords: carbon dioxide; electrocatalytic reduction; synthetic fuels; electrochemistry; electro-driven conversion; catalysis; gas diffusion electrode; electrolysis; photoelectrochemical reactor

1. Introduction

The increase of carbon dioxide (CO₂) in the atmosphere is claimed to be one of the major contributors to the greenhouse effect and will result in serious global warming issues (1–3). The electrocatalytic reduction of CO₂ to liquid fuels is a critical goal that would positively impact the global carbon balance by recycling CO₂ into usable fuels (4–8). However, CO₂ is an extremely stable molecule generally produced by fossil fuel combustion and respiration, returning CO₂ to a useful chemical state on the same scale as its current production rates is beyond our current scientific and technology ability (4). No commercially available processes exist for the conversion of CO₂ to fuels and chemicals yet. The challenges presented are great, but the potential rewards are...
enormous. To address this challenging scientific problem, we need to advance our fundamental understanding of the chemistry of CO₂ activation and develop novel multifunctional catalysts that could use electricity to efficiently break C-O bond and form C-H and C-C bonds (4). Appropriate energy input and reasonable productivity of fuels are also important considerations for practical industrial processes.

The CO₂ electrocatalytic reductions to usable fuels are ‘reverse’ electrochemical processes compared to the anode reactions occurred in fuel cells. CO₂ reduction converts electrical energy back to chemical energy stored in the chemical bonds of fuels. In thermodynamics, the Gibbs free energy of CO₂ reduction is always positive at medium and high pH range, and the theoretical potentials are negative. Thus, CO₂ reduction is an electrolysis process that requires electrical energy input. In kinetics, the overpotential needed to electrochemically reduce CO₂ is always >1.0 V, to get reasonable amounts of fuels, such as methane, ethylene, etc. In an aqueous electrolyte, the water reduction always occurs, and H₂ is a major by-product accompanied with CO₂ reduction. High hydrogen overvoltage metals, such as Hg, can suppress H₂ evolution, but it leads to formation of formate ions (HCOO⁻) at very high overpotentials (high energy cost).

A milestone work is that Hori group found the CO₂ reduction on copper (Cu) behaves very different from the other metals. Cu can directly reduce CO₂ to hydrocarbons (mainly methane and ethylene) with reasonable current density (i.e. 5-10 mA/cm²) and current efficiency (i.e. > 69% at 0°C) in aqueous electrolyte (6, 9). Cu-based catalysts (Cu single crystals, adatom Cu electrode, and Cu alloys electrodes) have been extensively studied from both fundamental and applied perspectives (9–17). Although the process has not been commercialized to produce hydrocarbon products yet, gas mixtures of hydrogen, methane, ethylene and CO would form ‘hythane’ that can be promoted as alternative fuel for existing vehicles (18).

CO₂ reduction in gas phase based on gas diffusion electrode (GDE) and solid polymer electrolyte (SPE) can greatly improve CO₂ transport, thus facilitating CO₂ reduction (19–23). Taking the advantages of established electrolysis cell and fuel cell technologies, electrocatalytic recycling of CO₂ and small organic molecule fuels appears to be a promising means to achieving sustainable, carbon neutral energy conversions. Recently, surprising long carbon chain organic molecules, such as iso-propanol and C≥₄ oxygenates, were found in the GDE based electrocatalytic reduction of CO₂ based on CNT-encapsulate metal catalysts (24, 25), although in very small amounts, they might open new avenues to CO₂ electrocatalytic conversion to liquid fuels.

Some excellent review articles are already available in this field. Frese reviews CO₂ electrocatalytic reduction on solid electrodes (5), Gattrell focused on fundamental mechanisms of electrochemical reduction of CO₂ to hydrocarbons on copper electrode in aqueous electrolyte solution (6), and Hori recently gave a comprehensive review on CO₂ reduction on metal electrodes based on his pioneer work in this area (7). This paper will introduce current knowledge of electrochemical CO₂ reduction on heterogeneous metal catalysts, review present CO₂ reduction techniques based on GDE and SPE, and discuss future research and
development needs in this area. Although homogeneous catalysis is an efficient approach to CO₂ reduction (8), it is out of the scope of this paper.

2. Review

2.1. Fundamental Challenges for Electrochemical Reduction of CO₂

The products of CO₂ reduction vary from liquid fuels (i.e. formic acid and isopropanol), hydrocarbons (i.e. methane and ethylene) to fuel precursors (i.e. CO). The reactivity of CO₂ reduction is very low, however, the equilibrium potentials of CO₂ reduction are not very negative (equation 123456), compared to hydrogen evolution reaction (HER) in aqueous electrolyte solutions (equation 7). The primary reactions that occurred on electrode in aqueous solution at pH 7.0 at 25°C, versus standard hydrogen electrode (SHE) are shown below (7, 26):

