FESC Research, Education and Outreach Project Progress Reports
(Attachment to Main Report)

November 1, 2012

UF Project Reports

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University of Florida
An Integrated Sustainable Transportation System

PIs: Eric Wachsman, Keith Duncan   **Co-PI:** Shirley Meng

Description: The proposed vehicle, operating on biofuel while in transit and charged by the sun while parked, is the ultimate sustainable transportation system operating completely on renewable American energy resources. Moreover, the use of solid oxide fuel cells (SOFCs) rather than an IC engine in this hybrid vehicle results in a dramatic improvement in efficiency and reduction in emissions. SOFCs are the most efficient technology for converting energy from hydrocarbon fuels to electricity on a "well to wheels" basis. In contrast, the more conventional fuel cells require hydrocarbon fuels to first be converted to H_2, with resultant efficiency losses, followed by losses due to H_2 transport and storage. Therefore, on a system-basis SOFCs hold the potential for producing the least CO_2/kWh from conventional fuels, and if designed to operate on biofuel would in effect be carbon neutral and operating on a renewable resource. *If developed this vehicle would be a transformational change in transportation technology.*

Budget: $594,000
Universities: UF
External Collaborators: Solid-State Energy Technology, Inc., Lynntech, Inc., Planar Energy Devices, Inc., CFX Battery, Inc.

Executive Summary

The proposed vehicle, operating on biofuel while in transit and charged by the sun while parked, is the ultimate sustainable transportation system operating completely on renewable American energy resources. Moreover, the use of solid oxide fuel cells (SOFCs) rather than an IC engine in this hybrid vehicle results in a dramatic improvement in efficiency and reduction in emissions. SOFCs are the most efficient technology for converting energy from hydrocarbon fuels to electricity on a "well to wheels" basis. In contrast, the more conventional fuel cells require hydrocarbon fuels to first be converted to H_2, with resultant efficiency losses, followed by losses due to H_2 transport and storage. Therefore, on a system-basis SOFCs hold the potential for producing the least CO_2/kWh from conventional fuels, and if designed to operate on biofuel would in effect be carbon neutral and operating on a renewable resource. *If developed this vehicle would be a transformational change in transportation technology.*

In this project, we made significant gains in the science of energy conversion, from fundamental studies of the atomistic underpinning for materials properties to the engineering of the highest performance solid oxide fuel cells in the literature. Fundamental studies of the two most promising materials for solid electrolytes, using computational modeling, enabled us to determine the optimal potentials to use (the Gotte potential) in predicting materials properties for oxides of interest in this field. Moreover, from a molecular dynamics study of bismuth oxide we were able to confirm that dopant polarizability was the key feature in determining oxygen vacancy mobility in the fluorite system. Undergirded by these results we are now positioned to use our computational tools to further optimize the material properties of known oxygen ion conductors as well as develop new ones with superior performance.

We have also expanded the application of our previously developed continuum-level electrochemical model to describe and predict the performance of SOFCs as a function of electrolyte thickness. We were able to show that, for maximum power density, mixed conducting electrolytes had an optimal thickness below which they were rapidly overwhelmed by electronic conduction and above which their ohmic

losses grew. We also are the first ones to predict the drop in open circuit potential with decreasing thickness for these materials.

Our development of record conductivity materials also continued with the highest conductivity ceria based and bismuth oxide based materials reported. We further studied their stability and optimal temperature window for operation. In so doing we have established our institution as the clear leaders in this area.

We are also leading in the area of anode development as the first to develop SOFCs with anode functional layers, which enabled a quantum step in SOFC performance. By comparison, our work on cathode performance is set to take off. We have already developed one of the highest conductivity cathodes (a bismuth ruthenate-bismuth oxide composite) in the literature. However, our fundamental studies on the oxygen reduction reaction (ORR) have positioned us to break further ground towards making a significant performance jump using conventional cathode materials. We have used multiple techniques to investigate the factors governing the ORR and the results of those studies point to new electrode architectures that should both improve performance and increase stability (especially, with respect to chrome poisoning and secondary phase formation).

Finally, we have also found time to complete our research efforts in hydrogen production, which is critical for the realization of a future hydrogen economy. In addition, we moved forward with our work on sensors, by indentifying the factors affecting the sensing process and developing high selectivity sensors with high signal-to-noise ratios. This has garnered interest from industry, leading to collaborations with General Electric (GE) and Energy Management Solutions (aka EPS) and RedOx Fuel Cells.

This project has been completed. The Final report is found here.

Both Dr. Wachsman and Dr. Meng left UF.

University of Florida
Biocatalytic Lignin Modification for Carbon Sequestration

PI: Jon Stewart
Students: Bradford Sullivan (postdoctoral fellow), Filip Boratynski (postdoctoral fellow)

Description: After cellulose, lignin is the second most abundant forma of carbon in plants. Lignin's complex structure makes it difficult to use this material in value-added products, and ahte vast majority of lignin is currently burned to provide energy for factory operations. While burning plant derived lignin does not add to global greenhouse gas levels, having options to remove lignin from the global carbon cycle would lead to diminished atmospheric CO2 levels. This could be accomplished by chemically altering lignin's structure to facilitate long-term terrestrial sequestration or using it in value-added products that would not be discarded immediately. We will use Nature's catalysts (enzymes) to tailor the chemical structure of lignin for both deep-well injection (by using lignin derivatives as drilling "muds") and for materials that can be used in building, packaging, and other manufactured products.)

Budget: $200,000
Universities: UF

Executive Summary

The overall goal for this sub-project was to develop biocatalytic strategies for modifying lignin, either for carbon sequestration or for conversion to value-added products. As part of this broader goal, we also carried out studies designed to improve biocatalyst stability since this is an essential element when judging the economic feasibility of a proposed process. Our objective in this area was to develop – and validate – methods that increase enzyme stability.

Lignin makes up approximately 20% of the carbon fixed by plants and must be separated from the cellulosic fraction in a number of processes including pulping and bioethanol production. Traditional Kraft pulping chemically derivatizes lignin with sulfonic acid moieties, allowing it to be soluble under basic conditions, but also imparting a strong odor that makes it difficult to employ the lignin for any purpose other than combustion. Steam treatment is typically employed in cellulosic ethanol processes, and this operation yields a lignin stream better suited to value-added uses.

Laccases are the best-known enzymes that accept lignin as a substrate. These multi-copper proteins are produced by a wide variety of species and play important roles in lignin degradation by white- and brown-rot fungi. These enzymes mediate the four-electron reduction of O_2 using lignin as the ultimate electron source. Because lignin can be highly crosslinked and interior portions are difficult to access by large proteins, laccases are paired with small molecule, diffusible electron carriers (mediators). Depending on reaction conditions, laccase / mediator systems can cross-link lignin internally, covalently add small molecules to lignin or degrade the lignin substrate.

The requirement for small molecule mediators poses significant economic drawbacks for using laccases in commercial-scale applications. We therefore investigated the possibility that oxidative enzymes might act on lignin and carve out mediators *in situ* that could then be used by laccases. We probed this possibility by using cinnamyl alcohol as a model compound for lignin-derived materials and *Pseudomonas putida* toluene dioxygenase as the oxidizing enzyme. While toluene dioxygenase convert cinnamyl alcohol to the corresponding diol, the yield was too low to be useful. For this reason, we did not pursue a dehydrogenase-catalyzed conversion of the diol to the corresponding catechol.

We next turned to the issue of biocatalyst stability under process conditions since this is a key factor in assessing feasibility. Because laccases are complex proteins with bound Cu^{2+} ions, we turned to a simpler model enzyme (*Pichia stipitis* OYE 2.6) for these studies. We first determined the crystal structure (the first structure determined solely by the Stewart group) and analyzed the atomic displacement (B) factors to determine which regions of the protein were most susceptible to motion. The hypothesis is that sites with high local mobility serve as nucleation sites for global protein unfolding. The solution is to replace amino acids with high relative B factors in the hope that the variants will exhibit lower mobilities in these areas. We chose the ten amino acids with highest B factors in Pichia stipitis OYE 2.6 and made site-saturation libraries in which each residue was replaced by all other amino acids. These variants were screened at elevated temperatures, using automated gas chromatography (GC). We found that one mutant (S388P) increased the protein's melting temperature by 4ºC. Efforts to increase the thermal stability further by making additional site-saturation libraries in which the S388P mutation was fixed were unsuccessful. We therefore decided to analyze the impact of the S388P mutation more carefully. Interestingly, while such studies have been carried out in the past, to the best of our knowledge, no crystallographic studies have ever been carried out on mutants with greater thermal stabilities to determine whether the mutations actually <u>did</u> yield lower B factors. Our goal was to answer this critical scientific question and the crystallographic studies are currently underway.

