

Research of Carbon Dioxide Reduction in New Energy Applications

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Abstract. Carbon dioxide is a significant byproduct from the usage of fossil fuels. Due to the rapid development of industry and the swift growth of urban populations, carbon dioxide has been accumulating in large quantities over the past decades. In terms of new energy research, carbon dioxide reduction has been given significant attention due to its non-toxic nature and the high utility of the products from its reduction. Electrochemical reduction, in particular, has been highlighted for its notable benefits. This paper introduces the mechanism of electrochemical carbon dioxide reduction, its current shortcomings, and methods of improvement, summarizing the recent deficiencies and advancements in electrochemical carbon dioxide reduction. The current belief is that refining the electrolytes like ionic liquids and using catalysts such as graphene and its derivatives can enhance the electrochemical reduction of carbon dioxide. This paper looks forward to research findings that will discover better electrolytes and catalysts to address the current deficiencies in carbon dioxide reduction and hopes to promote the full potential of electrochemical carbon dioxide reduction in future new energy applications.

Keywords: Electrochemistry, carbon dioxide reduction, graphene, Ionic liquids, catalysis.

1. Introduction

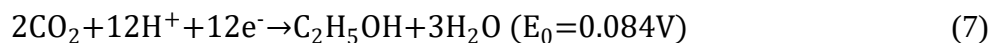
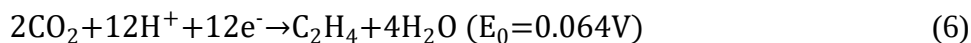
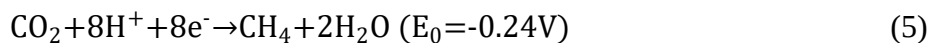
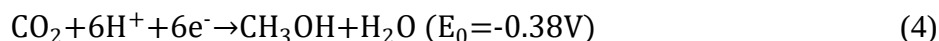
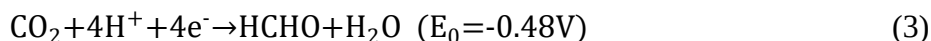
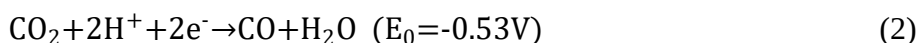
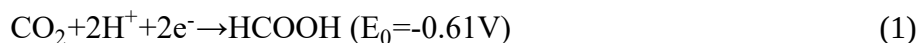
Carbon dioxide is a significant byproduct from the consumption of fossil fuels. Owing to fast industrial development and rapid urbanization, there has been a significant build-up of carbon dioxide over past decades [1, 2]. Currently, there are two global challenges related to carbon dioxide. First, the atmospheric concentration of carbon dioxide has surged to unparalleled levels and continues to climb, contributing significantly to global climate shifts, increasing sea levels, and the acidification of oceans. Second, given the finite nature of fossil fuels, the cost of using them may progressively rise, potentially resulting in an escalation of energy prices. Hence, there's a pressing need to develop greener and more sustainable energy alternatives. When it comes to innovative energy research, carbon dioxide reduction is spotlighted due to its benign nature and the significant applicability of its reduced products. The products from the reduction of carbon dioxide generally encompass high-value substances such as alcohols, hydrocarbons, and carbon monoxide [3]. These products often serve as raw materials for various reactions and have extensive applications in the new energy sector. Presently, in the realm of carbon dioxide reduction, there's a predominant emphasis on approaches like photoelectrochemical, electrochemical, and photocatalytic reductions. Electrochemical reduction stands out for its distinctive benefits: (i) Its system functions under ambient conditions of temperature and pressure; (ii) There's ease in modulating the entire reaction system by tweaking parameters like pH, choice of electrolyte, and overpotential; (iii) The energy propelling the reaction can be harnessed from green sources such as wind, solar, and geothermal energy, rendering the whole process eco-friendly [4].

Despite the numerous advantages of electrochemical reduction of carbon dioxide, due to the stability of carbon dioxide (CO₂) molecules, there remain many challenges in the actual reaction process. For example, the reaction demands excessive overpotentials, and the variety of reaction products complicates the precise extraction of required compounds [5]. This paper will discuss recent studies on electrochemical CO₂ reduction and provide a perspective on its future advancements.

2. Mechanism of Electrocatalytic CO₂ Reduction

2.1. Mechanism of Electrochemical Reaction

All the provided potentials are known as the Standard Hydrogen Electrode (SHE when pH is 7), as shown in equation (1)-(7).