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} + 2\text{e}^- &= \text{HCOO}^- + \text{OH}^- \quad (-0.43 \text{ V}) \\
\text{CO}_2 + \text{H}_2\text{O} + 2\text{e}^- &= \text{CO} + 2\text{OH}^- \quad (-0.52 \text{ V}) \\
\text{CO}_2 + 6\text{H}_2\text{O} + 8\text{e}^- &= \text{CH}_4 + 8\text{OH}^- \quad (-0.25 \text{ V}) \\
2\text{CO}_2 + 8\text{H}_2\text{O} + 12\text{e}^- &= \text{C}_2\text{H}_4 + 12\text{OH}^- \quad (-0.34 \text{ V}) \\
2\text{CO}_2 + 9\text{H}_2\text{O} + 12\text{e}^- &= \text{C}_2\text{H}_5\text{OH} + 12\text{OH}^- \quad (-0.33 \text{ V}) \\
3\text{CO}_2 + 13\text{H}_2\text{O} + 18\text{e}^- &= \text{C}_3\text{H}_7\text{OH} + 18\text{OH}^- \quad (-0.32 \text{ V}) \\
2\text{H}_2\text{O} + 2\text{e}^- &= 2\text{OH}^- + \text{H}_2 \quad (-0.41 \text{ V})
\end{align*}
\]

CO₂ reduction does not occur easily and the real applied electrolysis potentials for CO₂ reduction are more negative than the equilibrium values. This is mainly because the single electron reduction of CO₂ to CO₂⁻ (equation 8), which has been well recognized as the first step to activate CO₂ for subsequent reduction steps, occurs at -1.90 V, due to a large reorganizational energy between linear molecule and bent radical anion. This step has also been determined as the rate determining step (RDS) for CO₂ reduction.

\[
\text{CO}_2 + \text{e}^- = \text{CO}_2^- \quad (-1.90 \text{ V}) \quad (8)
\]

It should be noted that the theoretical equilibrium potentials decrease with pH increasing, governed by the Nernst equation (6). For example, the equilibrium...
potential is +0.17 V for CO₂ reduction to methane at pH 0 (Equation 9). The equilibrium potentials over the range of pH values around where the reactions are typically carried out are shown in Fig. 1.

\[
\text{CO}_2 + 8\text{H}^+ + 8e^- = \text{CH}_4 + 2\text{H}_2\text{O} \quad (+0.17\text{V}) \quad (9)
\]

The key problem of the conversion of CO₂ to liquid fuels is the assembly of the nuclei and formation of chemical bonds to convert the relatively simple CO₂ molecule into more complex and energetic molecules. The CO₂ reduction is greatly limited by reaction kinetics. Considering their low equilibrium potentials as shown in Fig. 1, thermodynamically, the products of methane and ethylene should occur at a less cathodic potential than hydrogen, however, kinetically this does not happen.

The products distribution for CO₂ reduction on Cu electrode as a function of potential is plotted in Fig. 2. Initially, CO₂ reduction produces CO and formate until below -1.12V, where hydrocarbons begin to form, with first ethylene (C₂H₄), then methane (CH₄) appearing. The methane production shows the stronger potential dependence, and these reactions accelerate, dominating over CO and formate at around -1.35V. Therefore, the fundamental challenges for CO₂ reduction come from both thermodynamics and kinetics.

In addition, hydrogen evolution reaction (HER) takes place in aqueous electrolytes by cathodic polarization, competing with CO₂ reduction, HER is prevalent in acidic solutions, while CO₂ does not exist in a basic solution. Therefore, most CO₂ reduction study was conducted in close neutral electrolyte solutions (i.e. 0.05 – 0.5 M NaHCO₃).

### 2.2. Classification of Electrocatalytic Metals and Reaction Selectivity

The product selectivity in CO₂ reduction depends on many factors, such as concentration of the reactants, electrode potential, temperature, electrocatalyst material and electrolyte solution (i.e. aqueous or non-aqueous electrolyte). As widely accepted by most researchers, the electrocatalyst materials govern the selectivity of CO₂ reduction, when the other conditions are identical. Hori’s group has carried out a series of elegant research on CO₂ reduction (9–13), and found electrocatalytic metals can be generally divided into four groups based on product selectivity, as shown in Table 1.

The 1st group metals include Pb, Hg, In, Sn, Cd, TI, Bi, etc. They have high hydrogen overvoltages, negligible CO adsorption properties, and high overvoltages for CO₂ to CO₂⁺, and hence weak stabilization of CO₂⁺. The major product is formate ion (HCOO⁻).

The 2nd group metals include Au, Ag, Zn, etc. They have medium hydrogen overvoltages and weak CO adsorption properties, and the major product is carbon monoxide (CO). Because they can catalyze the breakage of the C-O bond in CO₂ but allow the CO desorb, thus, the major product is CO.

The 3rd group metals include Ni, Fe, Pt, Ti, etc. They have low hydrogen overvoltages and strong CO adsorption properties and the major product is H₂, because the main reaction is water reduction to H₂.
The 4th group: Cu. Cu is unique for CO₂ reduction, because it is able to further react CO to more reduced species, such as CH₄ and C₂H₄ with significant amounts. The detailed mechanisms are discussed in section 2.3.