In conclusion, we have determined that it is possible to prepare small molecule laccase mediators by biocatalytic oxidations of lignin model compounds, although the yield is currently too low to be practically useful. We have also successfully increased the thermal stability of a model enzyme by protein engineering and are now in a position to test experimentally the central hypothesis of the methodology directly (do stabilizing mutations actually reduce local B factors).

This project has been completed. [Final report found here](#).

University of Florida
Combined Cooling, Heat, Power, and Biofuel from Biomass and Solid Waste

PI: Jacob N. Chung   **Co-PI:** William E. Lear

Description: The goal of this project is to provide the underlying research and demonstration of a novel technology which would enable the economic utilization of dispersed biomass and solid waste resources to produce electric power, cooling, heat, and transportation fuels. This integrated gasification and power generation system combines University of Florida advances in high-temperature gasification, hydrogen generation and separation, and advanced gas turbine systems. Their integration is expected to result in significant improvements in the cost, emissions, feedstock flexibility, and water requirements, all in a relatively compact, modular plant system. This in turn will enable much greater utilization of renewable energy supplies, helping the development of a sustainable energy supply infrastructure.

Budget: $576,000
Universities: UF
External Collaborators: Siemens Power Generation, Florida Turbine Technologies, Energy Concepts Co., Nu-Power Technologies LLC, PlanetGreenSolutions Inc., LPP Combustion, LLC.

Executive Summary

Part I – Biomass Gasification and Power Generation

PI : J. N. Chung
Co-PI: William E. Lear

The project goals are placed on two related parameters, firstly, to investigate the thermal profile of the trailer gasifier in different zones during the course of gasification and also to elaborate on the design, characteristics and performance of a trailer-scale gasification system using different biomass feedstock. Experimental data on the thermal profiles with respect to five different zones in the gasifier and a comprehensive thermal-chemical equilibrium model to predict the syngas composition was also developed. Four different feedstock- pine wood, horse manure, red oak, and cardboard were evaluated. The effects of C, H, O content variations in the feedstock on the thermal profiles, the efficiency, and viability of the trailer-scale gasifier are also discussed.

Secondly, to analyze the engine performance of the integrated system and the overall efficiency based on the calorific value of syngas produced from different feedstock. This part presents the feasibility study of a sound scientific, engineering, and technological solution for converting lignocellulosic biomass to electrical power using a trailer-scale down-draft biomass gasification system coupled with a spark-ignited IC engine/electric generator set for portable power applications in agricultural farms and in rural areas.

The main objective of this study is to investigate the coupling and integration between the gasification unit and the power generation unit. Also it is intended to emphasize on the effectiveness of distributed power generation systems and demonstrate the feasibility of such integrated systems in real world scenarios, where the lignocellulosic biomass resources are widely available and distributed across the board. Four feedstock materials, pine, red oak, horse manure and cardboard that represent a wide spectrum of lignocellulosic biomass resources were chosen for the study. The efficiencies for individual components and the overall integrated system efficiencies were evaluated using experimental data and a

thermal-chemical model for all four feedstock. Also to emphasize on the effectiveness of distributed power generation systems and demonstrate the feasibility of such gasification systems in real world scenarios, where the lingo-cellulosic biomass resources are widely available and distributed across the board.

The following results are derived based on the work carried out to accomplish the above mentioned goals. The feasibility and viability of a trailer-scale thermal-chemical system for the conversion of lignocellulosic biomass to biofuels have been demonstrated for distributed energy and rural applications. A thermodynamic equilibrium model that is capable of prediction the gasifier performance has been developed and validated by independent models in the open literature. Experimental results provided the system thermal profiles and quantitative hydrogen production rates. The thermodynamic efficiencies predicted by the model are in the range of 80 % for the four different feedstock used in this study that is in good agreement with other reports on similar biomass gasification systems.

The trailer-scale downdraft gasification unit was successfully coupled with a specially chosen spark ignition IC engine without any additional modification. The integrated system converted four different types of biomass feedstock into the electric energy form via an engine/generator set on the spot, which shows the possibility of portable power using various local feedstocks.

With a thermal-chemical model and experimental data, the individual component efficiencies for the gasifier and the engine together with the overall system efficiencies for all four feedstock materials used in this study were determined. The thermodynamic efficiencies for the gasifier were found in the range of 81.7% to 84.6%. The engine efficiencies fall in the range of 25.6% to 29.5% for horse manure, red oak and pine with only 20.3% for the cardboard. On the overall system performance, the integrated efficiencies were determined at 20.6%, 21.3% and 23.0% for red oak, horse manure and pine, respectively. Again, the cardboard delivered the lowest overall system efficiency at 15.8%. In summary, the overall system efficiencies are in good agreement with those from very limited other reports for the combined biomass to power applications.

Funding for this research from the Florida Energy Systems Consortium (FESC) was used for building and testing the trailer gasification system and also to upgrade the cleaning components to produce clean syngas. This would help the state immensely in taking the right step towards a cleaner and greener energy future, also the biomass resources would also provide valuable employment opportunities for the state. For further information regarding the project please refer to the full progress report posted on the FESC website.

Part II – Biomass Powered Power, Water Extraction, and Refrigeration Distributed Energy

PI : William E. Lear
Co-PI : J. N. Chung

This project has provided underlying research and demonstration of a novel energy conversion technology which would enable the economic utilization of dispersed biomass and solid waste resources to produce electric power, cooling, heat, and transportation fuels. This integrated gasification and power generation system combines University of Florida advances in high-temperature gasification, discussed above in Part I, and advanced gas turbine systems. Their integration is expected to result in significant improvements in the cost, emissions, feedstock flexibility, and water requirements, all in a relatively compact, modular plant system. This in turn will enable much greater utilization of renewable energy supplies, helping the development of a sustainable energy supply infrastructure.

The novel energy conversion technology is called the Power, Water Extraction, and Refrigeration (PoWER) cycle. It is an unusual integration of gas turbine and absorption refrigeration technology which results in a subsystem capable of simultaneous production of electrical power, heat, cooling, and fresh water captured from the combustion products. The combusion process is inherently fuel flexible with ultra low emissions of the key regulated pollutants, NOx, CO, unburned hydrocarbons, and particulates. The efficiency and economics of the plant are both favorable compared to competing distributed energy systems. When coupled to high temperature steam gasification, the overall plant has been predicted to provide unparalleled efficiency, emissions performance, and economic potential, while not requiring water to be supplied from outside sources. The elimination of local water requirement is viewed as a

The technical accomplishments in this portion of the overall project have included progress in demonstration of the PoWER system; development of testing facilities for characterizing fuel from the steam gasification system; and modeling of the integrated plant. The PoWER system demonstration consists of two developmental engine facilities, one being designed primarily to study the dilute combustion that inherently occurs in the PoWER cycle, and the other being a more modern demonstration system. The first is fully functional, and has been used for several purposes: 1) demonstrating complete operation of the PoWER cycle, including startup procedures, control, and varying load capability; 2) demonstration of multi-fuel operation; 3) demonstration of ultra low emissions on multiple fuels; 4) demonstration of water production; 5) validation of in-house system design models; 6) fundamental investigation of the reaction processes in dilute combustion.

The second engine is based on more modern technology, and is nearing completion, due in part to FESC support. Although both engines are brassboard design and far from optimal, the second engine is designed for significantly higher efficiency and power output, approximately 180 kW.

