Progress in the application of Cu-based catalysts in the electroreduction of CO_2 to produce C_{xs} products

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Abstract: Since the industrial revolution, human dependence on fossil fuels has resulted in increasingly severe atmospheric carbon dioxide (CO_2) emissions. Electrocatalytic CO_2 RR has attracted much attention because of its many advantages, such as mild reaction conditions, controllable reaction rate, low cost and scalable electrolyzer.[7] More importantly, electrocatalytic CO_2 RR can control the selective generation of target products by rationally adjusting the reaction potential, electrolyte and catalyst species. However, the CO_2 molecular structure is stable, and obtaining the key CO_2-based anionic intermediate CO_2^- from activated CO_2 molecules requires overcoming a huge energy barrier. Copper (Cu) catalysts are the only monometallic catalysts to date that can form two-carbon (C_2) products, which establishes their special position in the field. However, the poor selectivity of Cu for a particular product has led to a wide distribution of reduction products, covering the range from carbon monoxide (CO), a reduction product at $2e^-$, to ethanol ($C H_{25} OH$), a reduction product at $12e^-$. Meanwhile, Cu catalysts are generally less stable, which can seriously affect their commercialization. Currently, in order to obtain highly selective C_{2+} products (mainly ethylene and ethanol), [16]this article reviews the various methods developed by different scholars in China and abroad to modify Cu catalysts. Finally, this article suggests ways to improve the performance of Cu-based catalysts to enhance the Faraday efficiency of the C_2 product from the electroreduction of $C0_2$ and gives an outlook on the future direction of Cu-based catalysts.[19]

1. Introduction

The carbon cycle of nature can no longer accommodate the excessive amount of CO_2, and the resulting ecological problems such as global warming have had a significant impact on the natural environment and human development. Reducing greenhouse gas emissions and lowering the level of CO_2 gases in the atmosphere has become a broad consensus of the international community. Utilizing solar energy or other forms of renewable energy to create an artificial carbon cycle by converting CO_2 into valuable chemicals is an effective strategy for eliminating excess CO_2. This not only alleviates the energy and environmental crises caused by excess carbon emissions, but also creates a carbon economy of great economic value. Currently, the utilization of CO_2 reduction reaction (CO_2 RR) based on biological, thermochemical, photochemical and electrochemical methods has been widely studied.

Compared with other methods, it is therefore very difficult to achieve the reduction of chemicals, even selective reduction, which is one of the major reasons why CO_2 RR has not been industrially applied so far. Therefore, there is an urgent need to prepare efficient and stable electrocatalysts to improve the selectivity,

conversion, economy and stability of CO_2 RR. , including surface engineering, organic modification and addition of other elements to them.[14]The combination of other metal elements with copper may modulate the product selectivity by modulating the affinity of the product for carbon and oxygen, thus affecting the intermediate adsorption. However, due to the complexity of the mechanistic pathways, how many metal elements to add is still largely a matter of trial-and-error screening, which is very time-consuming. For this reason the development of high performance electrocatalysts remains one of the research priorities in this field.

2. Status of research

This chapter gives the current status of domestic and international efforts for the electroreduction of CO2 over copper-based catalysts.

2.1. Current status of foreign research

(Lin et. al., 2020) study operando time-resolved x-ray absorption spectroscopy reveals the chemical nature enabling highly selective co2 reduction. A systematic time-resolved study can provide key insights on selective carbon dioxide electro-reduction. (Wu et. al., 2020)