2.2. Reduction Products of Carbon Dioxide

Chemical remediation techniques are a relatively common means of remediating oil-contaminated land. The current classification of this technology includes chemical oxidation, chemical scrubbing, solvent extraction and photocatalysis. Fig. 1 is the market price of select CO₂ recycling products as a function of energy content.

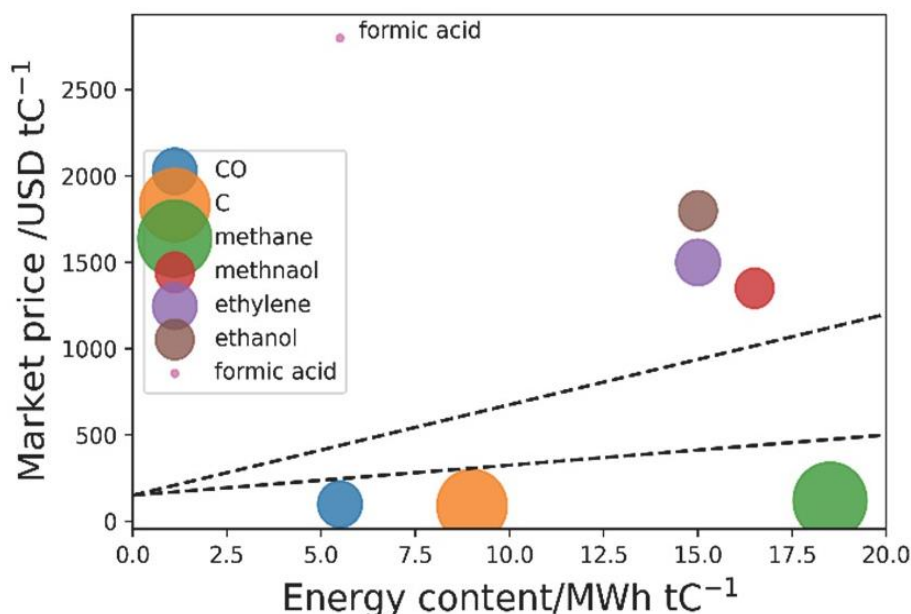


Figure 1. Market price of select CO₂ recycling products as a function of energy content.
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Recently, the primary focus of electrochemical CO₂ reduction studies have been on products like methane, ethylene, ethanol, and methanol. These are high-value energy-rich products. Their production involves different reaction pathways and mechanisms. For example, producing ethylene through electrochemical CO₂ reduction requires a transfer of 12 electrons.

Ethylene is primarily produced by reducing carbon dioxide using copper [6]. Ethylene is a critical chemical raw material and serves as an essential indicator of a country's petrochemical industry. Currently, ethylene is mainly produced through petrochemical processes, often by cracking petroleum. This process is not environmentally friendly and relies on non-renewable materials. Therefore, producing ethylene through electrochemical carbon dioxide reduction is a cleaner and more sustainable method. Ethylene products are primarily found in our daily life in the form of polyethylene and derivatives like PVC, styrene, and ethylene-propylene rubber. In organic synthesis, it is extensively used to produce ethanol, ethylene oxide, ethylene glycol, acetaldehyde, acetic acid, propionaldehyde, propionic acid, and other foundational organic synthesis materials. Additionally, in agriculture, ethylene promotes fruit ripening and is used to produce ripening agents.

Methane is also majorly produced by reducing CO₂ using copper. Its defining characteristic is the high calorific value, making it a superior fuel. Methane also serves as a critical chemical raw material for producing entities like acetylene and various chlorinated methane forms. Presently, methane's primary extraction method is from petroleum. Producing methane through electrochemical CO₂ reduction stands as a significant way to store energy within chemical bonds.

Methanol is also a product of electrochemical CO₂ reduction, with a comparatively simple reaction pathway. Conventionally, methanol is produced using synthesis gas derived from steam reforming of methane or naphtha and coal gasification. Methanol serves as an excellent fuel, being safer than hydrogen (64.7 °C). It can blend with gasoline, albeit at half the volumetric energy density of gasoline or diesel. Additionally, a unique methanol fuel cell has been researched where methanol directly oxidizes with air, generating CO₂, water, and electricity without the intermediate hydrogen generation step. This substantially streamlines fuel cell technologies for widespread applications. Moreover, methanol can replace petroleum in producing olefins like ethylene and propylene.