Overall system modelling efforts have centered on developing an optimal system architecture, then applying standard thermodynamic analysis in order to predict performance. Multiple system architecture configurations have been considered, and the most promising of those has been identified. Preliminary model results indicate water-neutral operation, with an overall efficiency gain of approximately 2% compared to not integrating the fuel and PoWER subsystems.

This project has been completed. The final report can be found here.

University of Florida
Database Infrastructure for Integrative Carbon Science Research

PI: Sabine Grunwald   **Co-PI:** Timothy A. Martin
Students: C.W. Ross (M.S.); X. Xiong (Ph.D.)
Technical staff: Brandon Hoover
Post-Docs: Nichola M. Knox

Description: Rising CO_2 concentrations in the atmosphere and effects on global climate change have been well documented, and future impacts are uncertain but potentially devastating. Florida's natural and agro-forest ecosystems have much potential to sequester carbon in biomass and soils due to unique climatic and landscape conditions. However, research gaps exist to accurately assess carbon pools and fluxes at coarse scales, ranging from county to the region and larger. The overarching objective of this project is to address these obstacles by developing a terrestrial carbon information system (called "TerraC") for the carbon science community, focused on ecosystems in Florida. The information system will be administered through the UF Carbon Resources Science Center (http://carboncenter.ifas.ufl.edu), a multi-disciplinary Center dedicated to research in support of enhanced agricultural and natural resource carbon management.

Budget: $199,440
Universities: UF
External Collaborators: Natural Resources Conservation Service-U.S. Department of Agriculture

Progress Summary

Our main accomplishments so far were to develop the TerraC database structure, functions to enter/download data, meta data tracking, tools to integrate carbon and ancillary environmental data, project menus, and user and administrative tools to manage the data. Several submenus have been developed to manage and store carbon specific data including: below-ground carbon (soils, geology/parent material), atmospheric carbon, vegetation (biomass carbon), and ecosystem (aggregated carbon). In addition, menus to accommodate ancillary environmental data were created that complement carbon dataset. The latter set of data is usually required for synthesis analysis.

Several improvements to handling of streaming out of large data sets with several thousands of records, additions of sub-menus, and a new spectral sub-module were developed. After beta-testing is completed they will be released to TerraC users.

Several large datasets, among them forest and climate data from the PINEMAP project and soil carbon data across the State of Florida, have been uploaded into TerraC. A soil carbon synthesis project conducted in the State of Florida has been completed. This analysis was based on soil carbon data and environmental covariates where machine learning and data mining techniques were used to integrate data and model soil carbon in dependence of environmental conditions (soils, topography, geology) and drivers (land use, climate).

Funds leveraged/new partnerships created

TerraC is now providing the data infrastructure for a $20 million integrated research, education, and extension project. This large-scale project funded by the United State Department of Agriculture (USDA) – National Institute of Food and Agriculture (NIFA) – Agriculture and Food Research Initiative

(AFRI) Regional Project "PINEMAP: Integrating Research, Education and Extension for Enhancing Southern Pine Climate Change" (2011-2016) allows to populate TerraC and will cross-fertilize several research idea centered around carbon budgets and assessments, carbon change in dependence of global climate change and other stressors, and carbon sequestration and regulation as an ecosystem service. Many other similar synthesis projects will be facilitated through TerraC-PINEMAP.

The PINEMAP project goals are to create, synthesize, and disseminate the necessary knowledge to enable southern forest landowners to:
- harness pine forest productivity to mitigate atmospheric carbon dioxide
- more efficiently utilize nitrogen and other fertilizer inputs
- adapt their forest management approaches to increase resilience in the face of changing climate.

PINEMAP has a multi-tier data structure representing different scales including:
- Tier 1 (historic measurements of tree response in dependence of treatments at about 700 locations across the southeastern U.S.)
- Tier 2 (new base measurements at hundreds of sites across the southeastern U.S.)
- Tier 3 (high-intensity measurements to capture water and carbon cycle at 4 sites)

Annual Progress Report

The main components of the TerraC database structure and web interface has been completed. Several submenus have been developed to allow integration of carbon and environmental covariates including: below-ground carbon (soils, geology/parent material), atmospheric carbon, vegetation (biomass carbon), and ecosystem (aggregated carbon). Submenus had to be standardized to give users the flexibility to enter (upload) carbon data created with different methods and protocols.

TerraC is now providing the data infrastructure of the PINEMAP (NIFA funded) project described above, which required to enhance TerraC to include not only carbon data, but also other types of environmental observations / measurements. For example, the atmosphere module in TerraC previously allowed storing of only carbon-specific properties (e.g., carbon flux measurements). Over the last year we extended its capabilities to include also ancillary environmental observations. For example, users can now also upload climatic properties (e.g., temperature, precipitation, vapor pressure, etc.) that impact and relate to the carbon cycle. These extensions to allow storage of ancillary environmental datasets in submenues of TerraC (such as soils and vegetation) have also been tackled.

The PINEMAP project has been utilizing the TerraC system as its data hub. The tier 1 PINEMAP dataset, which are historic data collected by Forest Cooperatives from hundreds of sites across the southeastern United States, have been integrated into TerraC. The legacy data consists of thirteen data sets that had to be standardized and harmonized, and meta datasets had to be developed. They are now being shared throughout the PINEMAP project via TerraC. With the addition of the legacy data, new standardized methods have been added to TerraC so that vegetation data (e.g., tree height and diameter) and treatment options (e.g., fertilization level) can now be uploaded into the system and shared among researchers, students, and other users.

Ancillary environmental data that are spatially extracted to tier sites were compiled to represent historic and future climate. To accomplish this, the spatial data layers (GIS data layers) from the (i) Parameter-Elevation Regressions on Independent Slopes Model (PRISM) [800 m grid resolution], (ii) (North American Regional Climate Change Assessment Program) (NARCAAP) [50 km grid resolution], and (iii) Idaho geospatial group [4 km grid resolution] were acquired (Table 1). The spatial data were

reformatted, harmonized to a common map projection, clipped and then extracted to tier site locations using GIS techniques.

Table 1. Summary of climate data complementing the tier 1 site locations.

Type	Variables (Properties)	Data source *Additional Information*
Climate	Precipitation Minimum temperature Maximum temperature Dew point temperature Mean temperature (average of Tmin and Tmax) Vapor pressure	Parameter-Elevation Regressions on Independent Slopes Model (**PRISM**) *Period: 1970 to 2010* *Monthly climatic data;* *Yearly averages of climatic data;* *Long-term (30 year) average of climatic data.* *Spatial resolution: ~4 km; 2.5 arcmin* *Spatial resolution (SE U.S.): 800 m; 30 arcsec*
Climate	Precipitation Maximum relative humidity Minimum relative humidity Mean specific humidity Mean downward shortwave radiation at surface Mean wind direction Minimum temperature Maximum temperature Mean wind speed	**Idaho Geospatial** *Period: 1971 to 2011* *Daily climatic data;* *Monthly climatic data;* *Yearly averages of climatic data;* *Long-term (30 year) average of climatic data.* *Spatial resolution: ~4 km; 2.5 arcmin*
Climate	Surface air temperature Precipitation Surface downdwelling shortwave radiation Surface pressure Surface specific humidity Num. frost days Minimum monthly temperature Maximum monthly temperature Mean daily minimum temperature Mean daily maximum temperature	**NARCAAP (North American Regional Climate Change Assessment Program)** *Historic climatic data (1971-2000);* *Climate change projections (6 different scenarios) (downscaled to the finest resolution in North America)* *Spatial resolution: 50 km*

The tier 1 (site-specific forest measurements and geographic coordinates) and climate data (PRISM, NARCAAP, and Idaho geospatial) were uploaded into TerraC and meta data created. These data are now useable for synthesis analysis to identify the effect of climate on forest treatments along geographic gradients in the southeastern U.S. (in progress).

The PINEMAP project also spurred a new development that has been named "Umbrella". Because the project has researchers from multiple institutions that needed to upload and share their data to entire groups of people inside the project, the TerraC team developed "Umbrella" to house multiple projects from multiple owners and assign group privileges to individual project datasets. So PINEMAP (and other Umbrella research projects) is able to assign all of the modeling researchers' permissions to all of the data they need by applying the group's read permission to the project data they need. Using the PINEMAP project, this function is still in the final stages of testing and will be released to all users soon.

