Micro-Additive Manufacturing Processes for Electrochemical CO_2 Reduction

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Primary CNF Tools Used: Nanoscribe GT2, AJA Sputter, Zeiss Ultra SEM

Abstract:

This work investigates the application of micro-additive manufacturing in the development of gas diffusion electrodes (GDEs) for electrochemical CO_2 reduction reactors. This technology relies on the principles of electrochemistry to convert CO_2 into useful chemical products. A key focus of this work is the reactor design and fabrication, as these elements impact the overall efficiency and functionality of the system. The gas diffusion electrode is identified as a common failure point in such reactors. To enhance the performance and durability of the GDE, we utilize the Nanoscribe Photonic Professional GT2 two-photon lithography 3D printer to print a microporous layer atop a carbon paper electrode. This effort aims to mitigate electrolyte flooding in our vapor-fed reactor. A copper catalyst will be deposited onto the microporous layer using the AJA sputter system. Subsequent analysis of the GDE surface will be conducted using a scanning electron microscope (SEM) to ensure structural integrity and optimal surface characteristics. To evaluate the performance of the CO_2 reduction reactor, measurements of open-circuit potential, electrochemical impedance spectroscopy, and cyclic voltammetry will be scrutinized. The results will highlight common failure modes, such as catalyst delamination and electrolyte flooding. Additionally, a long-duration, steady-state test will be performed to measure changes in potential at a fixed current, providing insights into the long-term performance and lifespan of the GDE. Our findings will deliver quantitative insights into the optimization of gas diffusion electrode synthesis, advancing the efficiency of electrochemical CO_2 reduction processes. This research underscores the potential of micro-additive manufacturing in addressing critical challenges in renewable energy and carbon capture technologies.

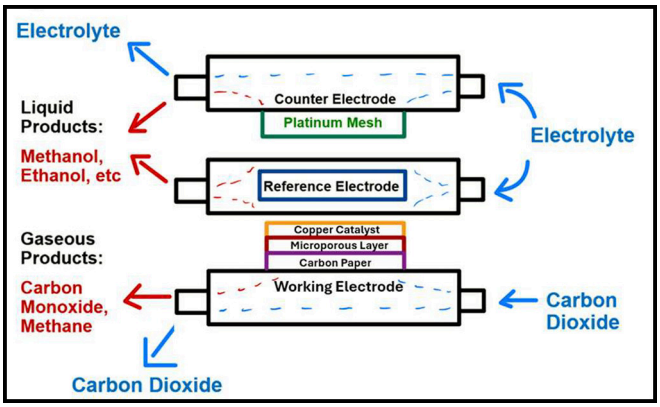

Figure 1: Diagram of CO_2 reduction reactor.

Summary of Research:

In the effort to optimize the fabrication and design of the CO_2 reduction reactor's Gas Diffusion Electrode (GDE), we addressed common failure modes such as catalyst degradation and flooding of the electrolyte into the vapor-fed reactor. To minimize these failure modes, we had to [1] characterize the reactor before and after long-duration trials, [2] design and print a microporous layer on the GDE, and [3] test the effect of electrolyte mixing into the reactor's expected liquid products.

The rate of degradation of the gas diffusion electrode's copper catalyst and the rate of flooding of electrolyte into the vapor-fed reactor are both dependent on the flow rate of CO_2 into the reactor. In order to measure these effects, we employed the characterization of the reactor before and after an hour long run of the reactor at different flow rates. Our characterization involved taking cyclic voltametric scans of the reactor, in which a voltage is applied across the working and reference electrodes, and its current density is measured. These scans display the reduction and oxidation reactions occurring at the copper catalyst of the GDE. Over the course of the long-duration trial, a galvanostatic scan was taken, in which a steady current of 350 mA/cm^2 was applied and the voltage

across the reactor was measured. The galvanostatic scan measures the rate of electrochemical reaction. Multiple trials were conducted at varying CO_2 flow rates of 5, 10, 20, and 40 standard cubic centimeters per minute (SCCM). The operating conditions in which we applied to our long-duration trials were influenced by previous literature, which concluded that 5 SCCM of CO_2 at an applied current density of 350 mA/cm^2 outputs the best reactor performance and efficiency [1].

3D-printing the microporous layer (MPL) offers control of the GDE's pore size and density. The MPL is printed on a layer of carbon paper using the Nanoscribe GT2, then a ~ 300 nm layer of copper is deposited on top of the MPL using AJA Sputter system. This design of the gas diffusion electrode allows the copper layer to be used as a catalyst for the CO_2 conversion, and the microporous layer to be used to prevent flooding of electrolyte into the vapor-fed reactor.

