Upgrading CO₂ Into Fuels And Chemicals Via Electrocatalysis

Yuxiang Li

School of Design and Engineering, National University of Singapore, 138600 Singapore, Singapore

Abstract. Converting carbon dioxide (CO₂) into useful chemicals through electrochemical reduction reactions (CO₂R) has received growing interest because it can be used to reduce greenhouse gas emissions and generate valuable chemical products. This report discusses the CO₂ electrochemical reduction for carbon recycling and the production of valuable chemicals and fuels. It provides an overview of CO₂ reduction reaction and a diverse of different CO₂ conversion pathway. This research focuses on the mechanisms and catalytic materials used in CO₂ electrocatalysis, with a specific emphasis on copper as a unique catalyst. It also highlights the factors that influence CO₂ reduction, such as pH, presence of ions, temperature, pressure, electrode fouling, and catalyst deactivation. Furthermore, the economic and environmental aspects of CO₂ reduction are explored, including the potential market prices and the positive environmental impacts. The report concludes by addressing the challenges and difficulties faced in electrocatalytic CO₂ reduction, such as high activation energy, competing reactions, catalyst poisoning, and low current density. Overall, electrochemical CO₂ reduction holds significant potential for sustainable and eco-friendly chemical production.

1 Introduction

In today's society, there is an increasing focus on environmental protection issues, and one of the most critical aspects is the reduction of greenhouse gas emissions. In all kinds of GHG, carbon dioxide is predominant. According to IEA (2023), from fossil fuels increased dramatically between 1900 and 2023, rising by more than 90% over that period. and according to IEA (2023), global carbon dioxide (CO₂) emissions related to the higher consumption of foils by 0.9% in 2022, resulting in a expansion of more release of the CO₂ over 36.8 billion tonnes. This represents a growth of 321 million tonnes compared to previous levels [1].

According to Fig. 1, carbon dioxide in fossil fuel industrial processes is 65% in the whole GHG emissions, so control the emission of CO₂ is an efficient way to control the greenhouse effect. There are three main approaches been taken to reduce net carbon dioxide emissions: decarbonization to eliminate fossil fuel use, carbon sequestration to capture and store carbon, and carbon recycling to convert CO₂ into valuable products [2, 3].

Manufacturing compounds like alcohols, olefins, and hydrocarbons from anthropogenic CO₂ emissions has the potential to reduce carbon emissions through the application of renewable energy sources and carbon capture technology. CO₂ can potentially be recycled through a process called CO₂ electrochemical reduction, which involves using electrolysis to reduce CO₂ into new compounds. One of the most promising processes for capturing and using carbon includes transforming CO₂ into a target substanc [4].

The CO₂ electrochemical reduction dates back to the 19th century, where early experiments demonstrated that CO₂ could be converted into carbon monoxide using a zinc electrode as the cathode. However, after the oil embargoes of the 1970s disrupted global oil supplies, study in this area accelerated in the 1980s. Prominent companies, including Dioxide Materials, Siemens, and Twelve, are actively engaged in the development of pilot-scale CO₂ electrochemical reduction devices. These endeavors aim to accelerate and endorse the adoption of this promising strategy, signifying a strong commitment to exploring sustainable solutions for CO₂ utilization [2].

![Fig. 1. Global greenhouse gas emissions by gas](Picture credit: Original)
Prior to the introduction of electrocatalytic CO₂ reduction, hydrogenation was a common method used for CO₂ reduction. However, electrochemical synthesis methods offer several potential advantages. One key benefit is that the electrochemical approach integrates water splitting and thermal hydrogenation into distinct processes, enhancing both the efficiency and cost-effectiveness of the procedure [5]. Additionally, electrochemical synthesis offers a distinct advantage over thermally driven processes by enabling the production of challenging-to-obtain products. This enhanced versatility makes it a highly adaptable and valuable method for chemical synthesis, opening up new possibilities for the creation of novel and complex compounds. Unlike traditional chemical synthesis methods, electrochemical synthesis can frequently be carried out at normal indoor condition, this attribute simplifies the experimental procedures, making them more manageable and efficient to conduct. The characteristics of electrochemical synthesis make it a compelling and sustainable approach for chemical production. In this report, the basic experimental principle will be firstly introduced and then the progress of the electrocatalysis of carbon dioxide will be illustrate, along with the faced difficulties during the experiment and the influence of develop this technology into industry.

