

Development of Active, Selective and Durable Metal on Metal Oxide Catalysts for Electrochemical Reduction of Carbon Dioxide to Carbon Monoxide

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Anthropogenic carbon dioxide (CO₂) emissions, resulting primarily from hydrocarbon combustion processes, have been correlated with detrimental climate change effects. Carbon capture for conversion and sequestration will play an important role in the future to lessen and possibly reverse the rate of global temperature increase. The energy efficient conversion of CO₂ into carbon monoxide (CO), a precursor for synthetic fuels, will increase the economic viability of developing large-scale carbon capture, utilization and storage (CCUS) processes/facilities. This project aimed to develop electrocatalysts and electrolysis cells that efficiently convert CO₂ to CO with a particular focus on catalyst supports and durability.

A primary outcome of this project was the synthesis, characterization, and electrochemical evaluation of a series of novel supported nanoparticle catalysts. The CO₂ reduction performance was analyzed via chronoamperometry experiments in an electrochemical cell with in-line product quantification via a gas chromatography system. Many combinations of metals (Ag, Au, Pd, etc.) supported on metal oxides (TiO₂, ZnO, CuO, etc.) and on carbonaceous materials (carbon black (CB), graphene) were investigated. In all cases, the carbon supported catalysts outperformed the metal oxide supported catalysts in terms of both CO production rates and current efficiencies. In many cases, the metal oxide supports either catalyzed hydrogen production (e.g., Ag/ZnO), lacked suitable electronic conductivity (e.g., Au/TiO₂), or reduced under operating conditions (e.g., Au/AgO). On a graphite foil substrate, gold supported on graphene (Au/Graphene) demonstrated the highest activity (8 A/cm²-g) and CO selectivity (80%). Stability testing on Au/Graphene, over a 48 hour period, revealed minimal catalyst decay, especially compared to CB and TiO₂ supports. Furthermore, advances were made in electrode engineering for improved activity and selectivity through tuning of the catalyst slurry formulation (e.g., catalyst : Nafion ratio, carrier solvent volume) using gold supported on carbon black (Au/CB) as a model material. The best performance, competitive with the state-of-the-art materials, was achieved with 40 wt% Au/CB. Specifically a CO selectivity of 93.5% and specific current density of 6.2 A/cm²-g were achieved at -0.62 V vs RHE.

A scalable continuous flow reactor was also developed to enable gas phase delivery of CO₂ to catalyst-coated gas diffusion electrode interfacing with a dynamic electrolyte stream. Significant engineering developments were required to control the interfacial pressure balance to prevent gas / liquid breakthrough between the two phases. A robust Au/Graphene catalyst served as the cathode in the reactor and selectivities as high as 80% were reached, albeit at a cell voltage of 5 V. Through further improvements to the cell design and operating protocols, cell voltage was reduced to 3 V with minimal sacrifice to catalytic performance.

Over the course of this project major improvements in catalyst performance and durability were realized and a prototype CO₂ gas-phase delivery reactor was developed. Hopefully, dissemination of the results gathered over the course of this collaboration will inform other researchers studying electrochemically-

Brushett & Bumajdad – CNRE Exploratory Project Outcomes

driven transformations of CO₂, an important and burgeoning research area. Future work involves the investigation of the performance and durability of emerging CO₂ reduction reaction electrocatalysts under application relevant conditions. Overall, the collaboration between MIT and KU was mutually beneficial as it enabled each laboratory to leverage their core competencies while creating a highly productive environment with open exchange of ideas.