Another facet in the effort to optimize the design of the GDE involved measuring the effect that of electrolyte mixing into the liquid products of the CO_2 reduction reactor. To address this, we performed a test involving measuring the rise velocity of the various samples through a capillary tube. The samples included deionized water to act as a control, the electrolyte (KHCO3), the alcohol and acid products, as well as the alcohol and acid products mixed with KHCO3.

Conclusions and Future Steps:

The cyclic voltametric scans taken before and after the long-duration trials suggest that the copper catalyst degrades more rapidly if there is a higher CO_2 flow rate input.

This can be determined because the reduction and oxidation reactions that are present in the characterization of the reactor before the long-duration trial are no longer present afterwards. The galvanostatic scans taken over the course of the trial also show that the CO_2 reduction reactor reaches steady-state operation after approximately half an hour.

Our 3D-printed microporous layer has pores approximately 1-5 microns in diameter, and also improves upon the previous method of 3D-printing the entire GDE. In comparison, printing the MPL takes ~ 6-9 hours, whereas printing the entire GDE takes ~ 35-55 hours.

Results from measuring the rise velocity of electrolyte and liquid products through capillary tubes suggest that KHCO3 has relatively low hydrophobicity, as it has the lowest rise velocity from our tests, and it lowers the rise velocity of the alcohol and acid products when they are mixed together. The results of these experiments will influence the hydrophobic coating used on the microporous layer.

Future work involves coating the printed microporous layer with a hydrophobic coating. The coated microporous layer will then be tested and its effectiveness against electrolyte flooding and catalyst degradation will be measured.

Acknowledgements:

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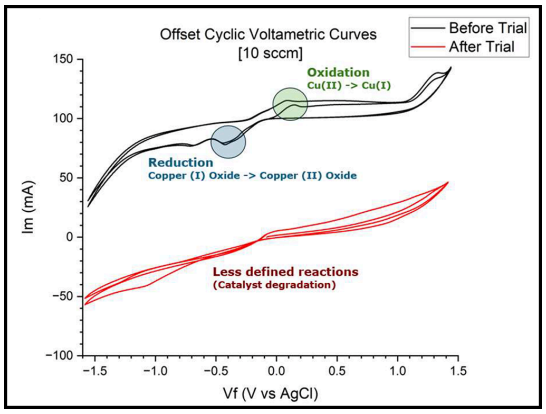

Figure 2: Offset cyclic voltametric scans taken of reactor cell before and after long-duration trial.

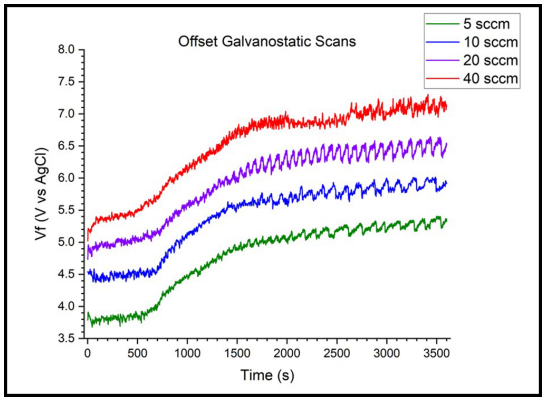

Figure 3: Offset galvanostatic scans of reactor cell at different CO_2 flow rates.

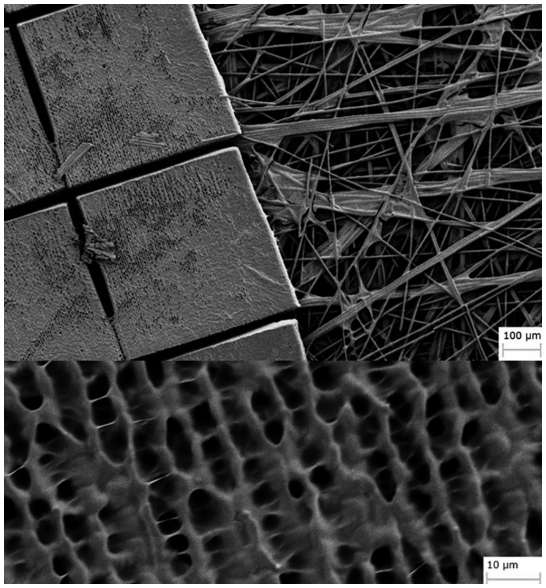

Figure 4: Scanning electron microscope (SEM) images of the microporous layer printed on carbon paper.

References:

[1] D. Corral, et al., "Advanced manufacturing for electrosynthesis of fuels and chemicals from CO_2," Energy Environ. Sci., vol. 14, no. 5, pp. 3064-3074, May 2021, doi: 10.1039/D0EE03679J.