

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 Roger Howe, Jens Norskov and Piero Pianetta are using first-principles simulations to discover materials with ultra-low work functions for energy conversion applications, in particular for high-efficiency thermionic conversions. Since the start of the project in October 2011, progress has been made in three areas: density functional theory (DFT) calculations of the work functions of multi-layer surfaces; fabrication of multilayer surfaces with low work functions; and measurements of surface properties of multi-layer surfaces. A systematic study of both work function and the energy of formation will be published, which provides a guideline for developing stable and efficient thermionic emitters. The work on a new DFT-based method for calculating thermionic emission currents using a non-equilibrium Green's function (NEGF) was completed and published. This paper was selected by the editors of *J. Chem. Phys.* as one of the most innovative and influential papers of 2013. Since the new model provides quantitative predictions of thermionic emission for adsorbate-coated surfaces, it is a breakthrough in the computational design of improved emitters. Low work function is a necessary, but not sufficient, condition for achieving high emission currents. Emitters for testing the DFT predictions for emission from tungsten thin films coated with mixed-oxide coatings are being fabricated. Finally, construction of a vacuum chamber in which these micro-emitters can be optically heated, with the thermionic current collected by a graphene-hafnia laminate is taking place.

Professor Mathew Kanan has a project on Nanostructured Cu Electrodes for Energy-Efficient Conversion of CO₂ to Fuel. Related to this work, Kanan has had recent success on converting CO₂ to ethanol, a result that was published in *Nature*. Building on this success, these researchers are well placed for more interesting science and potential

breakthroughs.

Professors Paul McIntyre and Christopher Chidsey are working on a project entitled, Schottky Tunnel Contacts for Efficient Coupling of Photovoltaics and Catalysts. This interdisciplinary project investigates the performance of nanoscale metal insulator semiconductor (MIS) contact structures that electrically couple optimized catalysts to high quality semiconductor absorbers in photoelectrochemical (PEC) cells, while chemically protecting the absorbers from oxidation during solar-driven water splitting. This work is making progress and the researchers have designed and are now assembling a small ALD reactor to investigate precursor chemistries for deposition of RuO₂-TiO₂ alloy layers that combine the capabilities of an efficient oxygen evolution reaction (OER) catalyst and a chemical protection layer for an underlying silicon absorber. The goal is to minimize utilization of RuO₂, a rare, but very efficient, OER catalyst. In the 2013-14 funding period, the researchers completed and published a study on water oxidation performance of varying the TiO₂ thickness (grown by atomic layer deposition – ALD) in the MIS structures. Among other things they have shown that ALD-TiO₂ protection can be used with three times less iridium with only small effects on device performance as well as with a variety of other metal catalysts. These findings together constitute a major advance in the coupling of general photovoltaic and catalyst systems. In light of their findings of the bulk-limited conduction through thicker TiO₂ oxide layers, they recently performed another set of experiments varying the SiO₂ oxide thickness

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 proposed research entails ligand synthesis, homogeneous catalyst screening, catalyst imprinting and immobilization, and mechanistic analyses, along with complementary density functional theory (DFT) calculations. A new strategy for the reductive integration of CO₂ into a polymeric elastomer with self-healing properties operative in humid to wet conditions has been developed. The highly efficient methodology for CO₂ hydrosilylation using an earth-abundant copper catalyst allows for efficient synthesis of polyformoxymethylsiloxane (PFMS) from two inexpensive and abundant waste products - polymethylhydrosiloxane (PMHS) and CO₂, in 1 hour. Further explorations of PFMS as a crosslinking component to make silicone rubbers may lead to a greener alternative for acetoxy silanes used in commercial products, in which the carbons are derived exclusively from fossil fuels. The remarkably high mass ratio of CO₂ in PFMS (ca. 40%) and the PFMS/PDMS elastomers (ca. 4-10%), as well as that in CO₂/epoxide copolymers (ca. 30-50%), unequivocally shows the great potential of CO₂ as a useful carbon source to make polymers. However, compared to the sheer scale of biosynthesis of lignocellulose biomass, mainly carbohydrate and aromatic polymers from CO₂, more research efforts to develop new CO₂ polymerization strategies are clearly needed.

Professors Robert Waymouth and Christopher Chidsey are also working toward the reduction of carbon dioxide. Their approach is through electrohydrogenation to produce a

variety of renewable fuels. In the past year, a series of molecular metal hydrides derived from transfer hydrogenation catalysts have been shown to activate and/or reduce methyl formate, carbon dioxide 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. Well-defined molecular complexes designed to activate and reduce carbon dioxide, alkyl formates, and protons have been tested. 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. They have also developed new classes of ketone reduction catalysts based on earth-abundant Mo and Co complexes.

Professors Tom Jaramillo, Jens K. 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*. 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 metal alloys and transition metal dichalcogenides. A setup to investigate the intermediates of CO₂ reduction through the use of ambient pressure X-ray photoelectron spectroscopy and mass spectrometry has been developed. They have also conducted in-depth analysis of CO₂ reduction on polycrystalline silver surfaces, synthesized AuPd thin films, and characterized their electrocatalytic CO₂ reduction activity.