2 CO₂ reduction reaction

Table 1 presents the chemical equations for the CO₂ RR and the equilibrium potentials associated with some of the frequently reported products.

Table 1. Equations involve in CO₂ RR.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>E₀/IV vs RHE</th>
<th>Name, abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2H₂O → O₂ + 4H⁺ + 4e⁻</td>
<td>1.23</td>
<td>Oxygen Evolution Reaction, OER</td>
</tr>
<tr>
<td>2H⁺ + 2e⁻ → H₂</td>
<td>0</td>
<td>Hydrogen Evolution Reaction, HER</td>
</tr>
<tr>
<td>xCO₂ + nH⁺ + ne⁻ → product + yH₂O</td>
<td></td>
<td>CO₂ Reduction, CO₂R</td>
</tr>
<tr>
<td>CO₂ + 2H⁺ + 2e⁻ → HCOOH (aq)</td>
<td>-0.12</td>
<td>Formic acid</td>
</tr>
<tr>
<td>CO₂ + 2H₂ → CO + H₂O (aq)</td>
<td>-0.10</td>
<td>Carbon monoxide</td>
</tr>
<tr>
<td>CO₂ + 6H⁺ + 6e⁻ → CH₃OH (aq) + H₂O</td>
<td>0.03</td>
<td>Methanol, MeOH</td>
</tr>
<tr>
<td>CO₂ + 4H⁺ + 4e⁻ → C₀(0) + 2H₂O</td>
<td>0.21</td>
<td>Graphite</td>
</tr>
<tr>
<td>CO₂ + 8H⁺ + 8e⁻ → CH₄(O)+ + 2H₂O</td>
<td>0.17</td>
<td>Methane</td>
</tr>
</tbody>
</table>