Among various catalytic methods, due to the high energy density of ethanol and its widespread applications, the electrochemical reduction of CO₂ to ethanol has significant prospects. Ethanol has a wide range of applications in the chemical industry, medical and health care, food industry, and agricultural production. As an organic solvent, ethanol is widely used in various chemical reactions as a solvent. Additionally, ethanol holds important research significance in the realm of drug delivery. Currently, ethanol has become an important blending component in the refining industry. In 2013, it was estimated in the US that 700 million gallons of blended gasoline ethanol had a high octane rating (RON~109) and four times the vaporization latent heat of gasoline on a stoichiometric basis. These characteristics improve the anti-knock quality of oil-based fuels, thereby enhancing engine efficiency and reducing greenhouse gas (GHG) emissions.

2.3. Chemical Oxidation

Choosing specific target products optimizes the economic viability of CO₂ electrolyzers. However, the design intricacies of the electrolyzer are paramount, even more so than in hydrogen production via water splitting [7]. Minor modifications in reaction parameters—such as temperature, pressure, flow rate, ion availability, contaminants, and pH—can induce significant variations in the selectivity of reactions within the CO₂ electrolyzer. Sustaining the requisite power, thermal energy, water, and other essential resources for CO₂ electrolyzers influences their adaptability and feasibility across diverse operational environments. Considering the vast economic disparities between electrolyzers extracting CO₂ from capture solutions and those demanding pure gaseous inputs, it's more beneficial to benchmark systems in line with feedstock prerequisites. The structure and properties of Gas Diffusion Electrode (GDE) involve the introduction of reactants to the metal catalyst. We have categorized the currently used electrolyzers into three types, summarized based on feedstock requirements covering all types of CO₂ electrolyzers, to simplify the various reactor architectures proposed so far. The key functionality of these electrolyzers lies in the structure and characteristics of their cathode GDE, where reactants are introduced to the catalyst metal. The three categories are: electrolytes with dissolved CO₂ at the cathode, gas-supplied cathodes, and high-temperature electrolysis.

2.3.1. Electrolytes with dissolved CO₂ at the cathode

This category includes electrolyzers that function with liquid anodes and cathodes and necessitate the dissolution of CO₂ in the cathode. They utilize a range of electrolytes, frequently relying on liquid ones for ion transport between the anode and cathode. Their architecture is analogous to that of water splitting electrolyzers; however, the cathode materials are more conducive to CO₂ reduction compared to platinum. Liquid electrolyzers can employ basic organic compounds as electrocatalysts and incorporate ionic liquids to enhance catalyst performance. However, ionic liquids have been proven to be unstable at high current densities. They also facilitate the direct reduction of CO₂, providing the ability to modulate pH and CO₂ capacity within the solution. In Type 1 electrolyzers, the CO₂ flux limitation to the catalyst is significant. The formation of bubbles should also be considered when designing these systems. Evaluating these electrolyzers involves looking at factors such as CO₂ capacity, additives, corrosion rates, and the ease of product separation.

2.3.2. Gas-supplied cathodes

This class of Proton Exchange Membrane (PEM) electrolyzers primarily introduces concentrated anhydrous CO₂ to the cathodic gas diffusion layer while supplying water to the anodic side. A hallmark of these devices is the CO₂ reduction at the juncture where the CO₂ gas, electrolyte, and catalyst converge. The membrane's pH and its surface acidity or alkalinity have a pronounced impact on the output of CO₂ reduction products. Contemporary designs employ hydrophobic materials, such as PTFE, to bolster the conveyance of gaseous CO₂ to the catalyst. A key advancement of these electrolyzers is the use of anion exchange membranes instead of cation exchange membranes, achieving nearly 90% Faraday efficiency in CO production. The localized pH on the catalyst's surface holds a key role in CO₂ electrolysis and is influenced by the membrane's composition and the design of the electrolyzer. The GDE design is vital for these electrolyzers, wherein the cathode GDE segregates the gaseous CO₂ feed from the liquid catholyte. The main strengths of these electrolyzers lie in their elevated current density, robustness, energy efficiency, and the ability to separate products. Nonetheless, in practical operating conditions, harnessing actual CO₂ streams necessitates the efficient use of dilute discarded CO₂.