Azuma et al. applied 32 metals to CO₂ reduction at similar conditions (-2.2 V vs. SCE, 0.05M KHCO₃) and confirmed these results given in Table 1 (from Hori’s group). They showed that Cu is the unique metal that can reduce CO₂ to appreciable amounts of hydrocarbons CH₄ and C₂H₄, while Ni and Pt catalysts
scarcely give products in CO\textsubscript{2} reduction at ambient temperature and pressure, but can reduce CO\textsubscript{2} to CO or formic acid under elevated pressure (i.e. 60 atm). They also provided a classical roadmap for CO\textsubscript{2} electrocatalytic reduction on metal catalysts (16), which can be found in Ref (16).

It is interesting that the presence of small amount of foreign atoms on the electrode surface could greatly change the reaction selectivity of CO\textsubscript{2} reduction (6, 27). These adatom modified electrodes were prepared by under potential deposition or overpotential deposition techniques. For example, at -1.44 V vs SHE, the CO selectivity of pure Cu is 69%, while that of Cd and Pd adatom modified Cu is 82% and 0, respectively.

2.3. Reaction Mechanisms

The CO\textsubscript{2} reduction on various metal electrodes has been extensively studied, but knowledge about CO2 reduction is still limited, the reaction mechanisms were mainly obtained base on observed charge transfer coefficients and reaction orders acquired from macroscopic electrochemical testing. The partially understood reaction mechanisms are discussed as follows.

a. Formation of CO\textsubscript{2}\textsuperscript{-} Is the Rate-Determining Step (RDS)

The CO\textsubscript{2} can be chemisorbed as a bent CO\textsubscript{2}\textsuperscript{-} molecule, which is promoted by surface defects, alkali metal promoted surfaces, and possibly through X-rays or photoelectrons during measurements. The exact geometry of CO\textsubscript{2}\textsuperscript{-} metal is unclear, and the possible structures for adsorbed CO\textsubscript{2}\textsuperscript{-} are shown in Fig. 3. CO\textsubscript{2} is an ‘amphoteric’ molecule possessing both acid and basic properties. The adsorption and stabilization of CO\textsubscript{2}\textsuperscript{-} are dominantly governed by the electrode metals. The electrode metals interact with carbon or oxygen or both in CO\textsubscript{2} to form carbon coordination or oxygen coordination, or mixed coordination adsorption mode, respectively. The CO\textsubscript{2}\textsuperscript{-} species is most easily produced at surface defects or in the presence of sublyer coverage of an alkali metal. It is generally agreed that the formation of CO\textsubscript{2}\textsuperscript{-} is the rate-determining step at medium and high overpotential regions. Jordan and Smith firstly proposed the formation of CO\textsubscript{2}\textsuperscript{-} anion radical by one electron transfer to CO\textsubscript{2} is the initial step for subsequent reduction of CO\textsubscript{2}, as shown in Fig. 4 (a) (28). Pacansky et al. studied scf ab initio molecular orbital energies and atomic population analysis of CO\textsubscript{2}\textsuperscript{-} at the minimum energy geometry and found the unpaired electron density at the highest occupied orbital is localized at C atom at 84% (29). This result suggests that CO\textsubscript{2}\textsuperscript{-} is ready to react as a nucleophilic reactant at the carbon atom. The standard potential of CO\textsubscript{2}\textsuperscript{-} formation is -1.90 V or -1.85 V vs SHE, -2.21 V vs. SCE in aqueous media (30–32). The transfer coefficient of RDS in the lower overvoltage region was found to be 0.67 (33). The CO\textsubscript{2}\textsuperscript{-} is mostly present freely in both aqueous and non-aqueous electrolyte solutions, and has been captured by ultraviolet spectroscopy (34).
Table 1. Faradaic efficiencies of products in CO₂ reduction at various metal electrodes. Electrolyte: 0.1 M KHCO₃ (T = 18.5 ± 0.5°C, Ref. (12)). Copyright (1995) with permission from Elsevier.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Potential vs. SHE V</th>
<th>Current density mA cm⁻²</th>
<th>CH₄</th>
<th>C₂H₄</th>
<th>EtOH⁴⁺</th>
<th>PrOH⁴⁺</th>
<th>CO</th>
<th>HCOO⁻</th>
<th>H₂</th>
<th>Total</th>
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<td>tr.</td>
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<td>99.7</td>
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</table>

⁴⁺ indicates formation of propylene oxide; tr. indicates trace amount.
Figure 3. Possible structure for adsorbed $\text{CO}_2^-$ on metals (Ref (7)). Copyright (2007) with permission from Elsevier.