Carbon measurements based on spectral techniques have become popular and are now commonly used to complement lab-based analytical techniques. For example, visible-near infrared (VNIR) and mid-infrared (MIR) spectroscopy has shown success to infer on soil carbon rapidly and cost-effectively. In addition, spectral data derived from remote sensing (e.g., Landsat Thematic Mapper satellite images) have been used extensively to infer on landscape features including vegetation indices, such as the Normalized Difference Vegetation Index or Biomass, which allows relating to the carbon cycle. Thus, we developed a spectral sub-module in TerraC that can handle spectral data. Hyperspectral datasets are large and complex consisting of hundreds of repetitive blocks of reflectance values or wavelengths. The spectral sub-module uses column names with incremental wavelengths. To accommodate this kind of data, and to make the system as user-friendly as possible, we are currently beta testing a new method of adding columns that will automate the process of adding large numbers of columns by allowing the user to input variables such as beginning wavelength, ending wavelength, and the increment in order for the system to automatically generate the columns needed. Otherwise data managers would need to add each column individually, which can be quite cumbersome. The design of the spectral module has been completed and is now being coded into TerraC to allow testing.

The most telling indicator that TerraC has been growing has been that a new backend must be developed in order to access larger datasets. The current system has served the TerraC community well, but, as datasets get larger, the system needs to grow in order to keep up with the demand. The PINEMAP project is utilizing datasets that are quite large. In order to output these datasets to users, the TerraC group is moving away from the ASP programming language that could only handle 15,000 to 20,000 rows of data. The new platform, based on Microsoft's ASP.NET, will be able to handle data chunks much larger and will be able to provide them to users much faster than the previous version. The recoding is underway and will be completed in the near future after successful beta-testing.

Another major accomplishment is to utilize carbon data hosted by TerraC to facilitate synthesis analysis. This has been demonstrated in a project where soil carbon data (n = 1,080 site locations) collected throughout the State of Florida were spatially correlated with a comprehensive set of 212 environmental covariates (representing soils, climate, topography, geology, and ecology). The environmental covariates were derived from various GIS and remote sensing resources. Machine learning and data mining techniques, such as ensemble regression trees (State Vector Machines and Random Forest), were used for data integration and to model soil carbon in dependence of environmental properties. This synthesis research found that land use / land cover and hydrologic properties impart most control on the variation of soil carbon.

Peer-reviewed Publications:

1. Cao B., S. Grunwald and X. Xiong. 2012. Cross-regional digital soil carbon modeling in two contrasting soil-ecological regions in the U.S. *In* **Minasny B.**, B.P. Malone, and **A.B. McBratney (eds.).** CRC Press, Taylor and Francis, 2012. ISBN: 978-0-415-62155-7.

2. Patarasuk R., S. Grunwald, T.A. Martin and B. Hoover. 20__. Integrative modeling of tree response along geographic and ecological trajectories in the southeastern U.S. Ecological Modeling J. (in preparation).
3. Ross C.W. 2011. Spatiotemporal modeling of soil organic carbon across a subtropical region. M.S. thesis. University of Florida, Gainesville, FL.

4. Ross C.W., S. Grunwald, and D.B. Myers. 20__. Spatiotemporal modeling of soil carbon stocks across a subtropical region. Soil Sci. Soc. Am. J. (in review).
5. Xiong X., S. Grunwald, D.B. Myers, J. Kim, W.G. Harris and N.B. Comerford. 2012. Which soil, environmental and anthropogenic covariates for soil carbon models in Florida are needed? *In* **Minasny B.**, B.P. Malone, and **A.B. McBratney (eds.).** CRC Press, Taylor and Francis, 2012. ISBN: 978-0-415-62155-7.
6. Xiong X., S. Grunwald, D.B. Myers, J. Kim*, W.G. Harris and N.B. Comerford. 2012. Which soil, environmental and anthropogenic covariates for soil carbon models in Florida are needed? The 5th Global Workshop on Digital Soil Mapping 2012, Sydney, Australia, April 10-13, 2012.
7. Xiong X., S. Grunwald, D.B. Myers, J. Kim, W.G. Harris and N.B. Comerford. 20__. Optimal selection of predicting variables for soil carbon modeling in Florida, USA. Geoderma (in review).

Presentations
1. Grunwald S. 2012. Soil carbon variability across large landscapes. Soil and Water Science Research Forum, Gainesville, FL, Sept. 7, 2012.
2. Grunwald S., B. Hoover, and R. Patarasuk. 2012. Terra C and Pinemap data resources. Webinar series Pinemap project. Gainesville, FL, July 13, 2012.
3. Grunwald S. 2011. Geospatial and spectral soil carbon modeling across large regions. NRCS, National Soil Survey Center (NSSC), Lincoln, NE, May 13, 2011.
4. Grunwald S., T. A. Martin, B. Hoover, G.M. Vasques, B. Zhong, and D.L. DePatieJr. 2010. Terrestrial carbon (TerraC) information system. 2010 Florida Energy Systems Consortium (FESC) Summit, Orlando, FL, Sep. 27-29, 2010.
5. Grunwald S., T.A. Martin, G.M. Vasques and B. Hoover. 2009. Database infrastructure for integrative carbon science research. Florida Energy Systems Consortium Summit, Tampa, FL, Sept. 29-30, 2009.
6. Hoover B., S. Grunwald, T.A. Martin, G.M. Vasques, N.M. Knox, J. Kim, X. Xiong, P. Chaikaew, J. Adewopo, B. Cao and C.W. Ross. 2011. The Terrestrial Carbon (Terra C) Information System to facilitate carbon synthesis across heterogeneous landscapes No. 264-10. Symposia Spatial Predictions in Soils, Crops and Agro/Forest/Urban/Wetland Ecosystems, ASA-CSSA-SSSA Int. Meeting, San Antonio, TX, Oct. 16-19, 2011.
7. Hoover B., N.M. Knox, S. Grunwald, T.A. Martin, X. Xiong, P. Chaikaew, J. Kim, and B. Cao. 2011. Synthesis tools for carbon assessment in ecosystems. FESC Summit, University of Florida, Gainesville, FL, Sept 28-29, 2011.
8. Hoover B., G.M. Vasques, B. Zhong, S. Grunwald, T. A. Martin, and D.L. DePatieJr. 2010. The terrestrial carbon (TerraC) information system Vers. 1.0. 11th Annual Soil and Water Science Research Forum, Gainesville, FL, Sep. 10, 2010.
9. Xiong X., S. Grunwald, D.B. Myers, W.G. Harris, A. Stoppe and N.B. Comerford. 2011. Are soil carbon models transferable across distinct regions or scales in Florida? No. 262-8. Symposia Spatial Predictions in Soils, Crops and Agro/Forest/Urban/Wetland Ecosystems, ASA-CSSA-SSSA Int. Meeting, San Antonio, TX, Oct. 16-19, 2011.

University of Florida

Development of Biofuel Production Processes from Synthetic and Biomass Wastes

PI: Pratap Pullammanappallil
Students: Diane Chaulic (PhD), Zhuoli Tian (PhD), Gayathri Ram Mohan (MS), Nicholas Locastro (BS)

Description: With the ever-increasing price of petroleum and its finite supply, it is of high priority to develop domestic sources of transportation fuel, as well as other chemicals. Ethanol is an attractive alternate fuel that is being produced from corn starch. It is necessary to target other feedstocks for biofuel production and develop processes that have a minimal environmental impact. There is considerable ongoing research on developing processes and catalysts for conversion of biomass to biofuels like ethanol (called cellulosic ethanol process). But this project addresses other feedstocks with the following objectives: 1) development of biocatalysts for the conversion of waste biodegradable poly lactic acid based plastics to ethanol and 2) development of processes that processes for the production of additional fuels like biogas, bio-oil and biochar from the waste and byproducts of a cellulosic ethanol plant for the clean-up and reuse of these waste streams

Budget: $192,000
Universities: UF
External Collaborators: UCF

Progress Summary

Process development for biogasification and clean-up of cellulosic ethanol stillage
- Demonstrated that struvite (a slow release fertilizer containing ammonia and phosphate) can be recovered from the anaerobically digested stillage.
- A process was developed to recover struvite along with other organic carbonaceous residue remaining in the digested stillage.
- Showed that this process can be applied with or without prior anaerobic digestion of stillage.
- Estimated that sufficient phosphorous is contained in the recovered sludge to grow the biofuel crop. The application of this sludge to grow the bioenergy crop offsets the need for addition of phosphate fertilizer.
- Demonstrated that nanoceria enhances anaerobic digestion of biomass.

