

Electrochemical Conversion of Carbon Dioxide

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The excess carbon dioxide emissions generated by the use of fossil fuels cause serious environmental problems and hinder the sustainable development of our society. Electrochemical CO₂ reduction reaction represents a viable alternative that could close the anthropogenic carbon cycle and convert intermittent electricity from renewable sources (i.e., solar energy and wind energy) into chemical energy in the form of fuels and valuable chemicals. However, CO₂ electrolysis technology is not yet well established, and there are significant hurdles to overcome for practical applications in terms of energy efficiency, reaction selectivity, and overall conversion rate. In this context, researchers have made significant efforts. This Special Issue aims to draw attention to CO₂ electrolysis technology. We have selected six research papers covering reactor design [1], catalyst design [2–5], and catalytic reaction mechanism [6] for electrocatalytic CO₂ reduction.

A brief summary of each selected paper in this Special Issue is as follows:

Ya Liu et al. [1] explore the effect of using an industrialized setup (large electrochemical cell) and a laboratory setup (small electrochemical cell) on the selectivity of the electrocatalytic CO₂ reduction reaction. Interestingly, when Ag is used as the catalyst, the small reaction cell shows a high CO Faradaic efficiency compared to the large reaction cell. However, when In is used as the catalyst, the HCOOH selectivity is almost the same in the two reaction cells. The results show that the reaction device only affects the gas selectivity but has no effect on the liquid product selectivity. The authors show that when a large reaction cell is used, the gas concentration on the catalyst surface is very high. A large number of bubbles could affect the mass transfer of CO₂, thereby affecting the CO selectivity, while the liquid product has no effect due to the absence of bubbles. The results could be a guide for industrial productions in the future.

Robert L. Sacchi et al. [2] prepare an inexpensive copper–tin alloy to convert CO₂ to CO in acetonitrile/imidazolium-based electrolyte and modulate the efficiency of the CO₂ reduction reaction by varying the alloy composition ratio. The authors discover that when using imidazolium-based ([Im]⁺) electrolytes, CuSn has a good synergistic effect with [Im]⁺ cations, exhibiting high CO Faraday efficiency. On the one hand, [Im]⁺ cations can be used as proton donors, which can stabilize the reaction intermediates formed at the cathode/electrolyte interface via the improved proton and electron transfer during carbon dioxide reduction, thereby improving the kinetics of electrocatalysis. On the other hand, a higher Sn content in the alloy leads to the less favorable reaction kinetics of electrocatalysis. The reaction kinetics can thus be tuned by regulating the ratio of bimetallic components in the alloy.

Ruggero Bonetto et al. [3] explore the effect of the electronic character of iron complexes on the reactivity of electrochemical carbon dioxide. Due to the rich chemistry of Fe metal centers, it allows for their application in oxidation and reduction processes. During the CO₂ reduction reaction, Fe^I can react with CO₂, so Fe complexes have received widespread attention. However, the characterization of the important intermediates of metal complexes involves the transformation of small molecules, which is crucial for the mechanism and design of catalysts. The authors study the electronic and spectroscopic characteristics of Fe^I intermediates in five Fe complexes and evaluate their effects on the



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reactivity of electrochemical carbon dioxide. The results show that the reduction potential of $\text{Fe}^{\text{II/I}}$ coupling is correlated with the electronic and spectroscopic characteristics of the Fe^{I} intermediates in the complexes. The results are instructive for the design of catalysts, which is beneficial for the development of efficient CO_2 conversion.

Gianluca Zanellato et al. [4] explore the effect of electrodeposition conditions on the catalyst morphology and selectivity of electrochemical carbon dioxide reduction. The authors prepare catalysts by adding different additives and applying different current densities and explore the influence of additives and current densities on catalyst morphology. Then these catalysts are applied to electrochemical CO_2 reduction reaction to explore the effect of additives and current density on the selectivity of electrochemical CO_2 reduction reaction. The results show that different catalyst shapes can be obtained by adding different additives (DATB, DAT, PEG), and the selectivity of catalysts can be significantly improved by controlling the type of additives. However, while the current density can control the morphology of the catalysts, the selectivity of the electrocatalytic CO_2 reduction reaction depends on the type of additives. This study provides assistance in further understanding the association between catalyst morphology and selectivity.

Amir Masoud Parvanyan et al. [5] review the application of porous materials for CO_2 reutilization. In this review, the authors introduce three techniques for CO_2 reduction, including solar thermochemical conversion CO_2 reduction, photochemical CO_2 reduction, and electrochemical CO_2 reduction. While these techniques are highly sensitive to the catalyst surface, their performance is closely related to the effective surface area of the catalyst. Porous materials have a porous structure, which can greatly increase the active reaction sites, thereby improving the kinetics of the CO_2 reduction reaction. Thus, porous materials are widely used as catalysts or catalyst substrates in CO_2 reduction technology. The authors review the applications and principles of porous materials in three CO_2 reduction technologies and summarize the problems and challenges existing in the application of porous materials to CO_2 reduction, which is of great help for the commercialization of porous materials in CO_2 reduction.

Giulia Tuci et al. [6] apply exohedral N-pyridine decorated carbon nanotubes instead of the traditional metal-based electrocatalysts in electrocatalytic CO_2 reduction reactions. Since N-doped carbon nanotubes prepared by chemical vapor deposition cannot exclude the influence of metallic substances, it is difficult to judge the nature of the active species during electrocatalysis. The authors prepare a series of exohedral N-type decorated carbon nanomaterials with differently substituted N-pyridine nuclei as metal-free electrocatalysts, revealing the role played by the N sites of the variable substituted pyridine nuclei adjacent to the carbon atoms. Studies show that the electrocatalytic performance of these metal-free materials depend on the basic character of each heterocycle and the electron charge distribution, and the effective balance of these two properties can achieve high CO selectivity. This study provides assistance in further understanding the reaction mechanism of metal-free electrocatalysts.

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