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report that a nanodendrite configuration for Cu catalyst can improve the electrocatalytic performance of Cu catalysts, especially multicarbon product formation, while suppressing HER and methane production. [8](Arán-Ais et. al., 2020) report improved efficiency towards ethanol by tuning the morphology and oxidation state of the copper catalysts through pulsed CO_2 electrolysis. [9](Li et. al., 2021) demonstrate a facile cation exchange method to synthesize Ag/Cu electrocatalysts for CO_2 reduction using Cu sulfides as a growth template. [11](Xiao et. al., 2021) summarize recent progress that has been achieved by tailoring the electrocatalyst architecture for efficient electrochemical CO_2 conversion to the target C_2 products.[12](Peng et. al., 2021) study double sulfur vacancies by lithium tuning enhance co2 electroreduction to n-propanol. The work suggests an attractive approach to create anion vacancy pairs as catalytic centers for multi-carbon-products. (Cao et. al., 2021) offer an effective avenue to design electrocatalysts for the highly selective CO_2RR to produce multicarbon products via a tandem route. Since the initial Cu^{2+} active sites are hard to retain, there have been few studies about Cu^{2+} catalysts for CRR.[13] (Zhou et. al., 2022) propose a solid-solution strategy to stabilize Cu^{2+} ions by incorporating them into a CeO_2 matrix, which works as a self-sacrificing ingredient to protect Cu^{2+} active species. [14]

2.2. Current status of domestic research

(Shengnan Wang et al.,2023)pointed out that the electrocatalytic reduction of CO_2 is expected to allev-iate the problems of depletion of fossil fuels and in-creasing concentration of CO_2 in the atmosphere at the same time.However,there is still a great challeng-e to improve the selectivity of the high-value-added multicarbon products for electrocatalytic CO_2 reductio-n.Therefore,they designed an activation strategy for oxide-derived copper electrodes to construct the Cu_2-O-Cu interface,and synergistically promoted the elec-trocatalytic CO_2 reduction with $Cu^+$and CuO to gen-erate $C_{(2+)}$products with high efficiency and high sele-ctivity.They demonstrated that the synergistic effect of Cu^G and Cu^+at the Cu_2 O-Cu interface could inde-ed enhance the selectivity of specific high-value-added multicarbon products in the electrocatalytic reduct-ion of CO_2.[2](Yongda et al.,20,21,22,23).(Y.D.Zhang et al.,2021)showed that Cu-based nanocatalytic material-s were prepared to facilitate the reduction of CO_2 t-o C_2 products at low overpotentials.The catalysts wer-e prepared,characterized,structurally and compositiona-lly analyzed and electrochemically tested.This stabili-zes the generation of C_2 products as well as improv-es the

electrocatalytic activity of Cu-based catalysts.[5](Niu Di et al.,2021)pointed out that the introduction of another metal to form a tandem catalyst on top o-f a Cu-based catalyst is an effective way to improv-e the selectivity of multicarbon products.The tandem catalyst can convert CO_2 to carbon monoxide(CO) over the introduced metal,which is subsequently redu-ced to the multicarbon product by the copper-based catalyst.Based on cuprous oxide(Cu_2O)catalysts,they introduced silver(Ag)and gold(Au)to form tandem cat-alysts with Cu_2O with the aim of achieving highly selective electrocatalytic reduction of CO_2 to C_2 prod-ucts and providing a new idea for the macro prepar-ation of nano-sized Cu_2O tandem catalysts.[6]

3. Commentary

The application of catalysts for the electroreduction of CO_2 to produce the C_{2+} product has been analyzed in detail by our scholars, and it has been found that most of the catalysts suffer from the problems of low selectivity for the C_2 product and weak catalytic activity. On the other hand, Cu is widely used as a CO_2 RR catalyst due to its moderate affinity for CO and can be used for subsequent C-C coupling, which can generate a large amount of C_2 product in aqueous solution with high efficiency and kinetic activity. [18]

Existing studies by our scholars show that the selectivity of Cu-based catalysts for highly reduced products is still low; on the other hand, Cu is the only active component reported so far that can be used for the production of highly reduced products, but it still suffers from the drawbacks of high overpotentials and low Faraday efficiencies (slow kinetics of the conversion of CO_2 to CO on Cu), which leads to the low efficiency of the CO_2 RR for the production of highly reduced products.

In this review, we summarize the recent strategies used by the scientific community (as shown in Table 1 below) including oxide and halide-derived copper nanoparticles. Specifically for the reduction of electrochemical CO_2 to polycarbon hydrocarbons and related oxygenated compounds. Obtaining C_{2+} products is a challenge because copper-based catalysts have different selectivities for different products.The researchers involved are trying to control the properties associated with copper-based catalysts to obtain the products we need.

