
Abstract

Renewable energy is being used to replace fossil fuels to mitigate global environmental problems (e.g., global warming) and reduce the risk of fossil fuel depletion. Renewable energy (e.g., solar energy and wind energy), however, is produced intermittently and thus requires storage systems to ensure the constant supply of energy. Electrochemical CO₂ reduction (eCO₂RR) towards value-added chemicals, powered by renewable electricity, is a promising technology for storing intermittent renewable energy in the form of chemical bonds. Among the various products of eCO₂RR, multi-carbon (C₂₊) molecules, such as ethylene and ethanol, are particularly interesting because they can be either important commodity chemicals or liquid fuels compatible with the current storage and transport facilities.

Production of C₂₊ molecules from eCO₂RR still suffers from low selectivity, reactivity, and stability, mainly due to the lack of proper catalysts and optimal reaction conditions. To develop proper catalysts for C₂₊ products, it is necessary to understand the reaction pathways and the key properties of the catalysts that affect the performance. Among the various catalysts that have been investigated, copper-based materials are most attractive, as they can catalyze eCO₂RR to C₂₊ products with substantial selectivity. Therefore, the main objective of this thesis is to develop advanced copper catalysts and understand the eCO₂RR process. The specific objectives are as follows: (1) revealing the active sites of different copper catalysts for C₂₊ products, (2) design of advanced copper-silver bimetallic catalysts for enhanced C₂₊ products, (3) understanding the effects of mass transfer and pH on the activity and selectivity of eCO₂RR to C₂₊ products, and (4) investigation of the transport of liquid products from eCO₂RR in a flow cell.

First, to reveal the active sites on monometallic copper catalysts for eCO₂RR C₂₊ products, we used copper phthalocyanine as a precursor, which contains a single copper atom in each molecule, allowing us to observe the evolution of single copper atoms to nanoclusters to nanoparticles. We found that the average size of the copper nanoparticles was correlated to the selectivity of the C₂₊ products and identified the grain boundaries as the active sites for C₂₊ products. In addition, the reaction intermediates, such as CO, were found to accelerate the reconstruction of the copper nanoparticles.

Next, we investigated the active sites of copper-based bimetallic catalysts. We designed and synthesized Ag@C@CuO core-shell nanoparticles to control the interface structure between silver and copper, making it possible to distinguish between the tandem and interface effects. By using this specially designed bimetallic catalysts, we found that the high local concentration of CO, generated mainly by the eCO₂RR on silver, suppressed the production of ethylene but showed little effect on the production of ethanol. In the absence of an interfacial carbon layer, the Ag@CuO catalyst improved the selectivity of ethanol but had no effect on the selectivity of ethylene. These results indicate that the tandem effect and interface effect play different catalytic roles on eCO₂RR.

Afterwards, we developed self-supported copper-based gas diffusion electrodes and achieved a current density up to 300 mA cm^{-2} with a high selectivity for C_{2+} products ($> 40\%$). The self-supported gas diffusion electrodes also allowed us to compare the selectivity and activity of eCO_2RR directly on the same catalysts in batch and flow cells. This comparison revealed that the copper catalyst in the batch cell was limited by the mass transfer of CO_2 . Thus, this cell had low current density ($< 20 \text{ mA cm}^{-2}$) and C_{2+} products selectivity ($< 19\%$). However, the Cu catalyst in the flow cell produced a much higher selectivity ($> 40\%$) of C_{2+} products at a higher current density ($> 100 \text{ mA cm}^{-2}$) due to the fast CO_2 diffusion and high pH. The electrode design strategies and the experimental findings presented in this section are valuable for the development of other self-supported electrodes for practical applications.

Finally, we found that more than 30% of the liquid products can pass through the gas diffusion electrode and anion exchange membrane (AEM) at commercial current densities from 50 mA cm^{-2} to 300 mA cm^{-2} . Volatile products (e.g., ethanol, propanol) pass through the gas diffusion electrode mainly by evaporation, and the migration rate increases linearly with the applied current density and CO_2 flow rate. Non-volatile products (e.g., formate ions) prefer to cross the AEM through electromigration, and the migration rate is affected by the current density and the flow rate of the catholyte.

To sum up, we developed different types of copper-based catalysts and identified their active sites for producing C_{2+} products from eCO_2RR . We also demonstrated the effects of mass transfer and pH on the selectivity and activity of C_{2+} products. These findings can help in the design of new catalysts and optimize the reaction environments to selectively produce ethylene or ethanol. We also showed the importance of considering product crossover in eCO_2RR in order to adequately assess catalytic performances in a flow reactor.

Keywords

CO_2 reduction; Electrocatalysis; Copper catalysts, Copper phthalocyanine, Copper-silver bimetallic catalysts; Gas diffusion electrode