Electrocatalysts for CO_2 Reduction

Subjects: Electrochemistry

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Given the environmental problems caused by burning fossil fuels, it is believed that converting carbon dioxide (CO_2) into chemical inputs is a great ally to generating clean energy. In this way, investigative studies related to electrochemical CO_2 reduction (CO_2RE) concerning the behavior of metal catalysts have received attention about the processes involved. CO_2RE can be an important tool to mitigate the presence of this gas in the Earth's atmosphere.

CO_2 electrochemical reduction electrocatalysts electrode

1. Introduction

Over the years, there has been an increase in the use of fossil fuels (oil, natural gas, and coal), which are responsible for the greenhouse effect [1][2][3]. Recent research, presented by Mikkelsen, Jørgensen, and Krebs, points out that the atmospheric concentration of greenhouse gases, including CO_2, nitrous oxide (N_2O), methane (CH_4), and chlorofluorocarbons (CFCs), reveals an excess of approximately 3.9% in relation to the natural cycle carbon [4].

CO_2 is naturally present in the atmosphere in quantities less than 0.035%, being essential to the life of the planet as it is one of the fundamental elements for carrying out photosynthesis, the process in which photosynthetic organisms transform solar energy into chemical energy, absorbing atmospheric CO_2 and transforming it into glucose and releasing oxygen (O_2), thus contributing to the chemical energy of living beings [5].

CO_2 can be captured directly from industrial sources through three methods: post-combustion capture, pre-combustion capture, and combustion of fossil fuels in a pure oxygen environment. Post-combustion capture, which uses chemical solvents such as monoethanolamine, separates CO_2 from the exhaust gas, which is composed mainly of a mixture of N_2 and CO_2 [6]. Researchers are directing efforts to reduce costs and improve the efficiency of post-combustion capture. This involves exploring more effective chemical solvents and membranes for separating CO_2 from N_2. At the same time, materials are being developed to reduce investment costs in large separation equipment required for industrial-scale capture. Research also focuses on the development of new materials capable of resisting higher temperatures and pressures, aiming to improve efficiency in energy generation with CO_2 capture [6].

One of the alternatives for reducing CO_2 emissions into the atmosphere is the conversion of atmospheric CO_2 into low-carbon fuels. It can be used as an energy storage carrier, demonstrating great importance in alleviating energy

shortages and global environmental pollution [7]. Currently, several methods for CO_2 conversion are being investigated, such as photocatalytic reduction, electrocatalytic reduction, and photoelectrocatalytic CO_2 reduction. Photocatalytic reduction of CO_2, similar to the photosynthetic process in plants, seeks to convert atmospheric CO_2 into oxygen, a function performed by green plants and photosynthetic bacteria. Over the years, scientists have developed and designed several types of photocatalysts, covering metal oxides, metal nitrides, metal phosphides, and semiconductors, among other materials [7]. Although there are a variety of photocatalytic materials, their practical efficiency has not yet reached an ideal level. Given this, researchers have explored techniques to improve photocatalytic performance, involving control of morphology and size, manipulation of the crystalline face, doping, application of noble metals, recombination of semiconductors, sensitization by dyes, and introduction of defects, among other approaches [7].

The other two methods to reduce carbon dioxide emissions are electrocatalytic reduction of CO_2 and photoelectrocatalytic reduction of CO_2. The first method is the process that uses the external electric field as the main source of energy to induce the redox reaction in the electrodes and the photoelectrocatalytic reduction of CO_2, as the two previous techniques present limitations for their application. Another method is the photoelectrocatalytic reduction of CO_2, which refers to the process in which the semiconductor photoelectrode generates electrons by photoexcitation, and then electrons migrate to the electrode surface under the guidance of an external voltage to carry out the catalytic reduction of CO_2 [7].

Concerning other processes that involve CO_2 capture, it is adsorption, because a good adsorbent should present high selectivity, high adsorption capacity at low pressure, fast adsorption/desorption kinetics, good mechanical properties, high hydrothermal and chemical stability, high regeneration capacity, and low synthesis costs. Some examples that have been studied are zeolites, metal-organic frameworks (MOFs), and carbon-based adsorbents [8].