2CO₂ + 2H⁺ + 2e⁻ → (COOH)₂(e) | -0.47 | Oxalic acid |

2CO₂ + 8H⁺ + 8e⁻ → CH₃COOH(aq) + 2H₂O | 0.11 | Acetic acid |

2CO₂ + 10H⁺ + 10e⁻ → CH₃CHO(aq) + 3H₂O | 0.06 | Acetaldehyde |

2CO₂ + 12H⁺ + 12e⁻ → C₂H₆OH(aq) + 3H₂O | 0.09 | Ethanol, EtOH |

2CO₂ + 12H⁺ + 12e⁻ → C₂H₄ + 4H₂O | 0.08 | Ethylene |

2CO₂ + 14H⁺ + 14e⁻ → C₂H₁₀ + 4H₂O | 0.14 | Ethane |

3CO₂ + 16H⁺ + 16e⁻ → C₂H₄CHO(aq) + 5H₂O | 0.09 | Propionaldehyde |

3CO₂ + 18H⁺ + 18e⁻ → C₂H₆OH(aq) + 5H₂O | 0.1 | Propanol, PrOH |

xCO + 6H⁺ + ne⁻ → product + yH₂O | CO Reduction, COR |

CO + 6H⁺ → CH₃OH(aq) + H₂O | 0.26 | Methane |

2CO + 8H⁺ + 8e⁻ → CH₃CH₂OH(aq)+H₂O | 0.19 | Ethanol, EtOH |

2CO + 8H⁺ + 8e⁻ → C₂H₄(0) + 2H₂O | 0.17 | Ethylene-|

2.1. Mechanism and pathway

Yoshio Hori and his team's groundbreaking study in 1985 marked a significant milestone as it allowed for the evaluation of both gaseous and liquid products, achieving a remarkable 100% Faradaic efficiency. Based on their product yields, these experiments and several that followed them that employed comparable techniques divided metal electrodes into four groups. While some metals, like Au, Ag, and Zn, largely make carbon monoxide (CO), others, like Pb, Hg, and Ti, mostly produce formate (HCOO) [6]. Some metals, such as Ni, Fe, Pt, and Ti, virtually completely convert water to H₂ while reducing very little CO₂. Contrarily, copper stands out as the sole pure metal with notable Faradaic efficiencies that can reduce CO₂ to special products. In addition, copper generates a variety of alcohols, aldehydes, and hydrocarbons. Following Hori's groundbreaking discovery in 1985, Following the remarkable demonstration of high Faradaic efficiencies achieved by copper electrodes in the process of CO₂ reduction, numerous researchers have been fervently engaged in investigating the intricate reaction mechanisms that govern the reduction of CO₂ on copper surfaces. The collaborative research endeavour exemplifies the ongoing enthusiasm and dedication towards exploring the untapped possibilities of copper as a catalyst in this groundbreaking process [2]. Despite extensive research, a consensus on the precise mechanisms governing product formation during CO₂
reduction (CO₂R) on copper remains elusive. Various studies have generated valuable insights, yet the complexity of the processes involved has led to ongoing debates and uncertainties among researchers, after three decades of research [7]. The creation of efficient catalysts that can suit our needs depends critically on our ability to comprehend these mechanisms. As a result, the presenter will discuss the current development on the molecular routes for CO₂ reduction on copper (Cu). One typical method is the conversion of CO₂ to CO, which can then combine with hydrogen to form fuels like methanol and methane. Typically, this process makes use of transition metal catalysts like copper, which can favor CO₂ reduction over rival hydrogen evolution events. CO₂ conversion into formate (HCOO⁻), serves as a valuable platform chemical, enabling the synthesis of other compounds such as formic acid and methanol, involves another process. Tin, silver, and gold are examples of catalysts that can be used to create this route [2].

Apart from these pathways, there exist various alternative routes for CO₂ reduction leading to the production of substances like ethylene. However, the selectivity and efficiency of these routes are contingent upon factors such as the catalyst used and the specific reaction conditions.

In Fig. 2, the potential pathway of CO₂ reduction reaction [2, https://pubs.acs.org/doi/10.1021/acs.chemrev.8b00705].

In the preceding section, the CO₂ reduction pathway was introduced, wherein one common route involves the stepwise reduction of CO₂ to CO before proceeding to subsequent reduction reactions. Electrocatalytic CO₂ reduction using metal catalysts, such as copper, silver, or gold, is a prominent method employed in this process. Metal catalysts are of utmost importance in facilitating the conversion of carbon dioxide (CO₂) to carbon monoxide (CO) by promoting a more favourable and energy-efficient reaction pathway. Copper emerges as a notable catalyst in driving this transformative process, in particular, has demonstrated high selectivity for CO production when utilized in conjunction with appropriate electrolytes and reaction conditions [8].

Electrocatalysts without metal components offer an alternative pathway for CO reduction by creating active sites that boost CO₂ to CO conversion by electrochemistry. The distinctive features of electrochemical CO₂ reduction make it more conducive to decentralization when compared to thermal methods. The flexibility in designing electrochemical CO₂ reduction technologies allows for quick adjustments in production to match fluctuations in electricity generated by intermittent renewable sources. The inherent adaptability of electrochemical CO₂ reduction renders it an exceedingly promising methodology for the synthesis of chemicals and fuels [9]. In Fig. 2, the potential reaction mechanisms associated with CO electrochemical reduction are depicted, showcasing the diverse pathways that can lead to the production of C₂-products or CH₄ [2].

The color-coded arrows depicted in the diagram represent the pH-dependent nature of the rate-limiting step for each reaction, as quantified on an absolute potential scale. The provided illustration offers a comprehensive depiction of the impact of pH on the rate-limiting step in various reactions. It showcases the diverse reaction pathways that result in the formation of either C₂-products or CH₄ during the process of CO₂ reduction on copper electrodes [10].

