Electrocatalytic reduction of CO2 to value-added products

Original
Electrocatalytic reduction of CO2 to value-added products / GUZMAN MEDINA, HILMAR DEL CARMEN. - (2021 May 31), pp. 1-296.

Publisher:
Politecnico di Torino

Published
DOI:

Electrocatalytic reduction of CO_2 to value-added products

Supervisors
Prof. Nunzio Russo, Supervisor
Prof. Simelys Hernández, Co-supervisor

Doctoral Examination Committee:
Prof. Daniel Milanese, University of Parma
Francesca Toma, CSD Staff Scientist at Lawrence Berkeley National Laboratory

PhD candidate
Hilmar Del Carmen Guzmán Medina

Summary

CO_2 electrochemical reduction, Copper, co-electrolysis, CO_2 utilisation, Boron-doped CuO, metal oxide electrocatalyst

An attractive approach of CO_2 Carbon Capture and Utilization is to exploit the protons (H^+) and electrons (e^-) from the oxygen evolution reaction to reduce CO_2 electrochemically to valuable products. Among these, the transformation of CO_2 to methanol or other high-octane alcohols (C_{2+}) like ethanol and propanol should bring a faster transition towards low C-based economy because they are compatible with the current energy infrastructure. **Chapter 1** presents a critical review of the state of the art of the electrochemical CO_2 conversion to these alcohols. Another product of high value is formic acid. The formic acid market is expected to grow at an estimated Compound Annual Growth Rate (CAGR) of around 4% to 5% by 2025 2027. CO and H_2 as syngas from CO_2 are also valuable because they can be used as feedstock for present chemical production technologies. However, this is a challenging task because CO_2 is a fully oxidized, thermodynamically stable and chemically inert molecule; and it involves proton-coupled-electron-transfer reactions. In this work, copper-based electrodes with different structures have been widely investigated to catalyse the CO_2 reduction reaction.

Therefore, inspired by the knowledge of the thermocatalytic CO_2 reduction process, metal oxides like ZnO and Al_2O_3 were proposed as promoters and support structures for copper catalysts. **Chapter 2-5** elucidate details on the preparation and the performance of these materials. The electrocatalytic activity of the CuZnAl-oxide materials was dependent on both the intrinsic properties of the electrocatalyst and the cell configuration used for testing. These are factors controlling the CO_2 availability at the active electrode surface. When moving from CO_2-saturated systems to a gas diffusion layer-type catalytic electrode configuration, the selectivity of the catalysts changed from syngas production (95% of FE at the most positive applied potential) to more liquid products (e.g. methanol or propanol), respectively. In this sense, the Cu/Zn/Al-based commercial catalyst was able to achieve ~25% of $FE_{2\text{-}PrOH}$. In contrast, the co-precipitated Cu/Zn/Al-based material promoted the formation of methanol (~32% of FE). However, the thermodynamically preferred hydrogen was the

main product in most cases, due to mass-transfer limitations issues. It must be pointed out that the formation and stabilization of different oxidation states of copper (during the catalyst synthesis or/and during testing), as well as the local pH, play an essential role on the selectivity of the reaction.

On the other hand, the use of ultrasonic irradiation in the co-precipitation synthesis was investigated. This topic is widely explored in **chapter 6**. The results indicated that precursor type and applied amplitude percentage influence morphology, crystalline planes and specific surface areas. In particular, US-synthesized CuZn-based catalysts resulted in nanocatalyst with smaller particles, more dispersed, and more uniform morphology than the conventional method. Indeed, a synergistic effect was observed and increased productivities (by ~1.4-fold) towards H_2 and C_1 products (CO and formate) with this US-synthesized CuZn-based catalyst. On the contrary, the synthesized CuZn catalyst by co-precipitation presented a higher Faradaic efficiency towards single alcohol (>10% FE_{EtOH}) than the commercial CuZn-based material (~6% FE_{EtOH} and ~2% FE_{1PrOH}). The bare US-synthesized CuO reached >14% of FE to alcohols in the CO_2-saturated system with a catalyst loading of 0.2 mg cm^{-2}.

Additionally, it was possible to tune the porous structure of the catalyst through the precursor concentration, Boron content (by different volume impregnation), US-assisted precipitation time, calcination temperature and atmosphere. The best diffusion properties were found in a range of mean pores of 20 nm and 30 nm. Besides, the volcano-like curve built with the results obtained from the different studied effects, revealed that the best prepared materials achieved a partial current density to liquids products higher than 2 mA cm^{-2}, mainly formate and ethanol. The electrocatalytic activities of these US-prepared catalysts were decreased when a gas diffusion layer was used to prepare these electrodes. In practice, the catalyst must produce CO until it has specific productivity, after which this CO is consumed in the dimerization to produce ethanol. In fact, the catalysts with the best productivity towards ethanol have low productivity towards CO.

Experimental and process simulation results were used to scale-up the CO_2 conversion to methanol via electrocatalytic and thermocatalytic routes. The details are given in **Chapter 7**. The environmental assessment suggested that both technologies can increase their sustainability if further efforts are made to reduce their energy demand. In fact, when a 100% of renewable energy was used, the carbon footprint is reduced by 62% for both technologies. Likewise, a techno-economic assessment revealed that CO_2-to-Methanol could be economically competitive at productivity > 20 kg h_{MeOH}^{-1}.

In this work, it was possible to highlight which properties are important in the Cu-based catalyst structure and how they affect the resulting electrocatalytic activity. The production of alcohols (e.g. methanol and propanol) was achieved using a mixed metal oxide ($CuO/ZnO/Al_2O_3$) catalyst, which has not been explored in a CO_2 electroreduction process. The nature of the surface and structure of this material was widely discussed. The current knowledge in gas phase catalysis could be incorporated to electrocatalysis for faster progress in the development of new electrocatalysts and to find and effective conditions for the reaction. For this reason, a zero-gap configuration must also be explored in the design of a more efficient system for the electrocatalytic reduction of CO_2. In this regard, **Chapter 8** provides future recommendations to the experimental setup to enhance the performance of the reaction.