Figure 4. The main reaction pathways at the electrode surface, with adsorbed blocking the majority of the surface and hydrocarbon products being formed by the further reduction of adsorbed CO. (Ref (6, 7). Copyright (2007) with permission from Elsevier. (see color insert)

There are two main pathways for further reduction of adsorbed $\text{CO}_2^-$ to respective final product of CO, and formate ion ($\text{HCOO}^-$), which is governed by the properties of metal electrocatalysts.

b. Formation of Adsorbed $\text{CO}_2^-$Leading to Further Reduction to $\text{HCOO}^-$

Erring et al. studied $\text{CO}_2$ reduction polarization data at Hg electrode in aqueous electrolyte with $\text{HCO}_3^-$, and obtained a major product of $\text{HCOO}^-$ (35). On Hg, $\text{CO}_2$ reduction is initiated by one electron transfer to form $\text{CO}_2^-$ at the potential negative of $-1.6$ V vs. SHE. The $\text{CO}_2^-$ will take a proton from a $\text{H}_2\text{O}$ molecule at the nucleophilic carbon atom, forming $\text{HCOO}^-$. $\text{H}^+$ will not be bonded to the O atom of $\text{CO}_2^-$, since $\text{pK}_a$ value of the acid-base couple ($\text{CO}_2^-$/CO$_2$H) is low of 1.4 (36). Hori et al found that the electrode potential is constant as the current density for $\text{HCOO}^-$ formation at a pH range of 2-8, thus, $\text{H}_2\text{O}$ is believed to be the proton donor in the formate formation from $\text{CO}_2^-$. $\text{HCOO}^-$ is subsequently reduced to $\text{HCOO}^-$ at the electrode in aqueous media. The reaction steps are:
CO$_2$"ads + H$_2$O $\rightarrow$ HCOO"ads + OH$^-$ (10)

HCOO"ads + e" $\rightarrow$ HCOO$^-$ (11)

Formate could also be produced directly by reaction with adsorbed hydrogen, which would be present as an intermediate in the hydrogen evolution reaction:

CO$_2$"ads + H$_{ads}$ $\rightarrow$ HCOO$^-$ (12)

Such a reaction mechanism would appear to be favored by CO$_2$" being adsorbed with oxygen coordination or being just close to the electrode. Other high hydrogen overvoltage electrodes, including Cd, Pb, Tl, In, and Sn, with weak adsorption of hydrogen, have high overvoltage for CO$_2$ reduction to CO$_2$", and hence weak stabilization of CO$_2$". The CO$_2$ reduction on these metals follows a similar mechanism as shown in Fig. 4 (b). In non-aqueous electrolyte, CO$_2$ electrolysis on Pb leads to formation of oxalic acid, due to formation of (CO$_2$)$_2$" (6).

c. Formation of Adsorbed CO$_2$-Leading to Further Reduction to CO

The other pathway also involves first protonation then reduction, which is similar to step b), however, the hydrogen appears to be added on oxygen not carbon in CO$_2$". The steps will occur more favorably on carbon coordination adsorption mode.

CO$_2$"ads + H$_2$O $\rightarrow$ COOH$_{ads}$ + OH$^-$ (13)

COOH$_{ads}$ + e" $\rightarrow$ CO$_{ads}$ + OH$^-$ (14)

CO could be formed by a direct reaction with adsorbed hydrogen:

CO$_2$"ads + H$_{ads}$ $\rightarrow$ CO$_{ads}$ + OH$^-$ (15)

In these reactions, the electrophilic reagents, H$_2$O in aqueous solution, react with the O atom of adsorbed CO$_2$", forming CO$_{ads}$ and OH$^-$ as depicted in Fig. 4(c). Sasaki et al used an ab initio molecular orbital approach to study the configuration of NiF(NH$_3$)$_6$(CO$_2$) as a model for CO$_2$ reduction and showed that C atom of CO$_2$ molecule is favorably coordinated with the transition metal atom in a complex and can be stabilized by a strong charge transfer due to back donation from Ni to CO$_2$, which indicates carbon coordination can facilitate protonation of oxygen (Eq.13), leading to formation of COOH not HCOO$^-$.

At Au electrode, H$^+$ will not take part in the CO formation, since the partial current of CO formation is independent of pH. The CO$_{ads}$ is readily desorbed from
the electrode as a gaseous molecule. The reaction scheme is suitable to other metal electrodes, such as Ag, Cu and Zn in aqueous media. The sequence of CO selectivity roughly agrees with that of the electrode potentials. This agreement verifies the hypothesis that CO is favorably produced from the electrode metals which stabilize CO\textsubscript{2}~ effectively. Because the CO adsorption on Au, Ag and Zn surface is weak, CO is the major product, as shown in Fig. 4 c. In comparasion, CO will be further reduced to hydrocarbon products on Cu electrode (as discussed in section 2.4).

d. Hydrogen Evolution Reaction (HER)

HER is a major side reaction that accompanies CO\textsubscript{2} reduction in an aqueous electrolyte. It has been found that the reaction kinetics of HER are pH dependent in the acid region and pH independent in the alkaline region. The HER can be written as

\[
\begin{align*}
H^+ + e^- &\rightarrow H_{ads} \quad (16) \\
2H_{ads} &\rightarrow H_2 \quad (17)
\end{align*}
\]

or

\[
H_{ads} + H^+ + e^- \rightarrow H_2 \quad (18)
\]

Adsorbed hydrogen H\textsubscript{ads} and/or H\textsuperscript{+} are the hydrogen source for hydrogenation in CO\textsubscript{2} reduction. Because CO is strongly adsorbed on Pt/Fe/Ni/Ti surface, in an applied potential range, the major product is H\textsubscript{2}, rather than CO, as shown in Fig. 4 d.