CO_2 captured from various sources can be reused in a process known as carbon capture and utilization. This not only reduces the CO_2 concentration in the atmosphere but also reduces dependence on fossil fuel raw materials. Research focuses on CO_2 storage and capture techniques, particularly the effective and long-term use of catalysts in various CO_2 conversion reactions. Transforming this pollutant into value-added products represents a significant challenge, but it also offers many opportunities to reduce CO_2 emissions [8].

Furthermore, other approaches to dealing with CO_2 include capturing and storing it or converting it into valuable chemicals. Another method that is being extensively studied and researched is the recycling of the CO_2 molecules by electrochemical reduction [9]. The electrochemical route is the most promising of the alternatives available for CO_2 reduction, as it does not require high temperatures or high pressures for efficient reduction, uses water as a source of protons, and allows greater product selectivity than that obtained with other reduction methods. In addition to having greater operational flexibility, it can be easily installed in places with difficult access and/or the availability of cheap energy [10][11][12].

2. Electrocatalysts Types in the Electrochemical Reduction of CO_2

An electrocatalyst participates in an electron transfer reaction (at an electrode) and facilitates the acceleration of a chemical reaction [13][14]. Electron transfer reactions are the most important processes at electrochemical interfaces. They are determined by the interaction between the interaction of the reagent with the solvent and the electronic levels of the electrode surface. Both electron transfer and kinetic chemistry must be fast for an efficient electrocatalyst [15]. Furthermore, an ideal electrocatalyst must present a good thermodynamic correspondence between the redox potential for the electron transfer reaction and the chemical reaction being catalyzed (e.g., reduction of CO_2 to CO) [13][14].

The effectiveness of the electrochemical reduction of CO_2 is directly linked to the electrocatalyst, making it possible to adjust its activity and selectivity by modifying its structure. To improve electrocatalysts, two engineering protocols are widely employed: (1) increase the number of active sites on an electrode, exposing more active sites per gram through optimization of the catalyst structure; and (2) improve the intrinsic activity of each active site. These strategies are not mutually exclusive and can be combined to achieve significant improvements. Several approaches, such as nanostructures, the use of supports, modeling, alloy formation, and doping with heteroatoms, among others, are used in the manufacture of high-performance catalysts [16].

The electrocatalyst used and the applied potential electrode have a great influence on the final reduction products [10][11][17]. Metallic electrodes, such as Cu, Au, and Sn, have been extensively explored in recent decades for CO_2 reduction. The generation of intermediate CO_2 is crucial to the rate of CO_2 reduction in most cases. Therefore, the main function of these electrocatalysts is to stabilize this intermediate to achieve high energy efficiency in reducing CO_2. Metal electrodes can be classified into three groups, depending on the binding tendency of intermediates and final products, as shown in **Figure 1**. Group I has difficulty binding to the CO_2 intermediate, resulting in the formation of formate or formic acid by an outer sphere mechanism. Group II, the intermediate *CO obtained, is weakly bound to the metal surface, being easily dissolved and emerging as the predominant product. Group III, represented only by Cu, is capable of binding and converting the *CO intermediate into higher value-added products, such as hydrocarbons and alcohols, through *COH or *CHO intermediates [18].