2.2. Catalysts

In the electrochemical reduction of CO₂, the catalyst is essential. Aspect from the experiment methods, Catalyst is essential, and there are some commonly studied and utilized metals for CO₂ electrolysis such as nickel (Ni) and Cu. However, among various metals, Cu stands out as a distinct catalyst, offering several advantages over its counterparts [2, 11]. Copper possesses numerous benefits when employed as a catalyst for CO₂ reduction (CO₂R). The polycrystalline and single-crystalline Cu-based electrodes demonstrate equal effectiveness and selectivity for the CO₂ electrochemical reduction, over time, the efficiency of CO₂ reduction (CO₂R) may decline, although the nature and extent of this degradation can be varied. The binding energy of CO adsorption is a crucial factor in determining how effectively a compound reduces >2e⁻ products. This intermediate will impede metals that bind CO too tightly, thus leading to desorb from the surface prior to further reaction. The Sabatier principle is well supported by the intermediate binding energy of copper for CO, which is a significant component to catalyze CO₂R into compounds that are more reduced than CO. Copper exhibits a notable advantage in terms of high Faradaic efficiencies (FE) for CO₂ reduction (CO₂R) products. Based on the experimental data obtained from metal electrodes immersed in a 0.1M KHCO₃ solution, it is noteworthy to highlight that copper demonstrates the highest total Faradaic Efficiency (FE). In fact, copper exhibits an impressive FE of 103.5% specifically for the reduction of CO₂R products [10].
Copper demonstrates the ability to suppress the competing hydrogen evolution reaction (HER) through a mechanism where CO$_2$ preferentially adsorbs on its surface. By stabilizing CO$_2$-derived intermediates such as CO$_2^-$, CO$_2$, and HCOO$^-$, which are crucial for desired product formation, copper inhibits HER activity. Moreover, employing copper-based alloys, oxides, or hybrid materials in combination with other metals or non-metals can further enhance the catalyst's selectivity and activity for CO$_2$ reduction.

2.3. Factors in the electrocatalyst

CO$_2$, formic acid, methane, ethylene, and other compounds are produced when CO$_2$ is reduced electrocatalytically, a process known as a CO$_2$ reduction reaction. The selectivity of these reactions depends on both electrocatalyst's properties and specific reaction conditions.

Though CO$_2$ reduction shows promise, there are some challenges that can limit its selectivity and productivity. Specifically, the hydrogen evolution reaction, in which hydrogen gas is generated through water electrolysis, competes with and detracts from CO$_2$ reduction, which can reduce the selectivity for CO$_2$ reduction. Similarly, the oxygen evolution reaction (OER) can also interfere with the desired CO$_2$ reduction process, leading to reduced selectivity and efficiency [11-13].

The pH level of the reaction environment is a key factor in influencing the kinetics and selectivity of the reaction. Lower pH levels tend to enhance the hydrogen evolution reaction (HER) activity, thereby reducing the selectivity of CO$_2$ reduction. Additionally, the presence of cations and anions in the solution has a significant impact on the reaction kinetics and selectivity. The presence of ions in the solution can alter the electrocatalyst's adsorption properties, thereby influencing the selectivity of CO$_2$ reduction.

Over time, electrode fouling can occur, resulting in reduced activity and selectivity. This fouling can happen due to the accumulation of intermediates or impurities during the CO$_2$ reduction process. Catalyst deactivation is another challenge that can arise during CO$_2$ reduction. This deactivation can occur through oxidation or poisoning by intermediates or impurities present in the reaction environment.

Temperature and pressure are crucial parameters that affect CO$_2$ reduction. Lower temperatures tend to increase the selectivity for methane production, although their impact on other products is not yet well understood. On the other hand, higher temperatures tend to decrease the overall selectivity for CO$_2$ reduction as HER become more dominant.

Increasing the pressure generally leads to higher total CO$_2$ reduction current, but its influence on product selectivity is not yet well-established [12]. Moreover, CO$_2$ reduction pathways can be influenced by temperature, with different reactions occurring at different temperature ranges [12]. To optimize CO$_2$ reduction for desired product selectivity, especially under non-ambient conditions, further investigation and research are needed. These initiatives will aid in the creation of effective and focused CO$_2$ reduction techniques.