2.4. Cu-Based Electro catalysts

Cu is a unique metal that can reduce CO\textsubscript{2} to CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{4} and alcohols in aqueous electrolyte at low temperature (6). Some known mechanisms are reviewed as below.

a. Formation of CO\textsubscript{ads} as Reaction Intermediate

From Fig. 2, at low overpotential, i.e. -0.9 V, the faradic yields of CO and HCOO\textsuperscript{−} are both appreciable, while C\textsubscript{2}H\textsubscript{4} begins to increase at -1.1V, CH\textsubscript{4} starts at -1.2V, these data indicate that CO and HCOO\textsuperscript{−} may be precursors to hydrocarbons and alcohols. However, FTIR and Raman spectrum show CO is linearly adsorbed on Cu polycrystal electrode at -0.6V, which suggests that CO is the reaction intermediate formed at Cu electrode, serving as a precursor for further reduction to hydrocarbons and alcohols (37, 38). The surface of the Cu electrode is covered by CO with coverage >90% as estimated from the current at -1.0V with and
without CO, this could severely suppress hydrogen evolution reaction. The heat of adsorption of CO on Cu is appropriate (-17.7 kcal/mol), which is higher than Au, but lower than Ni and Pt, as listed in Table 2 (39). Therefore, Cu allows efficiently subsequent reduction of CO to produce hydrocarbons and alcohols.

b. From CO$_{ads}$ to Hydrocarbons

Since CO has been identified as a primary reaction intermediate for formation of hydrocarbons, CO was used to investigate mechanisms of CO$_2$ reduction on Cu. Fig. 2 suggests that CH$_4$ formation starts at a more negative potential than C$_2$H$_4$ (-1.22 vs -1.12 V), but C$_2$H$_4$ formation is more favorable in high pH media. In addition, the Tafel slope for the two reactions are very different. All these strongly indicate that formation of CH$_4$ and C$_2$H$_4$ is through different reaction pathways from common starting substance CO. Interestingly, the evidence of lack of formation of methanol implies that the C-O bond of CO is broken early and consistently in the mechanism.

For the case of formation of CH$_4$, the transfer efficient of > 1 suggests that there is an initial electron transfer in equilibrium before RDS, this could result in a CO anion radical, as shown in Fig. 5 (a). Ab initio calculations were used to evaluate the state of the adsorbed CO anion radical, a slight decrease of the Cu-C bond and an increase of the C-O bond to about 1.25 Å were found, this predicts a mostly double bond character (40).

There are two possible reaction paths after formation of CO anion radicals. The first path is shown in Fig. 5 (b). This path involves a proton in the reaction, which must occur reversibly before the second electron transfer for RDS to yield the observed transfer coefficient. This is an acid-base reaction at the oxygen. The formation of four C-H bond would be not reversible, leading to production of CH$_4$. The second path involves reaction of C-O anion radical with an adsorbed hydrogen. Once the adsorbed CO has been electrochemically split, the hydrogen will add on carbon to form C-H radical and result in formation of CH$_4$, as shown in Fig. 5(c).

For the case of C$_2$H$_4$ formation, ethylene formation begins at a lower potential without a pH dependence and with first electron transfer as the RDS. As the first electron transfer begins a reaction pathway that subsequently results in a two carbon product, it is reasonable to assume that some type of bond formation occurs in this reaction step. A reaction is proposed that involves a “prior association” of two adsorbed CO (see Fig. 6). The postulation of a starting “associated pair” of adsorbed CO also would be consistent with the lower activation potential vs. the formation of CO (and hence methane).

The other possible reaction path is through the step of -CH$_2$ (ads) with CO. Since C(ads) is readily reduce to -CH$_2$ as shown in Fig. 5 b, two -CH$_2$ can dimerize to form C$_2$H$_4$, or alternatively, CO inserts into -CH$_2$ to form -COCH$_2$ which is further reduced to C$_2$H$_4$, as shown in Fig. 6.