2.3.3. Elevated thermal electrolytic process

Solid Oxide Electrolysis Cells (SOECs) employ specific gas inlet streams directed towards both the anodic and cathodic chambers, and depend on porous ceramic materials for electrodes and solid electrolytes to conduct ions. Operating within a temperature range of 300°C to 1,500°C, these devices have witnessed a surge in product development, attributed to their dependability and long lifespan. While SOECs offer superior thermal efficiency and show consistent performance in CO generation from pure CO₂ feedstock, their high operational temperatures limit their applicability for immediate CO production. Moreover, instances of these systems producing C²⁺ products are rare. These systems grapple with challenges stemming from contaminants in the CO₂ raw material and restricted transient functioning. Even with the mentioned limitations, this technology is on the brink of commercial adoption.

3. Problems and Solutions in Electrocatalytic Reduction of CO₂

3.1. Problems

Although the electrochemical reduction of carbon dioxide presents broad application prospects, especially in the realm of sustainable energy solutions, there are still many challenges that researchers face in current studies. Additionally, the reaction often requires a high overpotential, which can lead to low reaction efficiency. This not only hampers the scalability of the process but also increases the energy input, making it less cost-effective. Addressing these challenges is pivotal for the widespread adoption of this technology.

3.2. Solutions

In light of the prevailing challenges associated with the electrochemical reduction of carbon dioxide, the scientific community has embarked on rigorous investigations to elucidate potential solutions. Among the myriad of methodologies being probed, the quest for avant-garde electrode materials and the judicious selection of catalysts have emerged as paramount. Furthermore, the refinement of reaction apparatuses and the strategic choice of electrolytes are under intensive scrutiny. Presently, the research paradigm is distinctly oriented towards the identification and characterization of high-efficacy catalysts and the nuanced selection of electrolytes, given their intrinsic role in reaction kinetics and thermodynamics. This manuscript endeavors to provide a comprehensive discourse on these two pivotal domains, underpinned by empirical data and contemporary research findings.

3.2.1. Improvement of catalysts

Studies on the electrochemical reduction of CO₂ are centered on the discovery and enhancement of novel electrocatalysts. Lately, graphene and its derivatives, attributed to their expansive specific surface area, potent electron transfer capacity, exceptional stability, and modifiable structure and surface traits, have been deemed as superior catalysts for electrochemical CO₂ reduction, predominantly yielding an array of carbonaceous fuels and premium chemicals [8]. They primarily fall into two categories: electrocatalysts centered around precious and non-precious metal-based active centers (with a particular emphasis on the latter) and graphene-based non-metallic electrocatalysts characterized by their inherent structures, doping agents, and modifiers serving as active sites. Pertaining to catalysts formulated from graphene and metals, they predominantly segregate into unions of graphene paired with precious metals and graphene allied with non-precious metals.

Compared to precious metals, the most evident advantages of non-precious metals are their higher abundance, lower cost, and broader variety. Nonetheless, the majority of electrocatalysts based on non-precious metals grapple with challenges such as significant overpotentials, diminished conductivity, and compromised stability and selectivity. Materials like graphene oxide, derived from graphene, stand out as one of the frequently employed compounds to counteract the shortcomings of non-precious metals. By complexing, these materials can stabilize the properties of metals. Their mutual interactions have the potential to modify the metal's electronic structure, thereby amplifying the CO₂ reduction reaction (CO₂RR) activity [9]. Combinations involving graphene and metals typically outperform their standalone counterparts. Therefore, to achieve efficient carbon dioxide reduction, equal emphasis should be placed on designing active metal centers and adjusting the properties of the graphene substrate. The majority of research is centered on specific catalytic functionalities, like the standalone CO₂ reduction reaction or redox reactions. Limited research delves into the multifaceted nature of non-precious metal-based CO₂ reduction electrocatalysts when paired with graphene. Nonetheless, they showcase potential in catalyzing diverse electrolytic reactions. For instance, composite materials like nickel phthalocyanine (NiPc) combined with reduced graphene oxide (rGO) serve as electrocatalysts for both CO₂RR and ORR. Given their analogous catalytic routes, catalysts apt for CO₂RR might also exhibit potential in catalyzing ORR and the reverse holds true. This underscores the imperative for augmented research to unearth versatile electrocatalysts pertinent to other pivotal reactions associated with CO₂RR and devices dedicated to energy storage and conversion. In the context of precious metals, catalysts derived from precious metal-graphene combinations boast remarkable durability and catalytic prowess, garnering substantial interest from the research community. Typically, RuN₄ doped with graphene oxide (GO) and subsequently modified with oxygen atoms is used as an effective catalyst, which can reduce carbon dioxide to formic acid (HCOOH). Simultaneously, Density Functional Theory (DFT) calculations provide a theoretical underpinning for employing the noble metal rhodium (Rh) in conjunction with N-co-doped graphene as electrocatalysts for CO₂RR. By adjusting the Rh-N composition in RhN_x-graphene (where x values are 2.3 and 4), it's possible to optimize both catalytic activity and selectivity.

