

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 CO₂ 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 CO₂ 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 CO₂ 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 O₂. 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 CO₂ can be reduced at modest potentials under ambient conditions to oxalate as described in the literature, though DFT calculations suggest modest CO₂ coupling barriers using simple macrocyclic amine copper complexes. A 10-fold enhanced reduction reactivity of O₂ 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 Robert Waymouth and Christopher Chidsey are also working toward the reduction of carbon dioxide. Their approach is that of electrohydrogenation to produce a variety of renewable fuels. A series of molecular complexes have been prepared and shown to activate and/or reduce carbon dioxide, ketones, and protons. These advances illustrate the potential of highly reactive transfer hydrogenation catalysts to act as catalyst

precursors for the reduction of CO₂ and other biomass-derived feedstocks to energy dense liquid fuels. These studies have helped illuminate the electronic and structural features of coordination complexes whose metal and coordinated ligands can function cooperatively to facilitate reactivity with protons, electrons, and carbonyl compounds such as ketones, and carbon dioxide. New classes of ketone reduction catalysts based on earth-abundant Mo and Co complexes have also been developed. In the fourth year of this project a new class of CO₂ reduction catalysts based on Re and Mn complexes ligated by redox-active azopyridine ligands has been developed. If the ongoing efforts to develop efficient electrohydrogenation catalysts for the reduction of CO₂ to methanol prove successful, this research will provide a strategy for the more widespread use of renewable and/or intermittent energy sources, such as wind, hydroelectric and solar energy.

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 CO₂ and CO to Sustainable Fuels and Chemicals”. The objective of this project is to develop catalysts for electroreduction of CO₂ 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 CO₂ reduction. In particular, the focus has been on RuO₂ and metal alloys. A mass spectrometry setup to investigate the intermediates of CO₂ 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 CO₂ 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 CO₂”. 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.

Professors Norskov, Jaramillo, Bent, and Nilsson began a project in 2014 entitled “Sustainable Fuel Production from CO₂ 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 CO₂ 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 higher oxygenates production. 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. Conducting the same methodology, the function of several commonly used promoters will be investigated to obtain a deeper understanding of the key factors for converting syngas into higher oxygenates. Based on these fundamental understandings, optimization of the composition and structure of the Rh-based as well as other more earth abundant elements-based catalysts for higher oxygenates production will be carried out. A primary challenge of this system will lie in the selective promotion of the C₂+oxy pathway while not over promoting other reactions such as the production of hydrocarbons. For the alloy systems, this will also involve understanding how the promoters interact with the individual components of the alloy system through thorough characterization.

Professors Kanan and Martinez lead a project entitled “Carbonate-catalyzed CO₂ Hydrogenation to Multi-carbon Products” that began in September 2015. Using renewable energy to drive the synthesis of organic compounds from CO₂ and H₂O could provide a sustainable source of fuels and chemicals with no net CO₂ emissions. The key technical challenge is to efficiently transform CO₂ into multi-carbon compounds and CO₂ hydrogenation is a key step to obtaining these. Despite decades of research, currently available CO₂ 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 H₂ and CO₂ and mediates C–C bond formation in a controlled manner. The goal of this project is to develop a completely new approach to CO₂ hydrogenation that can directly

produce multi-carbon products. The innovative aspect is to use simple carbonate salts (M_2CO_3 or MCO_3) 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_2 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_3^{2-} -promoted CO_2 hydrogenation to oxalate, the first target product, and demonstrating that the *ab initio* molecular dynamics simulator, the nanoreactor, readily uncovers CO_3^{2-} -promoted reaction pathways relevant to the target catalytic cycles. These milestones provide the foundation for ongoing work aimed at developing CO_3^{2-} -based hydrogenation catalysts that produce the remaining target C2 products.