So far, we still lack convinced experimental data i.e. FT-IR / Raman spectrum under real reaction conditions, to clearly elucidate the elementary steps for the complex CO$_2$ reduction to hydrocarbons. It is still not very clear how H species
Table 2. CO reduction in 0.1 M KHCO₃ at various metal electrodes (Ref (11)). Copyright (1987) with permission from Japan Chemical Society.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Potential V vs.SHE</th>
<th>Faradaic efficiency/ %</th>
<th>CO heat of adsorption kcal mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>−1.49</td>
<td>0.0</td>
<td>101.6</td>
</tr>
<tr>
<td>Cu</td>
<td>−1.40</td>
<td>16.3</td>
<td>45.5</td>
</tr>
<tr>
<td>Ni</td>
<td>−1.46</td>
<td>2.6</td>
<td>94.2</td>
</tr>
<tr>
<td>Pt</td>
<td>−1.29</td>
<td>0.1</td>
<td>96.8</td>
</tr>
</tbody>
</table>

Figure 5. (a) the expected mechanism for initial electron transfer to adsorbed CO, (b) (c) the reaction mechanisms that could lead to the observed transfer coefficient and reaction order with pH. Grey particle: Cu atom, (Redrawn based on Ref (7)). Copyright (2007) with permission from Elsevier.

Figure 6. The proposed reaction mechanisms for producing a two carbon product. Grey particle: Cu atom, (Redrawn based on Refs. (6, 7)). Copyright (2007) with permission from Elsevier.

react with CO₂⁻ or CO to generate hydrocarbons on Cu electrodes, the detailed reaction steps are question marks, as shown in Fig. 4.
The crystal faces dominated by Cu(100) tend to result in a significant current efficiency for ethylene at relatively low overpotentials (41), one possible reason might be related to the hypothesized rate determining step in Fig. 7. Such step would require the π orbitals of the adsorbed CO to interact simultaneously with vibrational motions bringing the two oxygens close to Cu surface atoms. Such an intermediate state would be more likely with a right arrangement of surface atoms, preferably with wide Cu (100) terrace surfaces (see Fig. 7, ref (7, 41)).

The crystal faces dominated by Cu(111) tend to be polarised to more negative potentials and favor methane production. The Cu(110) type surfaces polarise to the most negative potentials and result in other 2 carbon and 3 carbon product, such as acetic acid (42). The product partial currents for methane and ethylene at polycrystalline Cu, Cu(100), Cu(110) and Cu(111) electrodes generally followed the same trends (7).

The overall CO2 reduction required a higher overpotential, and a greater difference in overpotentials was found between the different crystal faces. The results of single crystal studies show why the electrode preparation could have a strong influence on the results obtained. Metallic nanostructures will be expected to provide more opportunities in deliberately produce more advantageous crystalline (43, 44), i.e. nanocube is rich in (100), thus, improving the productivity of long-carbon chain organic molecules from CO2 reduction. In addition, it was found that no simple choice of rate determining steps from among reactions fit the data, it implies that shifting and/or parallel mechanisms operate, varying electrode preparation and possibly electrolyte compositions might change the mechanisms.

c. Surface Treatment and Cu Alloy Electro catalysts

Surface treatments affect the activity and selectivity of CO2 reduction on Cu catalysts (45–47). Formation of CH3OH was reported at intentionally preoxidized Cu electrodes, and the maximum partial current of CH3OH production reached 15 mA/cm2 (48). However, other researchers did not detect CH3OH from Cu electrodes oxidized in various manners (46). Steady formation of CH3OH from Cu electrodes at a high current density has not yet been confirmed by other researchers to date (6).

Cu-based alloys have been investigated for CO2 reduction. The modifications can be due to a combination of changes in the electronic structure and changes in the surface crystallographic characteristics, including the introduction of dislocations and vacancies, leading to major changes in the products distributions and reaction rates. Cu-Ni and Cu-Fe alloys, formed by in-situ deposition during CO2 reduction, gradually lose CH4 and C2H4 yields simultaneously with increased H2 evolution with the increase of Ni or Fe coverage on the Cu surface (49). A Cu-Cd electrode produced CH4 and C2H4. The yields gradually dropped with the increase of Cd coverage, but the CO formation increased (47). Watanabe et al. studied various Cu based alloys; Cu-Ni, Cu-Sn, Cu-Pb, Cu-Zn, Cu-Cd, and found that the major products are CO and HCOO-. Surface Cu-Au alloy electrodes showed that the surface alloying severely suppresses the formation of hydrocarbons and alcohols, leading to the increase of CO formation (14).
2.5. Major Issues Associated with Aqueous CO₂ Reduction

Numerous researches have been carried out to investigate electrocatalytic reduction of CO₂ in aqueous phase and advanced the understanding of the reaction mechanisms. However, liquid phase CO₂ electrocatalytic reduction suffers from serious problems which are difficult to overcome:

1) Sluggish reaction kinetics: this leads to >1.0 V overpotential, which greatly increases the energy cost for electrolysis process.
2) Low selectivity of CO₂ reduction. CO₂ reduction and hydrogen evolution are two competitive reactions, hydrogen is inevitably a by-product accompanying with CO₂ reduction in aqueous electrolyte.
3) Formation of various by-products: they mainly remain in electrolyte solution and separation and recovery are high energy-cost.
4) Low solubility of CO₂ in aqueous electrolyte (= 0.08M): high pressures are normally needed to improve CO₂ transport.
5) Deactivation: the electrode catalysts loose their high initial selectivity and reactivity after a short period of operation.
6) Low tolerance to impurities and contaminations: The surface contamination and non-pure electrolyte will often lead to low productivity and selectivity of hydrocarbon products.

