

Catalysis and Reactor Engineering for the Electrochemical Conversion of Carbon Dioxide to Carbon Monoxide

by

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Technical Summary:

Carbon dioxide (CO₂) utilization processes have garnered significant interest to both mitigate anthropogenic greenhouse gas emissions and increase the revenue of many chemical and fuel production processes. Low-cost renewable electricity provides impetus for exploring electrochemical methods to recycle CO₂ in cost-competitive and sustainable ways. Researchers have experimentally demonstrated CO₂ transformations into a variety of industrially relevant materials. Techno-economic assessments inform that the simplest transformations, such as generation of carbon monoxide (CO), appear to be the most feasible in the near future. Yet, widespread commercialization of this nascent technology has not occurred due to challenges that include synthesizing stable and active catalyst materials, understanding activity-driving force relationships, identifying appropriate reactor configurations, and developing comprehensive process models. Pursuant to these goals, this thesis advances both the experiment and theory of CO₂ conversion to CO through catalysis and reactor engineering.

Towards the development of an active and selective electrocatalyst, Au nanoparticles supported on carbon black (Au/C) were synthesized via a simple and scalable one-pot process and then tested for the electroreduction of CO₂ to CO. The bulk and surface properties of the Au/C materials were characterized using XRD, TGA, XPS, TEM, and HRTEM techniques to ensure complete reduction of the Au precursor and verify the composition. The synthesized Au nanoparticles have average diameters of 10 ± 2 nm and exhibit promising electrochemical performance. Selectivities as high as 93.5 % for CO formation over the undesired H₂ evolution were observed at competitive reaction rates. This demonstrates that the electroreduction of CO₂ to CO is, certainly, achievable with Au/C catalysts prepared by a low-cost route provided that the nanoparticles are suitably sized and optimally loaded on the carbon support.

In contrast to collective efforts towards catalyst development in electroanalytical cells, fewer studies have sought to characterize electrodes within operating electrolyzers. Therefore, we designed and manufactured a gas-phase reactant delivery, continuous-flow, CO₂ electrolyzer with a reference electrode centered between the polarized electrodes to study catalyst kinetics under conditions beyond what is achievable in traditional, batch, liquid-phase delivery devices. Using our Au/C catalyst deposited onto porous carbon electrodes, we examined CO₂ reduction capabilities by varying operating parameters, such as reactant gas and electrolyte flow rate, and exploring electrode durability under load. We observed a strong CO partial current density dependence on CO₂ flow rate below 2 mL min⁻¹, but only marginal increases at greater flow rates,

indicating kinetic control. While operating in a kinetic regime, we conducted a Tafel analysis and identified two linear regions with Tafel slopes of 60 and 350 mV dec⁻¹ at low and high overpotential regions, respectively. Extended electrolysis for 50 h at -0.60 V vs. RHE produced CO current densities initially at 20 mA cm⁻² with CO selectivities around 90%. The fade in selectivity was limited to ca. 5%. Significant current fade was observed which is tentatively attributed to gas diffusion electrode flooding, motivating future work on electrode engineering.

Despite advances in electrocatalysts and reactors, current understanding of the catalysis science remains limited, especially at conditions relevant for the commercialization of a CO₂ conversion technology. Most importantly, an accurate description of how the CO₂ reduction rate scales with the applied driving force is missing. The Butler-Volmer (BV) kinetic model defines the dependence of current density on electrode potential, predicting an exponential relationship when one of the complementary half-reactions occurs at a much greater rate than the other, producing a linear trend on a Tafel plot. In recent experimental literature on CO₂ conversion to CO, sublinear Tafel behavior is observed, demonstrating the need for alternate kinetic theories, modifications to existing theories, and/or other physical phenomena to describe the current-potential relationship.

To this end, we compare the ability of different electrokinetic models to explain the observations within the field of CO₂ reduction to CO on gold surfaces. While more difficult to quantify meaningful experimental parameters than the phenomenological BV model, the Marcus-Hush-Chidsey (MHC) model explains much of the observed nonlinear Tafel behavior. To quantify the goodness of fit, we computed the Bayesian Information Criterion (BIC) of representative data sets, harvested from literature, and the MHC model was identified as being most likely to be the “true” model. Additionally, we normalized literature data to the fitted kinetic prefactor in the MHC expression, effectively accounting for differences in catalyst surfaces, and the data collapsed to form a single super-set. Analysis of the super-set confirmed earlier findings that the MHC model was a better universal fit than the other models we investigated. This analysis serves as the foundation for determining an accurate activity-driving force relationship for CO₂ reduction on gold surfaces, which is necessary for sizing industrial reactors and informing process operation.

In summary, this thesis measured catalysis rates in a specialized reactor, which is unimpeded by mass transport, and advanced electrokinetic understanding with Marcus theory. This work aims to mitigate adverse climate change effects through the advancement of CO₂ utilization technologies.

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