

Engineering Gas Diffusion Electrodes for Electrochemical Carbon Dioxide Upgrading

McLain E. Leonard

Submitted to the Department of Chemical Engineering on 14 January 2021, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering

Electrochemical carbon dioxide reduction (CO₂R) is increasingly recognized as a viable technology for flexible generation of chemicals using carbon dioxide (CO₂) recovered from industrial exhaust streams or directly captured from air. If coupled with affordable carbon-free electricity, CO₂R has the potential to generate hydrocarbons that can replace petroleum-sourced feedstocks. Historically, three-electrode analytical cells have been used to study catalyst activity, selectivity, and stability with a goal of incorporating proven materials into larger devices. However, it has been recognized that the limited CO₂ flux through bulk volumes of liquid electrolyte suppress the reaction rate of CO₂ and inhibit the performance of otherwise promising catalyst systems. Gas-fed electrolyzers adapted from commercially successful water electrolyzer and fuel cell technologies have motivated CO₂R researchers to explore various combinations of porous electrodes, catalyst layers, liquid electrolytes, and membranes to achieve higher areal productivity while maintaining steady fluxes of species between flow channels and the active sites. For example, present art demonstrates that high current density production ($> 200 \text{ mA cm}^{-2}$) of valuable intermediates, such as carbon monoxide, at moderate cell voltages (ca. 3 V) is achievable at ambient conditions using cells with catalyst-coated gas diffusion electrodes (GDEs). However, beyond short duration operation (~1–10 h) stable performance in flowing electrolyte systems remains elusive as electrolyte often floods electrode pores, blocking diffusion pathways for CO₂, diminishing CO₂R selectivity, and constraining device productivity. Systematic study of the driving forces that may induce electrode flooding is needed to infer reasonable operational boundaries on gas fed CO₂R electrolyzers as full-scale cells are developed for industrial applications.

In this work, I combined experimental and computational methods to study the role of GDE wettability in determining durability of gas-fed flowing electrolyte CO₂ electrolyzers. First, I constructed a GDE flow cell to quantify the transient decline of CO₂R activity and selectivity that occurs alongside increasing electrode saturation. Results from this platform exposed relevant driving forces of porous electrode flooding, including liquid over-pressurization, electrolyte dry-out/salt precipitation, and electrowetting. Second, I explored how capillarity within GDEs evolves in response to high rates of liquid CO₂R product generation. To approach this, I combined insight from fundamental wettability correlations (i.e., relationships between fluid surface tension and solid surface energy) with reactor mass balances to approximate liquid product mixture thresholds that would challenge the flooding-resistance of common electrode materials (i.e., carbon and PTFE). Finally, I constructed computational electrode models to probe how microstructure and surface chemistry descriptors influence gas and liquid transport in partially saturated GDE layers. Computational variation of wettability parameters affirmed that modification or replacement of carbon-based GDEs is an effective pathway for improving cathode flooding resilience against liquid electrolyte intrusion.

Thesis Supervisor: Fikile R. Brushett

Title: Cecil and Ida Green Career Development Chair, Associate Professor of Chemical Engineering