Table 1 Kinetic activity, and is widely used as a CO_2RR catalyst.

Types	Catalyst	Electrolyte	Synthesis method	Performance parameters	Ref.
Oxide derived	cv treated copper electrode	0.1mol $KHCO_3$	Cu electrodes were prepared by PVD, then treated with Cv and electrodeposited on silicon wafers, and the prepared Cu electrodes were	Main products electrodeposited copper H_2, methane, formic acid finite elements 50%, 30% and 10%	[14]

			cycled and chemically deposited in the potential region of 0.55-0.3v, respectively.	
Halide derived	CuX (X = Cl, Br or I)	0.1 mol $KHCO_3$	Electropolished copper foil synthesized by electrophoresis in different 0.1 M potassium salt solutions	FE C2+: 80 % on cuprous iodide at 0.9 V, about 66-73 % on cuprous bromide and cuprous chloride at 1.0 V; partial geometric current density: about 31.2 mA cm 2 on cuprous iodide electrode [17]

To address such issues, this article reviews the modification strategies of Cu-based catalysts to improve the performance of the C_{2+} product from the electroreduction of CO_2 .

（1）The multi-step PCET (proton-coupled electron transfer) treatment of sequential intermediates suggests that tuning the adsorption energy of specific reaction intermediates on the catalyst surface to the appropriate level is an effective means of facilitating the selectivity of the C_2 product. In addition, the ease of C-C coupling depends on the surface coverage and adsorption sites of CO. Based on the above theoretical principles, researchers have carried out extensive modification and design of Cu-based catalysts to tune the adsorption capacity of the key intermediates.[1]

（2）Researchers can also construct environments with high CO concentrations, including designing unsaturated coordination atoms, controlling the oxidation state of Cu, preparing Cu nanocubes with different crystalline surfaces, and constructing tandem catalytic systems. The size, morphology and structure of the nanomaterials determine the average number of coordinating atoms in the catalyst.[3]

（3）The coordination number and atomic environment affect the orbital overlap between the surrounding electrons, changing the electronic structure of the active component, which can directly affect the reactivity of the catalyst and substrate. Monoatomic copper has the smallest coordination number.[4]

（4）Since the electronic structure of monoatomic Cu is fundamentally different from that of native Cu, this also leads to a general lack of C-C coupling ability of monoatomic Cu, whose electrolysis products are mainly C_1 products such as CH_3OH, CH_4 , CO. In oxide studies, it has been found that the near-surface oxygen of oxidized derivatives of Cu can reduce the σ-repulsion between CO and surface Cu atoms by extracting the electron density from the surface atoms, thus increasing the bonding strength of CO. CO dimerization is a key step in the formation of the C-C bond and is accompanied by the Cu surface after In addition, oxidized derivatives of Cu can also induce positive interactions between Cu^0 and Cu^+ through the formation of a mixed-valence state, thereby significantly increasing the C-C coupling capacity of CuO. The positive interaction between CuO and Cu^+ can be induced by the formation of mixed valence states, which significantly improves the selectivity of the C product.[10]

4. Summary and outlook

(1) In this article, we consider that the C-C coupling reaction, which determines the selectivity of single-carbon (C_1) or multicarbon (C_{2+}) products, is a thermocatalytic step that does not involve the transfer of protons and electrons, and thus the catalyst material and surface structure play a decisive role in it. [15]Therefore, our next research direction utilizes nanotechnology principles to design fine and rational electrocatalyst structures that can significantly affect the adsorption energies of some key intermediates and thus the inherent reaction pathways of Cu catalysts;

(2) The combination of other metal elements with Cu may affect the intermediate adsorption by modulating the product selectivity through regulating the affinity of the product for carbon and oxygen. However, due to the complexity of the mechanistic pathway, the amount of metal elements to be added is still largely a matter of trial-and-error screening. Therefore, in order to develop high-performance Cu-based electrocatalysts, our next step could be to explore composite Cu-based catalysts with better performance for the electroreduction of CO_2 product C_{2+} product by comparing the activities of different metal additions into the Cu-based catalysts.[20]

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