

## Introduction to Advanced Materials and Catalysts

The development and advancement of materials is an overarching need in systems that extract, distribute, store or use energy. The performance of these systems depends on the properties of the materials: plastics, coatings, alloys and catalysts are some of the broad classes of materials used in current energy devices. Advancements in these materials optimize energy conversion processes, improve system efficiency, extend lifetime, and reduce CO<sub>2</sub> emissions. Although initially developed for a specific application, material properties may cross-cut to other energy technologies or industries.

GCEP has several projects whose main focus is on materials development. Most of these are officially listed under their application area. Some projects have a materials component to their research. For example, research in the Hydrogen area includes studies of nanomaterials for hydrogen storage. Studies in the CO<sub>2</sub> Separation and Capture area on the development of innovative gas separation membranes involve preparation and testing of materials with highly specific properties. The Solar area is replete with materials research for nanostructured photovoltaic cells.

The studies listed above are all materials intensive investigations whose details can be found under their specific application areas in this report. In addition to these, six projects are underway in the advanced materials and catalysts area.

Professors Daniel Stack and Christopher Chidsey are working towards reduction of carbon dioxide using immobilized dinuclear copper complexes as electrocatalysts. This ongoing research focuses on the development of polynuclear copper catalysts attached to and specifically positioned on inexpensive carbon electrodes for electrocatalytic CO<sub>2</sub> reduction or water oxidation. The research entails ligand synthesis, homogeneous catalyst screening, catalyst imprinting and immobilization, and mechanistic analyses, along with complementary density functional theory (DFT) calculations. A template-imprinting method has successfully led to dinuclear sites with immobilized 1,10-phenanthroline ligands for faster and more selective electrocatalytic reduction of O<sub>2</sub>. Using this attachment strategy, a discrete ruthenium complex is now capable of electrocatalytic oxidation of methanol to formaldehyde for the first time. Yet, using copper catalysts, the researchers have found no evidence that CO<sub>2</sub> can be reduced at modest potentials under ambient conditions to oxalate as described in the literature, though DFT calculations suggest modest CO<sub>2</sub> coupling barriers using simple macrocyclic amine copper complexes. A 10-fold enhanced reduction reactivity of O<sub>2</sub> to water from an imprinting dimeric copper catalyst as compared to its randomly distributed monomeric counterpart highlights a new synthetic strategy for creating multinuclear metal catalyst sites for surface-immobilized electrocatalysis.

Professors Tom Jaramillo, Jens Nørskov, and Anders Nilsson are working on a project entitled, “Combining Theory and Experiment to Design and Develop Active, Selective Metal Alloy Catalysts for the Electrochemical Conversion of CO<sub>2</sub> and CO to Sustainable Fuels and Chemicals”. The objective of this project is to develop catalysts for electroreduction of CO<sub>2</sub> and CO. Developing catalysts for these reactions will enable

technologies that can produce carbon-neutral fuels and/or commodity chemicals when coupled to renewable energy sources, e.g. wind and solar. So far these researchers have performed theoretical studies for the discovery of materials of high activity and selectivity for CO<sub>2</sub> reduction. In particular, the focus has been on RuO<sub>2</sub> and metal alloys. A mass spectrometry setup to investigate the intermediates of CO<sub>2</sub> reduction on five different Cu surfaces has also been developed. A unique selectivity for ethylene on Cu cube surfaces was observed. In-depth analysis of CO<sub>2</sub> reduction on polycrystalline metal surfaces, providing new mechanistic insights into electrocatalyst selectivity has been performed and testing protocols to screen metal alloy thin films have been established. Preliminary experiments also show that physical vapor deposition can be used to epitaxially grow metals on single crystal substrates. This method can produce large format single crystal analogous thin films by using the interfacial energy from the substrate. In the future, these thin films will be electrochemically tested to explore the effects of surface structure on C-C coupling vs C1 pathways, and hydrocarbon vs oxygenate pathways. In addition, the effects of electrolyte additives such as ionic liquids on these well-defined surfaces will be explored.

Professors Cui and Hwang lead a project entitled “Integrated Electrochemical-biological Systems for the Production of Fuels and Chemicals from CO<sub>2</sub>”. Three important aqueous-based electrochemical reactions, hydrogen evolution (HER) oxygen evolution (OER) and oxygen reduction (ORR), hold the key to a number of electrochemical systems, such as fuel cell, water-splitting and metal-air battery devices. A very important component to maximize the energy efficiency of these systems is to explore highly efficient electrocatalysts with sufficient activity, prominent durability, and low cost. This project aims to electrochemically tune non-precious metal catalysts for these important reactions. The researchers have made significant progress so far. The catalysts they have worked on are transition metal oxides, lithium transition metal phosphate, and transition metal sulfides. The researchers have shown that after several times of inserting and extracting lithium into and out of the transition metal oxides, the catalysts become very porous with ultra-small interconnected nanoparticles, which provide a large amount of active sites and result in significantly enhanced OER and HER performance in base electrolyte. In another case, by continuously extracting lithium out from lithium transition metal phosphates, the catalysts become more efficient for water oxidation. The researchers have also developed an *in situ* electrochemical oxidation tuning approach to develop a series of binary, ternary, and quaternary transition metal (e.g., Co, Ni, Fe) oxides from their corresponding sulfides as highly active catalysts for much enhanced water oxidation. The researchers also have the ability to directly and continuously control the lattice strain of platinum catalysts, which allows precise tuning of the ORR activity. This work has led to eight peer-reviewed publications including two in *Science* and one in *Nature Communications*.

