Introduction to Completed Project Reports

In 2015, ten programs within six areas came to completion. Half the programs are in the area of CO_2 capture where there was a targeted solicitation, and funding for multiple institutions began in 2012. Other areas represented are in renewable energy (solar and biomass), advanced materials and catalysts, advanced coal, and grid storage.

Solar

An ambitious project entitled "Toward high-efficiency thin film solar cells combining multi-junctions and nano-scale light management" involving four investigators collaborating between the departments of electrical engineering and material science, Professors Harris, Fan, Cui and Brongersma, has been completed. It was aimed at specifically addressing the development of practical, ultra-thin single crystalline GaAs, AlGaAs and c-Si solar cell structures, as well as AlGaAs/c-Si tandem cells. Their work has been productive in the study of nanophotonic light management on ultra-thin film solar cells by demonstrating improved photon management, increasing efficiency for GaAs, fabricating lift-off methods, developing luminescent coupling for multijunction cells. A most surprising output from this work has been achieving waveguiding of the incident solar radiation under optimized period and height of nano-structured pyramids on c-Si, thus enabling nearly 100% absorption in <5μm thick Si. This discovery set into motion an entirely new design direction for the realization of higher efficiency and lower cost c-Si solar cells through a combination of photon management, ultra-thin c-Si and novel minority carrier blocking Ohmic contacts.

Biomass

Professsor Spormann and Professor Bruce Logan at Penn State University studied the fundamental processes that occur at cathodes during methanogenesis in microbes in a cathodic biofuel. The work involved collaborative design of a cathodic fuel cell, understanding the mechanisms of interaction of the microbes at the cathode and identifying species responsible for methane production. Understanding of the dynamics of the methane-producing microbial consortium and their capabilities for conversion of current into methane is a key challenge for maximizing methane formation in an energy efficient way. The project demonstrated that hydrogenotrophic methanogens belonging to the genera *Methanobacterium* and *Methanobrevibacter* are essential for high rates of methane production. It currently appears that there may be several routes for electromethanogenesis, which include production of hydrogen gas, conversion of electrical current to organic intermediates, and direct electron transfer. In general, the results to date suggest that methane is produced from intermediates released by bacteria or enzymes in solution.

CO_2 Capture and Separation

GCEP has five projects in the area of carbon capture and separation a result of a targeted solicitation. Three of the projects were focused on developing materials for pre-combustion or post-combustion carbon capture and separation. The other two projects performed systems analysis to define optimum design and performance parameters for various capture technologies, including those funded. Overall the aim of this portfolio

was to understand the inefficiencies in the processes and expand the opportunity to exploit fundamental advances in chemistry and engineering to drive down the operational penalties that CO_2 capture imposes on power production.

A multi-disciplinary team led by Professor Jennifer Wilcox at Stanford was involved in the "Surface Functionalization of Mesoporous Silica-Based Sorbents for Capture". The researchers developed high surface area carbon-based materials that have been functionalized with model complexes of carbonic anhydrases. The team synthesized promising nitrogen-doped porous carbons and developed a thermogravimetric analysis method for monitoring the absorption/desorption kinetics. The team brought new understanding that low-temperature carbonization and activation steps lead to abundant ultra-small pores and strong CO_2 binding nitrogen sites, which are essential in enhancing the CO_2-sorbent interactions and selectivity. They have also worked on synthesizing a class of highly porous carbon-based sorbents for applications of high-pressure CO_2 capture from natural gas.

A team of researchers led by Professor Randall Snurr at Northwestern University examined metal organic frameworks (MOFs) and interactions with water for post-combustion carbon capture in a scientific and modeling effort to determine "New Materials and Process Development for Energy-Efficient Carbon Capture in the Presence of Water Vapor". Computational screening and process-level modeling informed the experimental effort. Through the computational screening method that was developed, fluorinated MOFs showed promise of selectively adsorbing CO_2 in the presence of water vapor. The process-level modeling work indicated that it may be economically and technically feasible to remove water prior to carbon capture. However, the volume of water to be removed will be determined by the integration of materials development in future work. The process modeling also suggests that the total pressure for carbon capture may approach ~3 bar versus 1 bar that has been the focused target. This result may open up a broader range of possible material and process combinations for CO_2 capture.