2.6. Gas Phase CO₂ Reduction Based on Gas Diffusion Electrode (GDE) and Solid Polymer Electrolyte (SPE)

An excellent alternative to CO₂ reduction in aqueous electrolyte is the use of GDEs and SPE (including cation exchange membrane (CEM) and anion exchange membrane (AEM)) for a continuous CO₂ reduction system which could enable considerable enhancements of mass transfer of CO₂ (19–23, 49–69). GDE is a porous composite electrode developed for fuel cell technology, usually composed of Teflon bonded catalyst particles and carbon black. SPE membrane with GDE can provide gas phase electrolysis of CO₂. The acquired knowledge for CO₂ reduction over metal electrodes in aqueous electrolyte has been used to investigate the GDE/SPE-based electrolysis cells to convert CO₂ into usable fuels or syngas.
H$_2$/CO, with reasonably good energy efficiencies. The main advances in this area are summarized as follow.

a. From CO$_2$ to Fuel Precursors (CO and H$_2$)

It is relatively easy to electrocatalytic reduce CO$_2$ to CO using the 2nd group metals (Table 1), such as Au, Ag, etc, or to reduce H$_2$O to H$_2$ (HER) using the 3rd group metals (Table 1), such as Ni, etc.

Yamamoto et al conducted CO$_2$ reduction and water oxidation in a CO$_2$-reducing electrolysis cell with Ni catalyst, 1/1 CO/H$_2$ gas ratio at a current density of 10 mA/cm$^2$ at a cell voltage of 3.05V was obtained, the overall energy efficiency is 44.6% (49).

Newman group has demonstrated a method for CO$_2$ and water reduction for making syngas (CO+H$_2$) operated at room temperature by employing GDEs embedded with an aqueous KHCO$_3$ (pH buffer) layer between the Au/Ag based cathode catalyst layer and the Nafion membrane (4, 55). The schematic representation of the electrolysis cell is shown in Fig. 8. The cathode catalyst is Au or Ag, and the gas products are CO and H$_2$. Each catalyst was shown very selective for CO$_2$ reduction to CO at an overall current density of 20 mA/cm$^2$ for Ag and Au, respectively with the balance corresponding to H$_2$. A lower overpotential of 200 mV was observed on Au catalyst than Ag catalyst. As the overall current density efficiency increases, a decrease in CO current efficiency was observed, likely related to CO mass-transport limitation. Energy efficiency for the overall cell (with Pt-Ir as anode catalyst) is ca. 47% at 20 mA/cm$^2$ and decrease to ca. 32% at 100 mA/cm$^2$ for both catalysts, which is mostly due to joule heating losses. Their recent investigation show the CO partial current densities as high as 135 mA/cm$^2$ could be obtained for a short period based on supported Au catalyst (4). A CO/H$_2$ ratio of 1/2 was obtained, especially suitable for methanol synthesis, at a potential of ca. -0.2V vs SCE with a total current density of 80 mA/cm$^2$. Unfortunately, a decrease of catalyst selectivity for CO evolution with time has been identified as a critical technical issue (55).

b. From CO$_2$ to C$_1$-C$_2$ Fuels (Formic Acid, Methane and Ethylene)

An alternative possibility is to convert CO$_2$ to formic acid, that can be used as both fuels and chemicals. The ‘Formic Acid Economy’ was advocated by the UK government to promote sustainable energy development. Mahmood et al. demonstrated high rates of reduction of CO$_2$ to formic acid at Pb impregnated GDEs operated at 115 mA/cm$^2$ in aqueous acidic electrolytes (pH of 2) with a current efficiency of nearly 100% at an IR-corrected potential of 1.8 V (vs SCE) (19). Furuya et al. showed a current efficiency of 90% for the formation of formic acid at a GDE impregnated with Ru–Pd catalysts that can be obtained at the current density of 80 mAcm$^2$ (22).

The research efforts on CO$_2$ reduction to C$_2$ hydrocarbons (mainly methane and ethylene) using SPE cells were also studied. Hara et al. observed high
current density attainment up to 900 mA/cm² and 46% faradaic efficiency during the reduction of CO₂ with the formation of methane on the GDE using Pt electrocatalysts at increased CO₂ pressures of 50 atm (21). DeWulf et al. applied an SPE with Cu as the catalyst layer on a Nafion 115. CH₄ and C₂H₄ were produced, but the current density for CO₂ reduction dropped below 1 mA/cm² after 70 min electrolysis, which indicates a durability issue (56). Sammells et al.
preparing a Cu coated SPE electrode using a CEM Nafion 117, and they found CO₂ was reduced to C₃H₄ and C₂H₂ with the current density of 10 to 30 mA/cm² with the terminal voltage 1.5 to 3.5 V. The faradaic efficiency for CO₂ reduction remained < 10% (57–59). Kamatsu et al studied Cu deposited on cation exchange membrane (CEM, Nafion) and anion exchange membrane (AEM, Selenium) and found the total efficiencies for CO₂ reduction have maximum values of 19% and 27%, respectively. The use of CEM gave C₂H₄ as the major product, while, with use of AEM, the HCOOH and CO were obtained. It is also interesting to find that NO has no influence on the CO₂ reduction, but the removal of SO₂ is needed to obtain C₂H₄ on high current densities (61). The best results in term of hydrocarbon formation were reported using immobilized CuCl on Cu mesh electrodes, a Faradic efficiency of about 70% for ethylene was obtained, even if the presence of a fast deactivation (60).