Professors Norskov, Jaramillo, Bent, and Nilsson began a project in 2014 entitled “Sustainable Fuel Production from CO<sub>2</sub> and CO: Higher Alcohol Synthesis on Transition Metal Catalysts”. The production of higher oxygenates from syngas offers one pathway for the conversion of CO and CO<sub>2</sub> to useful fuels and chemicals; however, current catalysts known for this process have proved insufficient. This work seeks to improve the

performance of catalysts for higher oxygenate production through promoters and strengthen our understanding of how these promoters interact with the metal surfaces. By combining catalyst surface modification and DFT calculations, these researchers have gained a better understanding of the active sites for production of higher oxygenates. Such understanding can help improve the design of catalysts for converting CO into value added chemicals and transportation fuels. This study's methodology for controllable modification of catalyst structure and separation of various support or promoter effects could also be applied to other heterogeneous catalytic reactions. This method could provide improved understanding of the active reaction sites in supported metal catalysts and be applied to synthesize highly controllable heterogeneous catalysts. With extensive DFT studies and the development of different models for simulating the active site the researchers have improved the understanding of Rh catalyst promoted with MnO. Controllable modification of the catalyst surface and interface structure was achieved by preparing Rh catalysts with different Rh/promoter ratios by co-impregnation and ALD. The observed effects on catalytic rates and selectivity in the CO hydrogenation reaction can be explained by blocking of Rh stepped sites to reduce the production of the undesirable product; Furthermore, in the case of the presence of Rh- MO<sub>x</sub> interface sites, with M = Mn, Mo, increases in CO dissociation rate and the overall activity occur. Future work will focus on more detailed spectroscopic characterization of the Rh-MoO<sub>x</sub> catalyst. The work on Rh will continue to investigate new anionic modifiers. These researchers have also developed a tandem catalytic system for the direct conversion of syngas to ethanol or acetic acid using catalysts that are robust, contain earth-abundant metals, and are commercially available at large scales. The specific stages involved include methanol synthesis, methanol carbonylation to acetic acid, and acetic acid hydrogenation to ethanol. For the first time using the x-ray laser, LCLS, they have detected the intermediate HCO in the first hydrogenation step of CO on a Ru surface. It exists only transiently with a lifetime of around 3 picoseconds. The timescale of this step can determine the selectivity of hydrogenation reactions. So far this work has led to two publications and one under review in *Nature*.

Professors Kanan and Martinez lead a project entitled "Carbonate-catalyzed CO<sub>2</sub> Hydrogenation to Multi-carbon Products" that began in September 2015. Using renewable energy to drive the synthesis of organic compounds from CO<sub>2</sub> and H<sub>2</sub>O could provide a sustainable source of fuels and chemicals with no net CO<sub>2</sub> emissions. The key technical challenge is to efficiently transform CO<sub>2</sub> into multi-carbon compounds and CO<sub>2</sub> hydrogenation is a key step to obtaining these. Despite decades of research, currently available CO<sub>2</sub> hydrogenation methods are only useful for synthesizing methane, CO, or methanol. All of these methods use metal or metal oxide surfaces as catalysts. The absence of efficient multi-carbon product synthesis in this paradigm is understandable given the enormous challenges of designing a single surface that activates H<sub>2</sub> and CO<sub>2</sub> and mediates C-C bond formation in a controlled manner. The goal of this project is to develop a completely new approach to CO<sub>2</sub> hydrogenation that can directly produce multi-carbon products. The innovative aspect is to use simple carbonate salts (M<sub>2</sub>CO<sub>3</sub> or MCO<sub>3</sub>) as catalysts instead of transition metals or metal oxides. The target products include oxalate, acetate, ethylene, and ethanol. The research utilizes a highly synergistic collaboration between experimental studies in the Kanan lab and theory in the Martinez

lab to elucidate the chemical principles of carbonate-catalyzed CO<sub>2</sub> hydrogenations and use these insights to optimize reactions. In the first eight months, the researchers have made substantial progress towards the project goal with the discovery of reaction conditions for efficient and selective CO<sub>3</sub><sup>2-</sup>-promoted CO<sub>2</sub> hydrogenation to oxalate, the first target product, and demonstrating that the *ab initio* molecular dynamics simulator, the nanoreactor, readily uncovers CO<sub>3</sub><sup>2-</sup>-promoted reaction pathways relevant to the target catalytic cycles. These milestones provided the foundation for ongoing work aimed at developing CO<sub>3</sub><sup>2-</sup>-based hydrogenation catalysts that produce the remaining target C<sub>2</sub> products. In the past year the researchers have developed reactions conditions that convert alkali carbonate, CO<sub>2</sub> and H<sub>2</sub> into substantial quantities of acetate, propionate, succinate, and ethylene. They have revealed key reaction parameters that affect yield of C<sub>2+</sub> products and begun elucidating mechanistic pathways. Kinetic simulations of CO<sub>3</sub><sup>2-</sup>-promoted C-H carboxylation, are also underway.