Process development for preparation of enzymes to saccharify pectin rich biomass feedstocks.

- Developed a process that can be implemented in the biorefinery to prepare biocatalysts for saccharification of pectin-rich biomass and a method for saccharifcation of such biomass. This process has applications for pretreating citrus pulp, sugar beet pulp, apple pomace, fruit and vegetable wastes etc prior to production of liquid fuels.

Biocatalyst development for conversion of waste PLA based plastics to ethanol

- An *E.coli* mutant was constructed that is incapable of utilizing lactic acid.
- Into this mutant a Lactate dehydrogenase (LDH) gene was inserted. Currently experiments are underway to verify the expression of this gene.

University of Florida
Development of Low-Cost CIGS Thin Film Hot Carrier Solar Cells

PI: Gijs Bosman   **Co-PI:** Tim Anderson
Students: Yige Hu, PhD**.**

Description: PV has entered into a period of record growth. Most of the current production is based on crystalline Si technology. However, there are fundamental limits to the ultimate Si costs that may inhibit it from achieving the desired level of contribution to worldwide energy production. In contrast, thin-film PV technology can reach the desired outcome due to fast deposition rates and lower cost. Our study is focused on hot carrier solar cells for cell conversion efficiency improvement in a low cost, high throughput CIGS system. The rapid thermalizaton loss of hot photoexcited carriers interacting with the lattice can potentially be reduced through phonon engineering in the absorber layer; the subsequent extraction of the hot carriers may be realized through device engineering of energy selective contacts.

Budget: $ 126,112.00
Universities: UF

Progress Summary

Hot carrier solar cells allow hot carriers to be collected before energy is lost to the lattice. This ultimately leads to a higher open circuit voltage since the average energy of the collected electron is greater than the band gap energy. It also leads to a higher short circuit current, leading to an overall greatly improved efficiency.

Photocurrent measurements as a function of applied bias were carried out on fabricated CIGS solar cell structures to characterize the hot carrier effect. In a preliminary experiment the CIGS cell is exposed by LED light of wave length 365nm, 455nm, 630nm and 740nm, respectively. The incident photon energy defines the initial hot carrier energy. The resulting current shows a different bias dependency with respect to high energy carriers and low energy carriers. A relationship between the photocurrent and initial hot carrier energy is being formulated from which the relative density of hot electrons and its effect on cell operation can be determined from measured current voltage data.

FIGURE 1 CIGS PIN HOLE STRUCTURE

A study of the reverse bias dark JV characteristic helps in the separation of hot carrier effects from other device phenomena. The commonly used dark current model: $J_{dark} = J_0 \left[e^{\frac{q(V-IR_S)}{nk_BT}} - 1 \right]$ cannot explain the linear characteristic at low reverse bias and superlinear characteristic at high reverse bias of the CIGS solar cell. Space charge limited current (SCLC) via pinholes in the ZnO and CdS layers
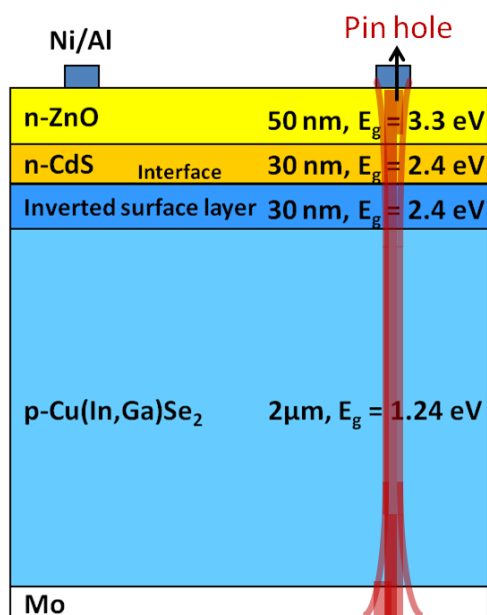
consisting of a metal-CIGS-molybdenum structure (Figure1) is proposed as contributing to the reverse bias leakage current [1].

The SCLC model helps to better understand the dark current and gives a baseline for separating the photocurrent contribution from dark current components in the CIGS cell. Therefore our hope is that photon induced hot carrier effects can be uncovered and demonstrated.

Annual Progress Report

The focus of this period is studying the dark IV characteristic of CIGS solar cells to extract photocurrent from the measured total current.

The dark current density is commonly modeled as $J_{dark} = J_0 \left[e^{\frac{q(V-IR_S)}{nk_BT}} - 1 \right]$ where $J_0 = J_{01} + J_{02}$ is the diode saturation current density. $J_{01} = q \left[\frac{D_n n_{p0}}{L_n} + \frac{D_p p_{n0}}{L_p} \right]$ is the diffusion related component and $J_{02} = q \frac{n_i}{2} W v_{th} N_t \sigma$ is the trap assisted generation-recombination related component. J_{02} dominates via generation the reverse dark current density for a non-ideal device. The depletion width $W \propto \sqrt{V_{bi} + V}$, therefore J_{02} follows a square root dependency of the bias. However, the experimental dark current density in CIGS solar cells reported in the literature is observed having a linear characteristic at low reverse bias and superlinear at high reverse bias. Mechanical scratches are proposed to explain the linear behavior since the reverse current increases dramatically with the increase of the load of scratches and the reverse current varies linearly over $1/T^{1/4}$ [2]. In our previous experiment on the 19% efficient "champion cell", the reverse dark current density (Figure 2) shows neither square root nor linear bias dependence. The generation related component and "scratch effect" are not able to exhibit the characteristic. Space charge limited current (SCLC) via pinholes in the ZnO and CdS layers consisting of a metal-CIGS-molybdenum structure is proposed as contributing to the reverse bias leakage current [1].
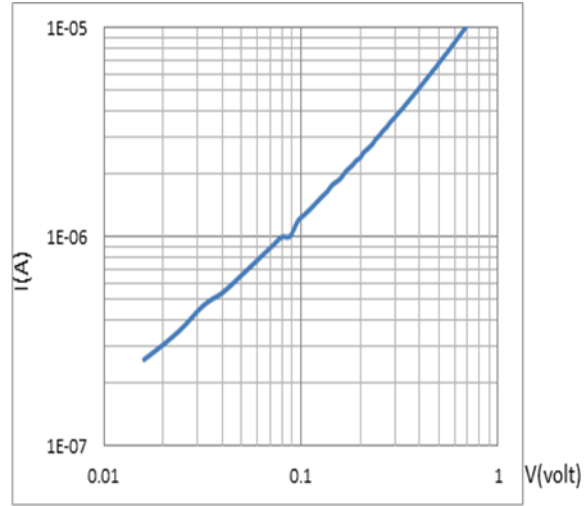
FIGURE 2 CIGS DARK IV REVERSE BIAS CHARACTERISTIC

Ohm's Law $J = q \mu n_0 \frac{V}{L}$ dominates at low applied voltage, where n_0 is the electron density from thermal generation. When the electrode injects carriers exceeding the number of thermal carriers, the linear relation of the current and voltage no longer holds. The resulting SCLC is proportional to the square of the voltage[1]. It is expressed as $J = q \mu n_s \frac{V}{L} = q \mu \frac{\epsilon_0 \epsilon_r V}{qL^2} \cdot \frac{V}{L} = \mu \frac{\epsilon_0 \epsilon_r V^2}{L^3}$. The crossover voltage V_T, where the current transitions from Ohm's law to the square law, can be calculated as $V_T = \frac{L^2 q n_0}{\epsilon_0 \epsilon_r}$ [Eq. 1.]