Within RhN_x-graphene catalysts, varying *x* values yield distinct primary products. Specifically, with *x* equating to 2, methane (CH₄) emerges as the predominant product; methanol (CH₃OH) dominates when *x* is 3, and HCOOH prevails for *x* set at 4. Additionally, recent experimental endeavors have led to the synthesis of precious metal Ru nanoparticles (NPs) integrated with N and S co-doped graphene (NS-G). This composite acts as a dual-purpose catalyst for both CO₂RR and CO₂ deposition within Li-CO₂ batteries. In terms of precious metal research, the emphasis should be on optimizing their efficiency and longevity, leading to the fabrication of a broader spectrum of precious metal-graphene catalysts.

3.2.2. Improvements in electrolytes

During the Electrolytic conversion of CO₂, the electrolyte plays a crucial role in the dissolution of CO₂ and its reaction mechanism. The dissolved CO₂ serves as the reactant, and the electrolyte solution provides the necessary protons for the reaction. Currently, most electrochemical CO₂ reduction reactions are conducted in aqueous solutions, such as Na₂SO₄, KCl, and K₂CO₃ solutions. However, under conditions of 25°C and one atmospheric pressure, the solubility of CO₂ in water is only 0.033mol/L, which significantly limits the efficiency of the reaction.

In recent years, ionic liquids (ILs) have emerged as a new avenue for the electroreduction of CO₂ when used as electrolytes [10]. Their unique physical and chemical properties offer advantages such as reducing the overpotential of the reaction, suppressing the hydrogen evolution reaction (HER), and enhancing product selectivity. ILs are gaining increasing attention in the electrochemical reduction of CO₂. When ILs are used as electrolytes in the electrochemical reduction of CO₂, they can modulate the reaction pathway of CO₂, reduce the required activation energy, and thus enhance the reaction efficiency. For instance, Rosen and colleagues studied the change in free energy for the reduction of CO₂ to carbon monoxide in water and ionic liquid electrolytes. The research found that the complex intermediates formed due to the reaction of cations in the ionic liquid with CO₂ significantly reduced the overall activation energy required for the reaction. This, in turn, lowered the overpotential, making the reaction more favorable.

Furthermore, ILs influence the selectivity of the reduction products of electro reduced CO₂. For example, Kang and his team prepared Zn-MOFs materials via a solvothermal technique, they were adsorbed onto carbon paper (CP), resulting in the formation of Zn-MOFs/CP electrode structures. This electrode, when used in an ionic liquid, primarily produced methane (CH₄) during CO₂ reduction, marking the first instance of selective CH₄ production in an electrocatalytic system. In the research indications are that the cations of ILs initially associate with the surface of Zn-MOFs. The CO₂ is subsequently sequestered by the ILs present on the Zn-MOFs interface. Following this, CO₂ undergoes an electron addition, which results in the formation of CO₂⁻, which is stabilized by the ionic liquid through coordination. Following this, it undergoes an additional electron acquisition, leading to the formation of CO. The generated CO₂ associates with the Zn-MOFs interface, undergoing a reduction involving the uptake of six electrons and six protons, culminating in the formation of CH₄. This research elucidates a mechanism for the electrochemical conversion of CO₂ to methane. Fig. 2 is ionic liquid electrolyzer

In conclusion, using ILs as electrolytes can reduce the activation energy of the reaction, enhance reaction efficiency, and effectively select reaction products. However, due to their relatively high cost and challenges.