3 CO$_2$R influence

![Fig. 3. Reference price of chemicals](https://pubs.acs.org/doi/10.1021/acs.chemrev.8b00705)

3.1. Economic aspects

Fig. 3 shows the CO$_2$R electrochemical reduction and the by-products produced. The graph illustrates a comparison between the energy content of various products (on the horizontal axis) and their corresponding reference market prices (on the vertical axis). The size of the circles on the graph represents the annual production quantities of each product. Additionally, from the graph it presents the minimum production cost for each product, factoring in a captured CO$_2$ price of $200 per ton of carbon (tC) and two electricity price scenarios: $50 per megawatt-hour (MWh) and $20 per MWh. The $50/MWh price corresponds to recent solar installations, while the $20/MWh price reflects the current record lows for solar installations, which are expected to become more prevalent in the future [10].

The graph is divided by a two-slope line that separates the chemicals based on whether their costs are higher or lower than the budget. Among the CO$_2$R products, CO (syngas), C (coal), and methane (natural gas) have lower costs compared to solar installations. On the other hand, CO (pure), methanol, acetaldehyde, ethylene, ethanol, propanol, and formic acid are considered lucrative due to their higher market prices. It is important to note that this comparison only considers the costs of captured CO$_2$ and electricity. There may be additional factors or errors in the analysis that could affect the feasibility of the project.

Researchers examined potential carbon dioxide reduction pathways by analyzing the net present value, which factors in capital expenses, operating costs, and product revenue over time. By adjusting assumptions until the net present value equalled zero, the analysis revealed the liquid product that would make the CO$_2$ reduction process economically viable. This modelling
approach helped identify profitable CO\textsubscript{2} reduction products and processes. Furthermore, as we look ahead, it is important to consider the potential advancements in CO\textsubscript{2}R technology and the subsequent economic advantages that may arise. The potential for a decrease in energy costs arises from the anticipated reduction in pollution levels, which could subsequently prompt the government to consider a reduction in tax fees.

3.2. Environmental aspects

The synthesis of lucrative hydrocarbon, alcoholic, and carbonyl compounds using CO\textsubscript{2}R in conjunction with renewable electricity from sources including wind, solar, and hydro power is a viable technique. Because of the wide range of uses for these goods in the chemical and energy sectors, CO\textsubscript{2}R is a potential technology for environmentally responsible and sustainable production. The process of CO\textsubscript{2} reduction (CO\textsubscript{2}R) presents numerous favourable environmental implications, notably the substantial mitigation of greenhouse gas emissions. Through the process of converting carbon dioxide (CO\textsubscript{2}) into valuable products rather than releasing it into the atmosphere, CO\textsubscript{2}R plays an active role in the mitigation of climate change. This process plays a crucial role in lessening the environmental impacts associated with global warming and helps in our collective efforts to create a more sustainable future. (2) Sustainable resource utilization: CO\textsubscript{2}R promotes the sustainable use of resources by relying on renewable energy sources to drive the process. By reducing dependence on fossil fuels for energy, CO\textsubscript{2}R helps minimize the environmental consequences linked to their extraction and combustion. (3) Waste reduction: CO\textsubscript{2}R plays a significant role in waste reduction by converting CO\textsubscript{2} into valuable fuels and chemicals. This prevents the accumulation of CO\textsubscript{2} in the atmosphere or oceans and turns it into useful products, thereby minimizing environmental harm.