A MEDICI simulation is carried out to check if the software can handle SCLC phenomena where specifically the contact boundary conditions play an important role. The heavily doped n-type CIGS, modeling a metallic pinhole shorting the contact to the absorber layer, provides excess electrons for injecting into the lightly doped p-type CIGS. The dark current density versus voltage is shown in Figure
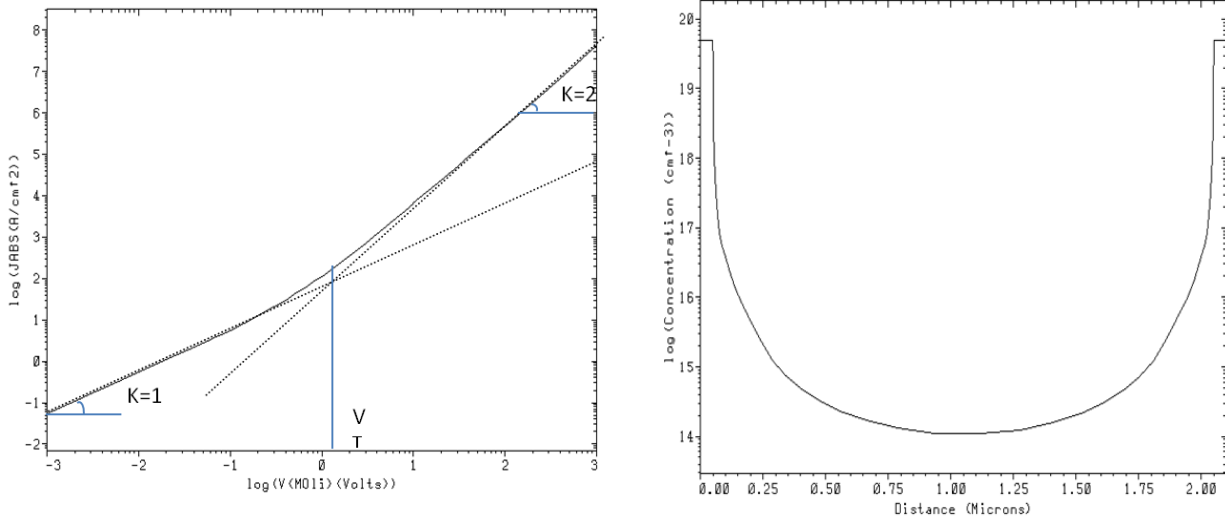
FIGURE 3 MEDICI SIMULATED CIGS ELECTRON DENSITY PROFILE

FIGURE 4 MEDICI SIMULATED CIGS SPACE CHARGE LIMIT CURRENT

3. The current density follows ohm's law at low bias and the square law in the high bias regime, as shown by the extrapolation lines with log slopes of 1 and 2, respectively. The doping density of the p-type CIGS is 6×10^{11}/cm^2. At V=10^{-3} volts, the ohm's law current density is calculated: $j = q\mu_p p\frac{V}{L} = q\mu N_a\frac{V}{L} = 1.44 \times 10^{-4} A/cm^2$. The plot in Figure 3 reads a current density of 5×10^{-2} A/cm^2 at the same voltage. The increased current density comes from the fact that the carrier density of the lightly doped p-region is converted to n-type by the adjacent heavily doped n$^+$ regions. The electron density is plotted in Figure 4. The heavily doped n$^+$ contacts make the effective carrier density between the contacts to become 10^{14}/cm^3 and the effective distance between contacts reduces to 1μm due to diffusion. The current density is then calculated as $q\mu_n n\frac{V}{L} = 4 \times 10^{-2} A/cm^2$. The crossover voltage V_T equals 1.2V as calculated from Eq. 1. In Figure 3, the point at where the extrapolated lines cross agrees with this value. At the crossover voltage, the total current density is twice the corresponding ohmic current density, since it is where the SCLC from the excess carriers equals the ohmic current from the thermal carriers. The total current density is the sum of these two components.

In a CIGS solar cell, the contact metal may penetrate the thin layers of ZnO and CdS causing "pinholes" that are essentially extensions of the metal electrode contacting the CIGS directly. In addition the CIGS layer may have regions with low densities of acceptor sites. If the pinholes contact an area of low-carrier density in the CIGS they form a SCLC structure, because the low-carrier density causes the crossover voltage to occur sooner and the metal electrodes are abundant electron carrier sources. Pinhole current is a parasitic loss in a CIGS device. The total current
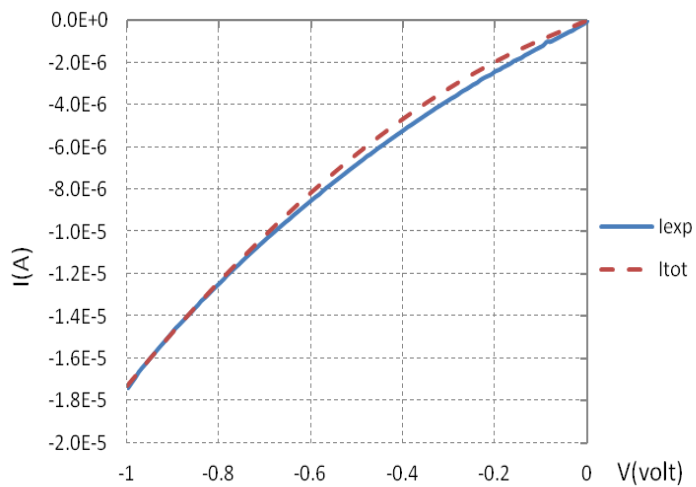

FIGURE 5 SPACE CHARGE LIMITED CURRENT MATCHING WITH THE MEASURED CIGS REVERSE BIASED DARK CURRENT DENSITY

is expressed as a sum of current through the pinholes and current through the rest of the device: $I_{total}=J_{SCLC}\times A_{SCLC}+J_{solar}\times A_{solar}$, where A_{SCLC} and A_{solar} are the overall effective pinhole area and the solar cell area, respectively. Under reverse bias, the total current is dominated by the SCLC giving weak voltage dependence. As the voltage increases in forward bias, the solar current increases exponentially and eventually dominates the total current. The SCLC matching with the CIGS "champion cell" dark current versus reverse bias voltage is shown in Figure 5, where measured reverse bias dark current is compared to current simulated via the pin-hole model. The pinhole area is calculated by $A_{SCLC}=I_{total}/J_{SCLC}$ in the reverse bias section. I_{total} is the experiment dark current and J_{SCLC} is obtained by the MEDICI program. The calculated effective pinhole area is about $0.147\mu m^2$, which makes up only $1/10^7$ of the solar cell contact area. The pinhole current is calculated from the simulated pinhole current flux multiplied by the pin hole area plus the dark current density simulated by the MEDICI program. Figure 5 shows that there is a good match between the experiment and the model.

[1] M.A.Lampert, "Universality of non-Ohmic shunt leakage in thin-film solar cells," *Journal of Applied Physics*, vol. 108, Dec. 2010, pp. 124509-124509-10

[2] O. Breitenstein, J. Bauer, A. Lotnyk, and J. Wagner, "Defect induced non-ideal dark characteristics of solar cells," *Superlattices and Microstructures*, vol. 45, 2009, pp. 182 – 189

University of Florida

Development of Novel Water Splitting Catalysts for the Production of Renewable Hydrogen

PI: Helena Hagelin-Weaver
Students: Justin Dodson (Ph.D.)