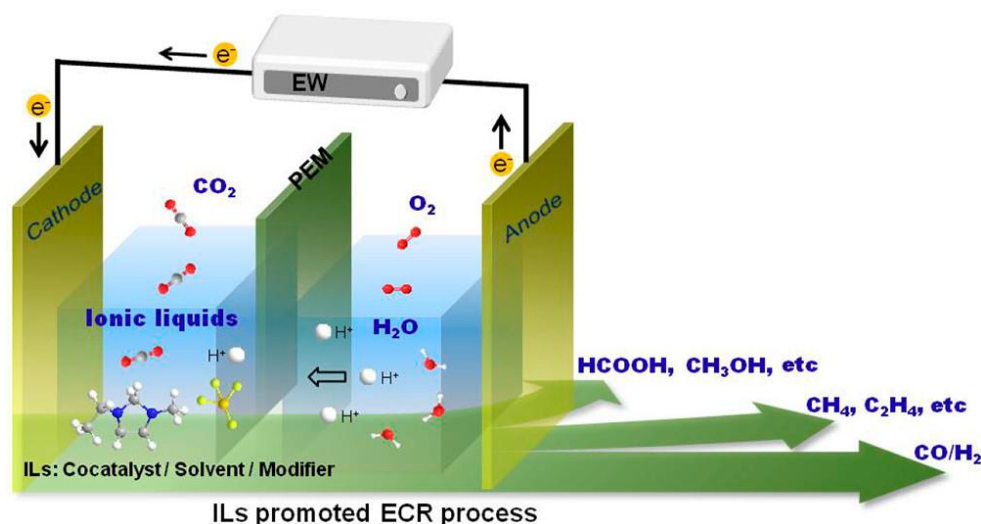


Figure 2. Ionic liquid electrolyzer. <https://doi.org/10.1021/acs.iecr.0c04037>

4. Conclusion

The technology of electrochemical reduction of carbon dioxide holds significant implications in energy utilization and environmental protection. It has now become one of the most active fields in electrochemistry and materials science. This article has discussed the mechanism of electrochemical reduction of carbon dioxide, the application of its products, and summarized the current challenges and issues. The products of CO_2 reduction are diverse and have extensive economic benefits and applications. However, the selectivity of its products is poor, making it difficult to choose the desired products. Moreover, the CO_2 molecule is very stable, requiring a high overpotential for the reaction. To address these challenges, this article has discussed the catalysts and electrolytes required for the reaction. Currently, in terms of electrolytes, ILs have demonstrated excellent performance. Graphene and its derivatives have attracted researchers' interest due to their outstanding advantages as catalysts. However, at present, due to its high reaction cost and low efficiency, there is still a vast room for development in the electrochemical reduction of carbon dioxide. In the future, researchers should focus on addressing the aforementioned shortcomings, developing more efficient and economical reaction systems, and realizing commercial applications. This article offers some suggestions for the further development trend of electroreduction of carbon dioxide.

References

- [1] Mikhail G.I.D., Marc A., Rosen, Greenhouse gas emissions reduction by use of wind and solar energies for hydrogen and electricity production: Economic factors. *International Journal of Hydrogen Energy*, 2007, 32 (8): 927 - 931.
- [2] Seyed E.H., Mazlan A.W., Ghobad B., A review on green energy potentials in Iran. *Renewable and Sustainable Energy Reviews*, 2013, 27: 533 - 545.
- [3] Zhao L., et al., Efficient photoreduction of carbon dioxide into carbon-based fuels: a review. *Environmental Chemistry Letters*, 2023, 21 (3): 1499 - 1513.
- [4] Lee S., Choi M., Lee J., Looking Back and Looking Ahead in Electrochemical Reduction of CO_2 . 2020, 20 (2): 89 - 101.
- [5] Seger B., Robert M., Jiao F., Best practices for electrochemical reduction of carbon dioxide. *Nature Sustainability*, 2023, 6 (3): 236 - 238.
- [6] Sturman M., Oelgemöller M., Process Parameters in the Electrochemical Reduction of Carbon Dioxide to Ethylene. 2021, 8 (3): 149 - 188.
- [7] Chen C., Khosrowabadi Kotyk J.F., Sheehan S.W., Progress toward Commercial Application of Electrochemical Carbon Dioxide Reduction. *Chem*, 2018, 4 (11): 2571 - 2586.

- [8] Delgado S., et al., Electrochemical Reduction of Carbon Dioxide on Graphene-Based Catalysts. 2021, 26 (3): 572.
- [9] Hu H., et al., Graphene-assisted construction of electrocatalysts for carbon dioxide reduction. Chemical Engineering Journal, 2021, 425: 130587.
- [10] Cui Y., et al., Ionic Liquids-Promoted Electrocatalytic Reduction of Carbon Dioxide. Industrial & Engineering Chemistry Research, 2020, 59 (46): 20235 - 20252.