

Development of Functional Gas Diffusion Layers for use in CO₂ Reduction Reactors via Microscale Printing

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Primary CNF Tools Used: NanoScribe GT2, Objet 30 Printer, AJA Sputter Deposition, Zeiss Ultra SEM

Abstract:

In a world reliant on the burning of fossil fuels to run some of its major industries, there is concern as to how we dispose of the carbon dioxide (CO₂) waste produced. One approach is to reprocess the CO₂ into simple hydrocarbons using a CO₂ Reduction Reactor (CO₂RR). A CO₂RR's ability to produce useful products relies heavily on its gas diffusion electrodes (GDEs), which consist of porous membranes called gas diffusion layers (GDLs) coated in a metal catalyst. GDLs act as a barrier against unwanted liquids, letting only gasses pass through.

A conventional GDE, consisting of PTFE and copper covered carbon paper, typically operates for a few hours before its efficiency begins to drop and it floods. Printing GDLs using a 3D printer would allow for optimization of the layer through the customization of the pore size, structure, and density of the layer.

Summary of Research:

The CO₂RR used consisted of three SLA-printed compartments: gas, anolyte, and catholyte compartments. The anode, ion-exchange membrane, and cathode used in the reactor were respectively a platinum mesh, nafion ion exchange membrane, and 3D printed GDL created using the NanoScribe GT2, attached to an adapter made by the Objet 30 printer, and sputtered in copper. The reactor was constantly being pumped with carbon dioxide gas and electrolytic solution, consisting of water and potassium bicarbonate. The process of creating functional GDLs was broken into three parts: designing a GDL, creating the gas diffusion electrode, and assembling the reactor and testing it.

The NanoScribe GT2 sweeps a femtosecond near IR laser across resin, curing sections with two-photon polymerization. The two resins experimented with to produce the GDLs were the IP-S and IP-Q resins. The general workflow for the NanoScribe consisted of creating a CAD model and generating an STL, slicing the STL using DeScribe, prepping the resist on a silicon wafer, loading the wafer into the printer, and printing, unloading, and developing the sample. The first design attempt to generate the full-scale layer of 10.095 mm × 10.095 mm × 400 μm thickness was too computationally intensive. The NanoScribe slicer, DeScribe, can work

with files up to two gigabytes, but the full-scale GDL, in its lowest quality, was six gigabytes.

The next design created an STL out of 1/16 of the full-scale layer, one block, and used a for-loop of arrays and an overlap of 5 μm to build the full layer. The layer printed using this design began to deteriorate and peel off the silicon wafer after development. The final GDL design made and used was a 2 × 2 array of 5 mm × 5 mm × 100 μm each block, layered on top of each other four times, to create a thickness of 400 μm.

Using the IP-S resin and 2 × 2 array design, a second GDL print was made. After development, the GDL layers began to fall apart, and the layer began to peel off the wafer. At this point, the suitability of the IP-S resin was put in question.

The IP-S resin was initially chosen because it was not sensitive to overdevelopment and was the freshest resin available. It was only after printing the third gas diffusion using IP-Q resin instead that the layer turned out better than previous prints, with the IP-Q resin layer having no visible discoloration, excess uncured resin, or separation of layers from each other or off the wafer (see Figure 1).

After developing the layer in PGMEA for 45 minutes and IPA for 30 min, it was soaked for another 30 minutes in IPA. Next, it was sonicated for 10 minutes at 21°C, then placed on a hot plate of 90°C for 20 seconds and moved onto a cool plate. After doing this twice, the layer popped off the wafer.

Then the layer was glued to an adapter printed on the Objet 30 and cured using UV light. Afterwards, the glued pieces were sputtered with a 254 nm layer of copper, using the AJA sputter deposition tool (see Figure 2). Finally, the CO₂RR was assembled, and the finished gas diffusion electrode was incorporated into it (see Figure 3).

The CO₂RR was connected to a power source, potentiostat, and peristaltic pump. However, the gas chromatograph, a machine that would collect and quantify the gas products, was not working. The IR drop was collected and was found to be similar to an IR drop of a conventional GDL on the market. Then a cyclic voltammetry (CV) scan, which measures the change in current as different potentials are applied, was generated. Ideally, the plot should have multiple peaks, each peak representing the reduction/oxidation process. However, as shown in Figure 4, there's no current in the cell until about -1.2 V of potential is applied. This conclusion informs us that there is an electrochemical reaction taking place. However, there is another issue preventing a proper CV scan from being generated.

When the GDL was taken out of the cell, it was discovered that the copper wasn't adhering well to the GDL. A possible solution to try down the line would be to coat the layer initially with another metal, like chromium, then coat it with copper.

Conclusion and Future Steps:

Through the lengthy process of designing the gas diffusion layer, 3D printing it, and running it in a CO₂RR, we were able to produce a GDL that has a similar IR Drop to a conventional market GDL. More importantly, the GDL did not flood during the process of running the cell, showing the potential of using microscale manufacturing in producing optimized GDLs. The next steps would be to try coating the printed GDLs with a hydrophobic coating, as well sputtering it with chromium and copper. Afterwards, it would be tested in the CO₂RR when the gas chromatograph is working.

References:

- [1] Energy Environ. Sci., 2021, 14, 3064 Wakerley, D., Lamaison, S., Wicks, J. et al. Gas diffusion electrodes, reactor designs and key metrics of low-temperature CO₂ electrolyzers. Nat Energy 7, 130-143 (2022). <https://doi.org/10.1038/s41560-021-00973-9>.

Figure 1, top: IP-Q resin layer with no visible discoloration, excess uncured resin, or separation of layers from each other or off the wafer. Figure 2, second from top: A 254 nm layer of copper was added using AJA sputter deposition. Figure 3, third from top: Assembled CO₂RR with gas diffusion electrode incorporated. Figure 4, bottom: Electrochemical reaction.

