

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. The recent discovery and development of the 2D material, graphene, opens a wholly unexplored avenue for achieving ultra-low work functions. By combining both electrostatic gating and surface engineering approaches to simultaneously lower the vacuum level and raise the Fermi level of graphene it is possible to maximize the work function reduction.

Professor Mathew Kanan has a project on “Nanostructured Copper Electrodes for Energy-Efficient Conversion of CO₂ to Fuel”. The goals of this project are to elucidate

the structural origin of the catalytic properties of oxide-derived copper (Cu) and use these insights to prepare improved catalysts. In the past year, this research group has made major progress on both of these objectives. Toward the first goal, they have used temperature programmed desorption to discover that the surfaces of oxide-derived Cu have a significant portion of sites that bind CO with higher affinity than either Cu terraces or stepped surfaces. Because adsorption energy directly impacts the potential energy surface for electroreduction reactions, the results suggest that these high-affinity sites are critical for the reduction of CO on oxide-derived Cu. Insights from experiments with oxide-derived Cu will be used to develop the first experimentally validated design principles for nanoparticle CO₂ and CO reduction catalysts. In particular, results show that the specific activity for CO₂ reduction to CO is directly correlated with the density of grain boundaries in gold (Au) nanoparticles, and the specific activity for CO reduction to ethanol and acetate is directly correlated to the density of grain boundaries in Cu nanoparticles. The most grain boundary-rich Cu catalysts are the most active and selective CO electroreduction catalysts reported to date. These results provide validation for the use of grain boundary engineering to create highly active fuel-synthesizing catalysts.

Professor 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. In the 2014-15 funding period, the researchers have performed four core studies: the first on photovoltage design principles – and achieved the current record for photovoltage in water-splitting silicon anodes; the second on the SiO₂ interlayer in the stack and its role in determining overall device efficiency; the third on alloyed TiO₂-RuO_x catalysts for water oxidation by atomic layer deposition (ALD), and the fourth, in moving toward a complete photosynthetic device, on implementing a tandem solar cell architecture for higher overall performance. A report on photovoltage design principles applicable to all types of oxide-protected water splitting cells has been submitted for publication in a high impact journal. This study focused specifically on achieving high voltages in stable devices to maximize overall efficiency. The novel observation of a linear photovoltage loss with oxide thickness, and by eliminating it, achieve photovoltages as high as 630 mV, was the highest yet reported for single-junction water-splitting silicon cells. The loss mechanism is systematically probed in MOS Schottky junction cells compared to buried junction p+n cells, revealing the need to maintain a characteristic hole density at the semiconductor/insulator interface. A capacitor model predicts a photovoltage loss that is linear with oxide thickness and that can be related to the materials properties, achieving excellent agreement with the data. These findings help to inform design principles for the simultaneous optimization of charge transfer resistance and series resistance to maximize the photovoltage of MOS water splitting devices.

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 template-imprinting method has successfully led to dinuclear sites with immobilized 1,10-phenanthroline ligands for faster and more selective electrocatalytic reduction of O₂. The researchers reason that the distance between the two nuclear sites is an important factor affecting the rate and selectivity of the electrocatalysis. Further work will probe initially the effect of various bridging anions on the reduction of O₂ with the same 1,10 phenanthroline ligands, which will establish methodologies to prepare dinuclear sites on GCE surfaces with different dinuclear separations.

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. Several well-defined molecular complexes designed to activate and reduce carbon-dioxide, ketones 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. New classes of ketone reduction catalysts based on earth-abundant Mo and Co complexes have also been developed.

Professor's 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 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.