Advancing Carbon Dioxide and Carbon Monoxide Electrolysis for Sustainable Chemical Production

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Friday, November 13, 2026, 8:00 AM (EST)

ISE 322 | https://udel.zoom.us/j/91096012204 | Password: CO2

Decarbonizing the chemical and energy sectors is essential to reduce greenhouse gas emissions and address climate change. With the declining cost of renewable electricity, electrochemical CO_2 reduction (CO_2R) offers a promising pathway for converting captured CO_2 into value-added fuels and chemicals. However, its practical implementation faces challenges related to economic viability, operational stability, and product selectivity. This dissertation addresses these challenges through techno-economic analysis (TEA), the development of strategies to maintain stable CO electrolysis under intermittent operation, and *operando* characterization of electrochemical systems.

First, a comprehensive TEA is conducted for major CO_2R products, including CO, formate/formic acid, ethylene, ethanol, and acetate/acetic acid, based on recently reported experimental data. Five electrolyser configurations–proton exchange membrane, anion exchange membrane, bipolar membrane, porous solid electrolyte, and tandem systems–are evaluated to identify suitable configurations for each product. The analysis shows that single-pass conversion and product concentration largely determine downstream separation costs, which can account for more than 50% of the total production cost when either is low. For gaseous products, increasing single-pass conversion beyond 30% for CO and 10% for ethylene provides limited additional reductions in separation costs. Similarly, for acetic acid, increasing the concentration beyond 3 M provides minimal additional reductions in separation costs.

Next, the operational stability and economic viability of CO electrolysis under intermittent operation are investigated. Repeated power-off/power-on cycles cause Cu catalyst degradation through carbonate accumulation under CO and Cu oxidation under Ar, leading to increased hydrogen evolution and reduced carbon-product selectivity. To mitigate these degradation pathways, a controlled power-down strategy is developed to maintain the cathode at a slightly more negative potential than its open-circuit potential. This strategy enables stable dynamic operation for more than 750 hours. TEA shows that dynamic operation can reduce acetic acid production costs by up to 26% compared with steady-state operation in regions with large electricity price fluctuations.

Finally, *operando* neutron imaging is employed to investigate the relationship between water accumulation and product selectivity during high-rate CO electrolysis. The increase in hydrogen evolution at high current densities has frequently been attributed to cathode flooding. However, changes in H_2 selectivity during operation at high current densities and elevated temperatures were not consistently accompanied by corresponding changes in neutron-inferred cathode water accumulation. These findings suggest that water accumulation alone cannot fully explain the observed selectivity shifts, indicating the need to consider additional transport and interfacial electrochemical processes.

Together, these studies highlight the importance of combining techno-economic evaluation, operational strategies, and *operando* characterization to improve the economic viability, stability, and selectivity of CO_2 and CO electrolysers. The findings provide insights into the design and operation of electrochemical systems for sustainable chemical production.