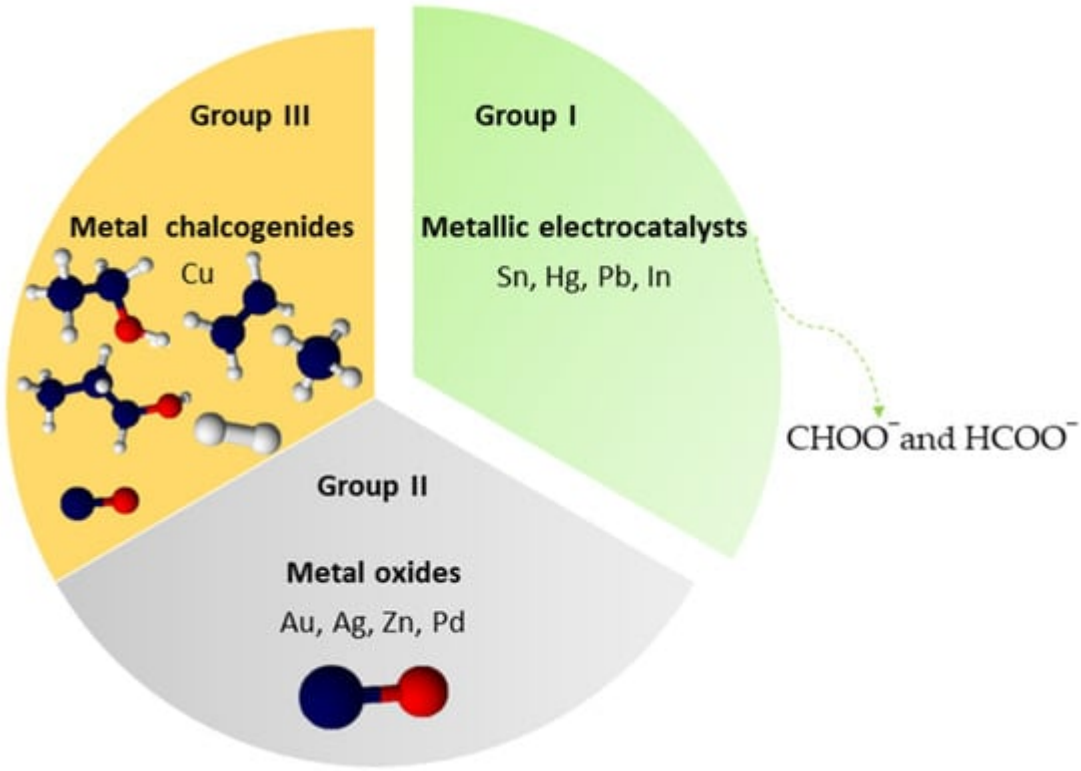

Figure 1. Classification of metal electrodes with their respective products.

To implement practical applications in the electrochemical reduction of CO_2, it is necessary to develop electrocatalysts efficient in electron transfer that operate close to the thermodynamic potential of the reaction to be conducted. Therefore, it is essential to choose a catalyst that contributes to accelerating the reaction of interest as well as the supporting electrolyte that favors the processes [19][20].

Electrocatalysts can be classified into three types, such as metallic, non-metallic, and molecular. The materials used in the preparation of the catalysts are what designate their characteristics. Therefore, metallic catalysts can have a metal in their composition or a combination of two metals, termed monometallic or bimetallic. For non-metallic catalysts, the most commonly used materials are carbon nanofiber, nitrogen-doped carbon, metal-organic structure, known as MOF, and covalent-organic structure, Covalent-Organic Framework (COF). On the other hand, molecular catalysts present in their composition the formation of macrocyclic complexes linked to some metals [21][22]. The electrocatalyst material involves the conversion of CO_2 into various products, as listed in **Table 1**.

Table 1. Main electrocatalysts described in the literature with their respective Faradaic efficiency, stability, and final products.

Electrocatalyst	Electrolyte	Main Product	Faradaic Efficiency	Stability	Ref.
$FeF_{20}TPP$/CNT-CF/CC	0.5 M $NaHCO_3$	HCOOH	95%	50 h	[23]
CuSn-4	0.5 M $KHCO_3$	HCOOH	93.7%	-	[24]