Description: This project focuses on the development of iron-based catalysts for the thermochemical splitting of water into hydrogen and oxygen. The thermochemical process of splitting water is particularly well-suited for the utilization of solar energy to provide the heat for the reaction and is a way to produce a renewable hydrogen fuel. As hydrogen is difficult to transport and store, producing hydrogen on site for power plants using proton exchange membrane (PEM) fuel cells or internal combustion engines to generate electricity or for the production of chemicals, such as liquid hydrocarbon fuels, is a very attractive approach. The project uses a two-step process in which water is passed over a reduced iron oxide to generate hydrogen while the oxygen is taken up by the oxygen-deficient iron oxide (Step 1: $FeO_{x-1} + H_2O \rightarrow FeO_x + H_2$). In the second step the resulting iron oxide is heated to desorb oxygen and regenerate the oxygen-deficient iron oxide to close the catalytic cycle (Step 2: $FeO_x \rightarrow FeO_{x-1} + \frac{1}{2}O_2$). The main objectives of the project are to develop mixed metal oxide catalysts that 1) will release oxygen at temperatures lower than 1500°C (Step 2), while still maintaining water-splitting activity (Step 1) and 2) are stable up to the temperature necessary for the oxygen desorption step.

Budget: $ 100,000
Universities: UF

Progress Summary

The high-temperature reactor for testing of water-splitting catalysts has been constructed (Figure 1) and calibrated. An iron oxide catalyst supported on zirconia has been tested in the reactor system and some preliminary data has been colleced. Initial results reveal that the catalyst can be regenerated at temperatures of 1,300°C, which is lower than the typical 1,500°C. We are currently working on lowering the temperature further by modifying the catalyst composition.
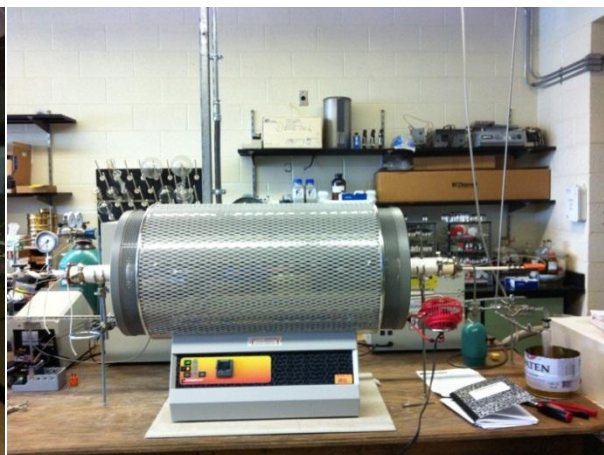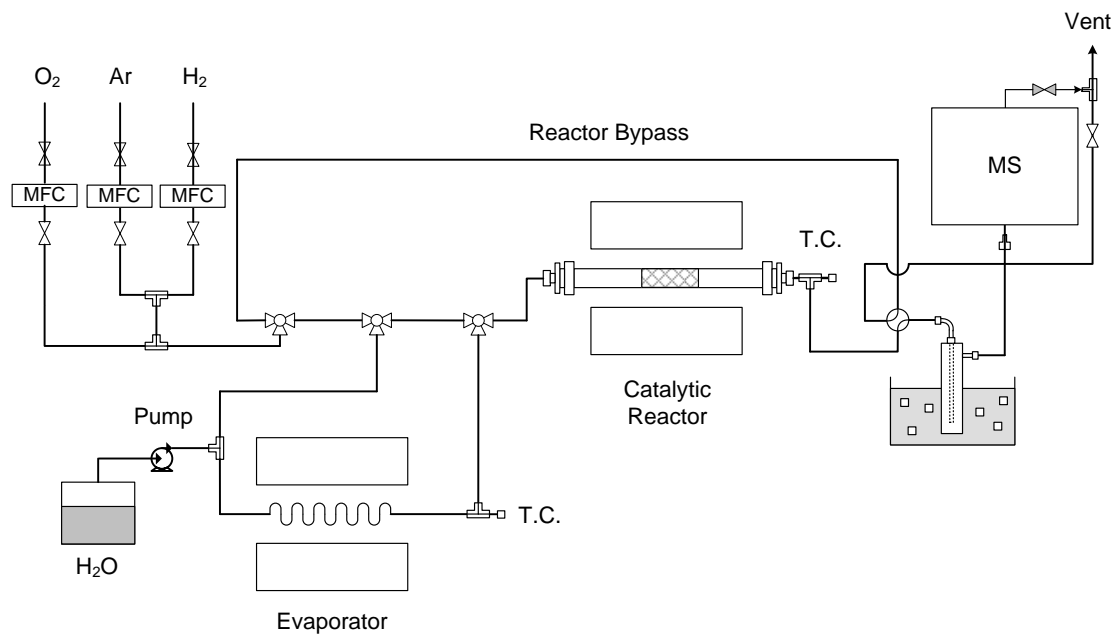
Figure 1. Top: drawing of reactor system. Bottom left: photo of syringe pump and evaporator. Bottom right: photo of high-temperature reactor (mass spectrometer for product analysis is visible in the right hand corner of the photo).

Funds leveraged/new partnerships created

The PI has initiated a collaboration with Dr. Juan Nino in Materials Science and Engineering to design the second generation catalysts. Dr. Nino has extensive experience with solid oxide fuel cell materials, i.e. high-temperature ceramics with oxygen mobility. These materials will be produced as foams by Dr. Nino's group, and the PI will use these as catalysts or catalyst support in the water splitting reaction. Data collected from these foams will be used in future proposals to funding agencies, such as DOE and NSF.

Annual Progress Report

Reactor Construction and Calibration. The reactor system for water splitting has been constructed and calibrated. Figure 1 presents a drawing of the reactor configuration and Figure 2a is a photograph of the assembled system. The reactor system has two modes of operation. The first step is water decomposition, where water (steam) is decomposed over an oxygen-deficient iron oxide catalyst to produce hydrogen and iron oxide. In the second step, the catalyst is heated in a flow of argon until the oxygen desorbes from the iron oxide and the oxygen-deficient iron oxide is regenerated. In both steps the reaction products are monitored on-line using a mass spectrometer.
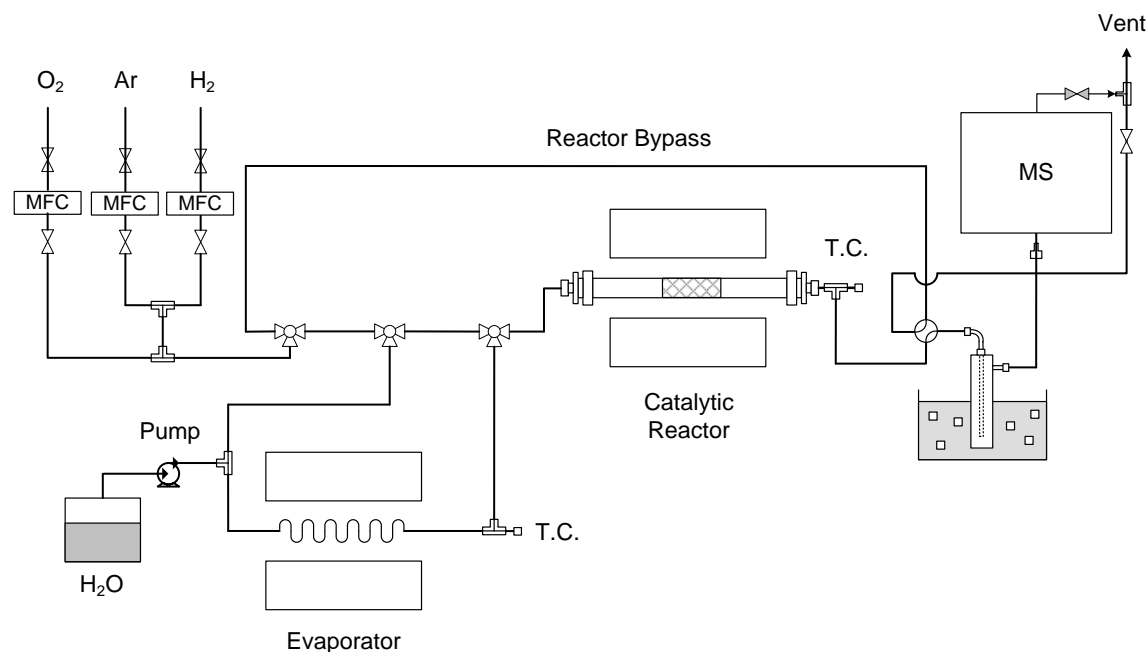

Figure 6: Drawing of The Reactor System For High-Temperature Water-Splitting.