c. From CO₂ to Long-Chain Carbon Fuels

An ultimate goal for CO₂ cycling is direct reduction of CO₂ to liquid long-chain carbon fuels. It is still very challenging to achieve direct reduction CO₂ to such fuels based on current science and technology ability. Both the selectivity and productivity are very low and they are far from real applications.

It was reported that very small amount of paraffins and olefins up to C₆ hydrocarbons can be obtained in CO₂ electroreduction at room temperature and atmospheric pressure through commercially available Cu-electrode. Certain Cu-electrodes produce products in CO₂ electroreduction with a distribution as typically obtained in the Fischer–Tropsch reaction of syn-gas over heterogeneous Co- or Fe-based catalysts. The paraffin products fit to Schultz-Flory product distribution with an exception of olefins C₂H₄, which suggests that C₂H₄ is produced via another reaction path than chain propagation (70).

A new concept of photoelectrocatalytic (PEC) reactor was proposed in Fig. 9. At the anode, the water is photooxidized to oxygen and produce electrons and protons, which electrocatalytic reduce CO₂ to liquid fuels at the cathode (71). This concept was originally proposed by Hitachi Green Center researchers (72, 73). Centi group reported Fe and Pt nanoparticles / carbon nanotubes (CNTs) exhibit encouraging electrocatalytic selectivity to CO reduction, the isopropanol can be the major product at a formation rate of 0.06 μmol.h⁻¹.cm⁻², besides CO and H₂ (Fig. 10 a). Other long carbon-chain hydrocarbons were detected in trace amounts.

It has been reported that the selectivity of CO₂ reduction to C₂ hydrocarbons with the micropores of activated carbon fibers could be significantly enhanced, due to a special nanospace effect, which gives rise to a similar high-pressure-like effect at ambient pressure (52). As a unique support material, CNTs-based catalysts have demonstrated high activity and superior durability in low temperature fuel cell applications (76–79). The Bao group recently revealed that CNTs channels could provide an intriguing confinement environmental for Fisher-Tropsch synthesis (80, 81). The strategy of design and preparation of catalysts could be widely applied to other gas-liquid reaction systems, such as CO₂ reduction to liquid fuels. As what Centi group demonstrated in their recent publications, the CNTs encapsulated Fe
nanoparticles (Fig. 10b) can effectively promote long-carbon chain oxygenates, due to ‘space-restriction’ effect (24, 25, 74, 75).

3. Conclusions and Future Directions

CO2 is an extremely stable molecule generally produced by fossil fuel combustion and respiration, electrocatalytic approaches have potentials to direct convert CO2 to small carbon chain fuels. The energy-efficient CO2 reduction demand catalysts that can operate near thermodynamic potentials with high rate of electrochemical reaction. However, our current understanding on the reaction mechanisms is still very limited, and controllably returning CO2 to useful carbon-fuels on the same scale as their current production rates is beyond our current scientific and technology ability. Conversion of CO2 to liquid fuels and useful chemicals will require new methods and approaches for activating the CO2 molecule. Novel complex catalysts and catalyst assemblies including hybrid catalysts, hierarchal nanostructured catalytic systems, and multi-site catalysts, that can work in concert, should be studied to achieve the overall efficient CO2 reduction process.

It is imperative to advance our understanding of the reaction mechanisms of C-O bond cleavage and C-C and C-H bonds formation (especially for >2 carbon-chain molecules). Multi-step, multi-electron chemical transformations, coupled charge and atom transfer reactions are needed to be thoroughly investigated. At the mean time, developing advanced in-situ / on-site characterization tools under ‘real’ electrochemical operations is demanded to identify the key reaction intermediates and elucidate reaction pathways. The ‘space-restriction effects’ were discovered to change the reaction pathways, investigations on the interplay between various catalytic sites and catalyst environments in multifunctional catalysts are required. Extensive study on the model catalysts, including single crystal, atom, and electro-deposited catalysts for CO2 reduction have been carried out, bridging the gap between model catalysts and ‘real-word’ nanostructured catalysts is highly demanded. Nano-techniques
provide exciting opportunities in this area by precisely controlling the surface facets, morphologies and structures of multi-metal nanoparticles.

In the future, research efforts should also be focused on addressing the engineering issues related with design and construction of electrolysis cells and photoelectrocatalytic reactors, fabrication of electrodes, assembly of membrane electrode and solid electrolyte, etc. The efforts will help realize efficient CO₂ recycling processes and devices.

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References