4 Challenge

Despite the challenges, CO\textsubscript{2} reduction remains a vital area of research for energy and sustainability. CO\textsubscript{2}, with its high oxidation state, needs to be converted into more valuable products by transferring electrons and reducing its oxidation state. This process, known as CO\textsubscript{2} reduction, aims to produce energetically favourable and useful products while reducing CO\textsubscript{2} emissions. Following is a succinct summary of the challenges in electrocatalytic CO\textsubscript{2} reduction:

(1) High activation energy: CO\textsubscript{2} has high stability, requiring a high overpotential to drive the electrocatalytic reaction. This leads to energy inefficiency and decreased selectivity.
(2) Competing reactions: Besides CO\textsubscript{2} reduction, competing reactions like hydrogen evolution and oxygen evolution can occur on the electrocatalyst surface. These reactions reduce the efficiency and selectivity of CO\textsubscript{2} reduction.
(3) Catalyst poisoning: Reaction intermediates or impurities can poison the electrocatalyst, reducing its activity and selectivity.
(4) Low current density: The CO\textsubscript{2} reduction reaction often exhibits low current density, limiting production rates and efficiency.
(5) Catalyst stability: The durability of the electrocatalyst plays a vital role in ensuring its sustained performance over extended periods. Numerous catalysts tend to deteriorate and lose their effectiveness when exposed to the challenging conditions of the reaction environment.

5 Future overlooks

Cu-based catalysts have drawbacks in electrocatalytic CO\textsubscript{2} reduction, including poor durability and stability. Factors such as high current densities, acidic electrolytes, and prolonged reaction times can lead to decreased catalytic activity and surface changes.

Recent research has highlighted the potential of copper oxide (CuO) as a promising electrocatalyst for CO\textsubscript{2} reduction. Notably, CuO demonstrates significant advantages over pure copper (Cu) in terms of selectivity towards CO production, rendering it highly attractive for industrial utilization. Moreover, CuO's enhanced surface stability contributes to mitigating the risk of declining catalytic activity over prolonged operation.

CuO also possesses a higher surface area and more active sites, resulting in enhanced catalytic activity by facilitating CO\textsubscript{2} adsorption and activation. Other bimetallic catalysts, such as CuPb or CuAg, are used for several reasons:

Enhanced selectivity: Bimetallic catalysts, like CuAg, can exhibit improved selectivity for valuable chemical feedstocks such as ethylene and ethanol. CuPb has shown enhanced selectivity for formic acid.

Lower overpotential: Bimetallic catalysts often have lower overpotentials, reducing the energy required for the reaction and improving energy efficiency.

Improved stability: Bimetallic catalysts, including CuPb, offer enhanced stability, resulting in longer catalyst lifetimes and reduced replacement needs.

Tunable properties: Bimetallic catalysts can be tailored in composition and structure to optimize activity and selectivity for specific products or reaction conditions.

6 Conclusion

In conclusion, electrochemical CO\textsubscript{2} reduction shows great potential for carbon recycling and sustainable chemical production. It offers a pathway to mitigate greenhouse gas emissions, utilize renewable energy sources effectively, and contribute to a more sustainable future. This report discussed various aspects of CO\textsubscript{2} reduction, focusing on mechanisms, catalytic materials (such as copper), and influencing factors like pH, ions, temperature, pressure, electrode fouling, and catalyst deactivation. From an economic standpoint, CO\textsubscript{2} reduction can be cost-effective for certain products,
especially when considering captured CO₂ prices and electricity costs. Chemicals like CO, methane, and methanol can be produced at viable market prices, surpassing the costs of solar installations. As CO₂ reduction technologies advance and pollution decreases, the cost of energy may further decline, leading to additional economic benefits.

Furthermore, electrochemical CO₂ reduction aids in reducing greenhouse gas emissions, promoting sustainable resource utilization, and minimizing waste accumulation. By converting CO₂ into valuable products, this process helps mitigate climate change, reduce reliance on fossil fuels, and prevent environmental harm. However, challenges remain, such as high activation energy, competing reactions, catalyst poisoning, and low current density. Addressing these limitations necessitates further research and development to enhance efficiency, selectivity, and scalability.

In summary, electrochemical CO₂ reduction holds promise for sustainable chemical production and carbon recycling. Advancements in catalyst design, reaction optimization, and process scaling are crucial for realizing its full potential and achieving a sustainable future. Electrocatalytic CO₂ reduction can significantly contribute to the transition to a low-carbon economy and the creation of a greener planet by overcoming these obstacles.

References