During the water decomposition step, water is pumped into the evaporator using a syringe pump (Figure 2b). Argon is used as the carrier gas for this step, as well as an internal standard for the mass spectrometer and allows quantification of reaction products. The argon is supplied via a mass flow controller, which is displayed in Figure 3a (the figure also includes the mass flow controllers which are used for the calibration of the mass spectrometer). After the evaporator, the lines to the high-temperature furnace, a Carbolite STF 1650 (Figure 3b), are heated to prevent condensation of the steam. The steam then enters the high-temperature furnace, where the catalyst is located. The water in the product stream leaving the reactor is condensed before the gas phase products are analyzed. Steam is continuously introduced until no hydrogen is detected in the products. At this point, the syringe pump and the

evaporator will be bypassed and only argon is fed to the reactor. The temperature in the reactor is then increased until the oxygen desorbs and the catalyst is regenerated.

Figure 2: a) (left) Completed water-splitting reactor system, and
b) (right) evaporator furnace used to produce steam for the water-splitting step.

The completed reactor system has been calibrated, which was done by feeding known flow rates of hydrogen and oxygen to the mass spectrometer (MS). In both cases, the argon flow rate was kept constant at the flow rate used during reaction, and the hydrogen and oxygen flow rates were varied. The calibration data is then stored in the MS software and is used to quantify the amounts of hydrogen and oxygen produced during reaction.
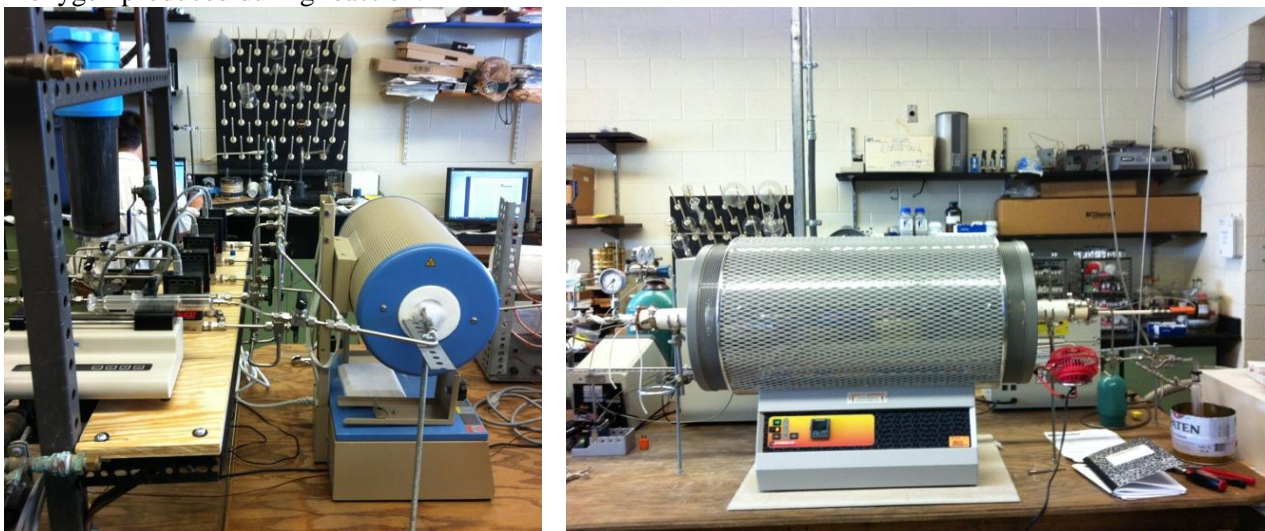

Figure 7: a) (left) the mass flow controllers (MFCs) are the black boxes used to flow argon for the reaction and to calibrate the mass spectrometer. The syringe pump is located in front of the MFCs in the picture and is used to introduce water into the system. The water is evaporated in the furnace to the right of the MFCs and the syringe pump, and
b) (right) high temperature furnace.

Activity Measurements. Two catalysts catalysts have been prepared for initial catalyst testing, an iron oxide deposited on zirconia (FeO_x/ZrO_2) and iron oxide deposited on yttria-stabilized zirconia (FeO_x/YSZ). Initial thermal reduction experiments of the FeO_x/ZrO_2 have been performed and are shown in Figure 4. In these experiments, the unreduced catalyst (Fe_2O_3/ ZrO_2) is heated under a flow of argon and the oxygen partial pressure in the reactor outlet is monitored as a function of temperature and time. During these experiments, the catalyst was first heated to 1,000C and the O_2 signal monitored. When no more oxygen could be detected, the reactor temperature was increased in 100°C increments first to 1,100°C and then 1,200°C and so on, while monitoring the O_2 signal. This will continue until 1,500°C, or until no more O_2 is detected in the product stream, whichever comes first. Once a suitable O_2 desorption temperature has been established, this temperature will be used to run several water decomposition and catalyst regeneration (O_2 desorption) cycles.

Future Work. Once data has been collected for the FeO_x/ZrO_2 and FeO_x/YSZ catalysts, the catalyst compositions will be modified in attempts to increase the hydrogen yield from the water-splitting step and decrease the catalyst regeneration (O_2 desorption) temperature.
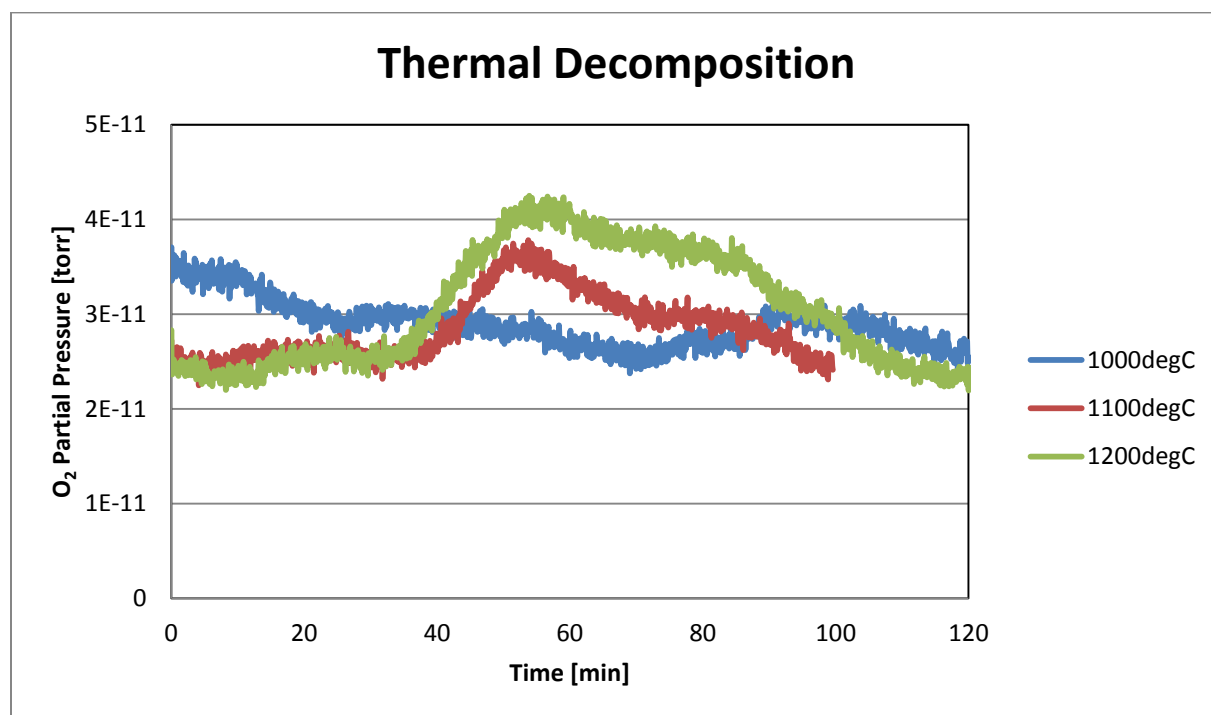

Figure 4: Oxygen evolved during thermal reduction at different temperatures.