Pre-combustion capture research in the GCEP carbon capture portfolio was conducted by a team of chemical and biological engineers led by Professor Joan Brennecke at the University of Notre Dame. They researched "Chemically-Complexing Ionic Liquids for Pre-combustion CO_2 Capture". They designed and developed ionic liquid systems (ILs) for pre-combustion in applications such as integrated gasification combined cycle systems. The team was able to develop new ionic liquids that showed cooperativity and CO_2 uptakes well above 1 mole CO_2/mole IL. However, the physical properties were not attractive for industrial applications. The investigators also showed how physical cooperativity can be used to enhance CO_2 uptake and now better understand the CO_2 uptake chemistry. New molecular modeling and simulation methods were developed and used to design the new ILs and predict gas solubilities. Process modeling was used to identify the optimal physical and chemical properties. High viscosity and, subsequently, poor mass transfer, remains a challenge for using the ILs developed for practical CO_2 capture applications.

System analysis work was conducted in two separate programs by researchers at Stanford

University and Carnegie Mellon University. At Stanford, Professors Christopher Edwards and Adam Brandt led an effort on "Carbon Capture Systems Analysis: Comparing Exergy Efficiency and Cost of Electricity of Existing and Future Technology Options". Their objective was to develop a framework based on an exergetic analysis at the local (system) and global (life cycle) level in addition to a techno-economic evaluation of capture technologies. Four types of CCS technologies were studied under this framework: MEA/NGCC as a reference system, MOFs-based adsorption, biomimetic sorbents and ionic liquids absorption. The work showed that both existing, well-developed systems and proposed future systems are well below theoretical performance limitations, perhaps by as much as an order of magnitude. The analyses also showed that there are immediate improvements to be made—for example in process integration or component choices—but also more challenging and less-intuitive improvements are needed—such as process *de-intensification* (reducing the driving gradients that destroy exergy during a separation).

Professor Edward Rubin led a team at Carnegie Mellon University on "Systems Analysis of Advanced Power Plant Carbon Capture Technologies". The work expanded on the existing Integrated Environmental Control Model (IECM) framework, allowing for carbon capture technology evaluation. The team is still in the process of completing a final report that analyzed and compared the performance, emissions and cost of new power plants employing three advanced capture processes: ionic liquids, metal organic frameworks, and activated carbon.

Advanced Materials and Catalysts

Professor Mathew Kanan completed a project on "Nanostructured Copper Electrodes for Energy-Efficient Conversion of CO_2 to Fuel". The genesis of this GCEP project was the discovery of "oxide-derived Cu"—a thin-film metallic Cu material synthesized by reducing a Cu_2O precursor. Compared to conventional Cu electrodes such as polycrystalline Cu foil, single crystal Cu electrodes, or commercial Cu nanoparticles, oxide-derived Cu has higher selectivity for CO_2 vs H^+ reduction and much higher activity for CO reduction to multi-carbon (C^{2+}) oxygenates such as ethanol and acetate. The goals of the project were to elucidate the structural origins of these improvements and apply these principles to the preparation of even more active and selective catalysts. In particular, results showed that the specific activity for CO_2 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. These results provide validation for the use of grain boundary engineering to create highly active fuel-synthesizing catalysts.

Professors Paul McIntyre and Christopher Chidsey worked on a project entitled, "Schottky Tunnel Contacts for Efficient Coupling of Photovoltaics and Catalysts". This interdisciplinary project investigated 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.

Advanced Coal

A project started in the spring of 2013 on the "Co-generation of Carbon-Free Hydrogen and Electricity from Coal in a Steam-Carbon Fuel Cell with Carbon Capture" led by Professor Reginald Mitchell of Stanford University. The steam-carbon fuel cell is a novel concept where steam gasification of coal in a fuel cell arrangement can generate electricity and physically separated streams of hydrogen and CO_2. The objective of the project is to gain better mechanistic and operational understanding of the steam-carbon fuel cell through experimental, materials and modeling efforts. Research during the previous years involved screening, synthesizing, and assessing materials to serve as sulfur tolerant anodes. In the final year the researchers addressed the design and construction of a coupled cell that was gas-tight with proper access to electrical leads and carbon and gas feeds that also showed stable electrochemical behavior.

Grid Storage

Professor Hongjie Dai and his team from Stanford researched large-scale batteries for grid storage, looking carefully at different chemistries and the electrocatalytic reactions at the electrodes. Their work was titled "Photoelectrochemically Rechareable Zn-Air Batteries" and attempted to develop novel nanocarbon-inorganic hybrid materials for the hydrogen evolution, oxygen reduction and oxygen evolution reactions. Novel battery concepts were also developed such as an ultra-fast Zn-Ni battery and the aluminum ion battery. Their work has resulted in ten publications including in several high impact journals such as Science, Nature and Nature Communications**.**