Electrocatalyst	Electrolyte	Main Product	Faradaic Efficiency	Stability	Ref.
Ni@HNC	0.1 M $KHCO_3$	CO	98.7%	-	[25]
Ag-NP	2 M KOH	CO	99.9%	-	[26]
Cu-polyamine	1 M KOH	C_2H_4	72%	3 h	[27]
Cu/PTFE	0.1M $KHCO_3$	C_{2+}	80%	24 h	[28]
Cu-12	0.1M $KHCO_3$	C_2H_4	64%	190 h	[29]
Cu/Ni(OH)	0.5 M $NaHCO_3$	CO	92%	22 h	[30]
4H/fcc Au-MMT	1.0 M $KHCO_3$	HCOOH	92.3%	12 h	[31]
CNT@mC/Ni	0.5 M $KHCO_3$	CO	98%	24 h	[32]
Ag_{75}/C	1 M KOH	CO, H_2, and HCOOH	90.1%	30 h	[33]
Pd/PdOx	0.5 M $KHCO_3$	CO	90%	24 h	[34]
ZnO	1 M KOH	CO	91.6%	18 h	[35]
Ni-N_2-C	0.5 M $KHCO_3$	HCOOH	98%	10 h	[36]
Bi-N_4	0.1 M $NaHCO_3$	CO	97%	4 h	[37]
CuNNs	5 M NaOH	C_2H_4	52%	6 h	[38]
Sn	0.1 M Na_2SO_4	HCOOH	95%	10 h	[39]
Cu–In	0.1 M $KHCO_3$	CO	55%	24 h	[40]
CuO–Sn	0.1 M $KHCO_3$	CO	90%	14 h	[41]
Cu nanowire	0.1 M $KHCO_3$	CO, HCOOH, C_2H_4	17.5%	5 h	[42]
Cu (dendrite)	[EMIM](BF_4)/H_2O (85/15 *v*/*v*)	HCOOH	87%	8 h	[43]
Ag	0.5 M $KHCO_3$	CO	30–80%	285 min	[44]
Sn	0.5 M $KHCO_3$ + 2 M KCl	HCOOH	70%	4 h	[45]
Cu-based metal–organic porous materials	0.5 M $KHCO_3$	CH_3OH, C_2H_5OH	56%	90 min	[46]

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Electrocatalyst	Electrolyte	Main Product	Faradaic Efficiency	Stability	Ref.
Cu_2O/ZnO	0.5 M $KHCO_3$	CH_4 C_2H_4	31.4%	90 min	[47]

Analyzing the work presented in **Table 1**, it can be observed that several types of electrocatalysts enable the reduction of CO_2 with high efficiency. Furthermore, it is noted that the most enterprising venture is metallic [22][48], with copper being used. This factor is related to its characteristic of continuing the reduction of CO_2 into aldehydes, hydrocarbons, and alcohol with high efficiency [49].

In previous publications regarding CO_2, Hori et al. studied the intermediate products by reducing CO at Cu electrodes, which is subsequently reduced to hydrocarbons and alcohols. CO is also formed on Ni and Pt electrodes and subsequently adsorbed on the electrode. And in this way, the adsorbed CO prevents further reduction of CO_2 in Ni and Pt. These points lead the metal electrodes to be classified into two groups: CO formation metals (Cu, Au, Ag, Zn, Pd, Ga, Ni, and Pt) and $HCOO^-$ (Pb, Hg, In, Sn, Cd, and Tl) [50][51][52].

In 2019, Zhou and collaborators [53] highlighted the need to recycle CO_2 in the atmosphere due to the greenhouse effect and the energy crisis. It addresses electrocatalytic CO_2 reduction as a viable solution but highlights the challenge of developing electrocatalysts with high activity, selectivity, and durability for this reaction. Explores recent advances in nanostructures of different dimensions as promising catalysts to accelerate CO_2 conversion, discussing the challenges and prospects for achieving high efficiency in this process.

Moreover, in 2020, Tang and collaborators [54] discussed the carbon dioxide reduction electrochemistry along transition metals, addressing a complex network of reactions. The research combines experimental observations from the literature with theoretical analysis to explain that not all intermediates in CO_2 reduction are formed by direct protonation steps. A selectivity map for two-electron products (carbon monoxide and formate) on pure metal surfaces is derived, using only the CO and OH binding energies as descriptors. The analysis rationalizes the experimentally observed product distributions in CO_2RE in pure metal systems, highlighting the need for additional descriptors for screening materials in CO_2 reduction and the importance of considering the competition in the elementary steps of the hydrogen evolution reaction.

Johnson and collaborators [55] highlighted the significant role of carbon dioxide in global warming, with the burning of fossil fuels being the main source of pollution. The capture and reduction of CO_2 for the production of valuable chemicals using renewable energy sources is an important area of research. Catalysts, support structures, and electrolytes are key factors affecting the electrochemistry of CO_2 reduction for the production of value-added chemicals and fuels. The research covers the field of CO_2RE electrocatalysts, focusing on non-precious transition metal-based catalysts and highlighting design, synthesis, characterization, and mechanisms. Advanced catalyst design, including two-dimensional metal carbide and nitride materials, and state-of-the-art in situ/operando spectroelectrochemical techniques are emphasized. The text concludes by highlighting the remaining challenges and perspectives for future research and opportunities.

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