

GIULIA CUATTO – PhD 38TH CYCLE, POLITECNICO DI TORINO

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ABSTRACT

Electrochemical CO₂ reduction (CO₂RR) plays a crucial role in the CO₂ abatement. Indeed, CO₂RR can valorise waste CO₂ into value-added products. C₂₊ chemicals such as ethylene and ethanol can be obtained from CO₂RR on a copper-based catalyst, under optimized operating parameters. All these studies underwent a Design of Experiment (DoE) workflow in order to maximize the information extraction from raw data. DoE has been employed from the preparation of the experimental plan to the data analysis.

Firstly, a commercial Cu powder has been used as a catalyst after thermal treatment. Two DoE have been built on the thermal treatment and the electrochemical (EC) test. From the EC-DoE turned out that CO₂RR has a multidimensional domain, where different parameters, such as catalyst nature, flow, water content management, and currents employed during the CO₂RR, affect its performance. A D-Optimal analysis has been employed to reduce the experimental matrix in order to fit the experimental budget. The statistical-based data analysis turned out that longer residence time, low water content, and high electron availability lead to enhanced ethanol production. The thermal treatment DoE revealed that Cu, Cu₂O, and CuO content can be precisely controlled by managing the thermal treatment conditions. A model validation has been carried out, confirming the model prediction.

In order to enhance the ethanol production and C-C coupling, bimetallic Cu–Ag catalysts have been evaluated. An extensive DoE has been carried out: presence of a surfactant, silver amount, pulse conditions with both anodic and cathodic current variation. A modest amount of silver, around 2%, turned out to be the best compromise to balance *CO generation and Hydrogen Evolution Reaction (HER) suppression, without an excessive CO production. The surfactant helped during the Ag precipitation on Cu nanoparticles. Notably, it can mitigate both migration and distribution-related inhomogeneities in surface wettability during pulsed operation, contributing to the overall robustness of the electrode. Pulsed electrolysis consistently suppresses HER, stabilizing Cu⁺ and enhancing C-C coupling. However, charge losses due to surface reconstruction under operation and potential re-oxidation processes of both copper and newly reduced products are still a limiting factor for this technology. Charge availability confirms its importance as a threshold for C₂₊ production.

Electrodeposition of bimetallic Cu-Ag (2%) catalyst has been evaluated by varying deposition time, current, and precursor concentration. Two different morphologies have been widely evaluated: one

with branched-Cu₂O particles, one with denser nanometric particles. EC tests with long pulses (1h under reduction, 3 min in oxidative conditions) have been employed in order to reduce electrode stress and membrane crossover. SEM/EDX and XRD analyses have been carried out on fresh and tested electrodes, revealing reconstruction during the EC tests. Specifically, Cu reconstruction and Ag migration over the electrode have been observed. A custom-made reactor has been produced, with an interchangeable flow field for effective flow management. Simulations on CO₂ pressure were pivotal in choosing the flow fields to be tested. A higher CO₂ pressure turned out to affect the CO₂RR selectivity, together with an activation pre-treatment of the electrode. A final 10-hour EC test has been carried out to check the stability of the system, which led to an ethanol faradaic efficiency of ~30 % during the first hours, decreasing to ~10 % at the end of the test.

Further studies should be done to optimize CO₂RR-to-ethanol and C₂₊ products in general. This work suggests a valuable way to study this kind of system, with a high complexity level and a multidimensional experimental domain.