

***Beyond Photovoltaics - Nanoscale Rectenna for Conversion of Solar and Thermal Energy to Electricity***

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**Students:** Rudran Ratnadurai, Electrical Engineering/ Ph.D., Michael Celestin, Chemical Engineering/ Ph.D. Justin Boone, Electrical Engineering/ Ph.D.

**Description:** The main objective of the proposal is to commercialize and scale up a new technology, rectenna to convert waste heat energy to electricity. Although the prediction of highly efficient (~85%) solar rectennas was published almost 30 years ago, serious technological challenges have prevented such devices from becoming a reality. Since the ultimate goal of a direct optical frequency rectenna photovoltaic power converter is still likely a decade away, we plan to convert optical solar radiation to thermal radiation (~30 THz regime) using an innovative blackbody source. Leveraging the research efforts of the world-class team members, we plan to further develop the rectenna technology that is within reach of efficient radiation conversion at 30 THz. A fully integrated, blackbody converter and 30 THz rectenna system will be capable of converting at least 50% of solar and thermal energy into usable electrical power, clearly demonstrating a truly transformational new technology in the renewable energy technology sector.

**Budget:** \$598,500

**Universities:** USF

**External Collaborators:** Bhabha Atomic Research Center, India, Florida International University, Miami

## **Progress Summary**

### **Objectives:**

The research objective of this project is to develop a high efficiency solar/ thermal energy conversion using antenna coupled MIM tunnel junction. Towards this, the follow tasks were charted,

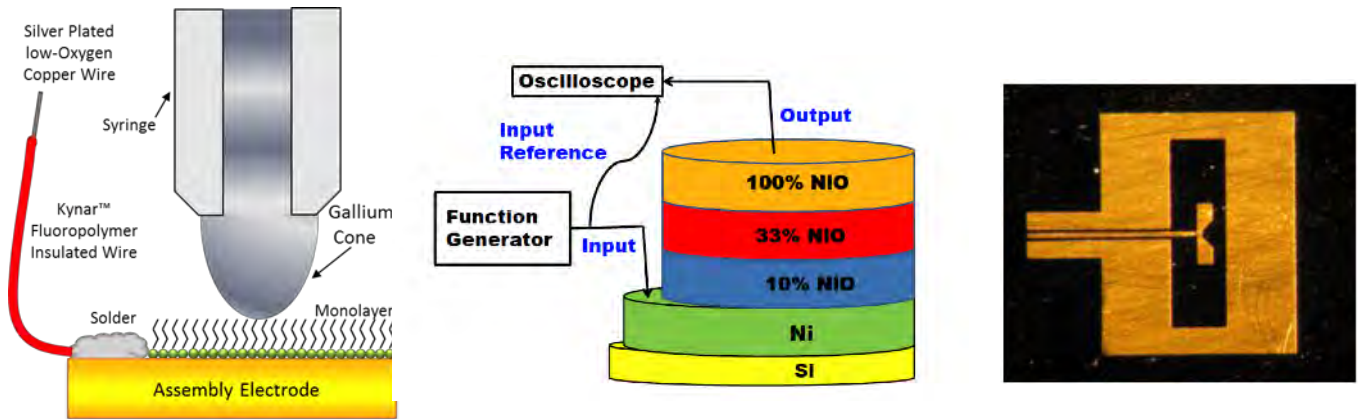
- Fabrication, characterization and testing of Metal-Insulator-Metal tunnel junction,
- Design, fabrication and testing of antenna,
- Integration of antenna and MIM junction.

### **Approach:**

- Determine the AC and DC behavior of SAM based MIM using a novel microinjection contact
- Characterize the organic insulator layer to yield reliable electrical response
- Investigate the effect of varying the oxygen concentration on tunneling response of MIM junction
- Determine the efficiency and gain of the antenna

**Accomplishments:**

- MIM junctions with nanometer thin SAM layer was successfully deposited on Au and made contact with liquid metal to determine the electrical behavior. The organic tunnel junctions exhibited highly asymmetric I-V response with 1:200 rectification ratio.
- Nickel oxide layer was deposited with varying oxygen gradient, which exhibited a novel electrical response when subjected to low frequency AC measurement. The Device exhibited clipping behavior, which could be reproduced reliably. Moreover, the devices were tested over a period of time and observed to be reliable.
- A novel antenna structure consisting of dual design was developed and was observed to resonant at the designed frequency with 25% bandwidth. The radiation pattern also matches with the simulated plot.



**Funds leveraged/new partnerships created:**

We have submitted a proposal to NSF in collaboration with UCF for an Engineering Research center. The proposal is entitled “*Nanosystems Engineering Research Center for Transformational Sensor and Detection Systems*”.

We are currently collaborating with Bhabha Atomic Research Center, India in developing a organic based tunnel junction.

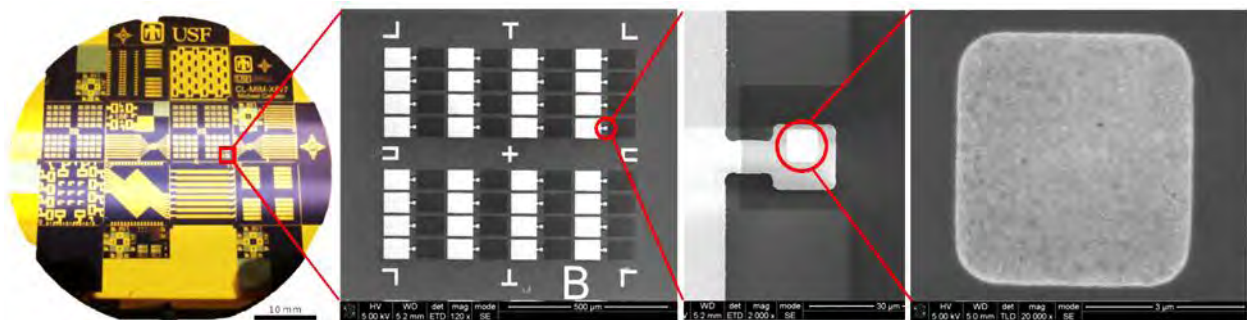
## 2011 Annual Report

Based on the research objective, during the current reporting period of the project, the main focus was to characterize the tunnel junction with organic insulator. As a preliminary approach, several organic films (self-assembled monolayers) were procured and characterized for the thickness uniformity using impedance spectroscopy technique. A novel-processing scheme was used, which incorporates microinjection of liquid metal to small contact areas. MIM tunnel junctions were fabricated with Au-SAM-Ga. In order to provide better electrical behavior, the SAM layer was optimized to yield maximum uniformity. Furthermore, the MIM junctions fabricated with inorganic insulator layer using NiO as the insulator layer was investigated for its electrical characteristics by varying the oxygen concentration in the NiO layer. Specifically, the gas ratio used for depositing the inorganic insulator layer was varied and its effect on electrical behavior of the junction was determined. Additionally, a folded dipole-slot antenna operating at 60 GHz were deigned, fabricated and characterized.

### Research Accomplishments

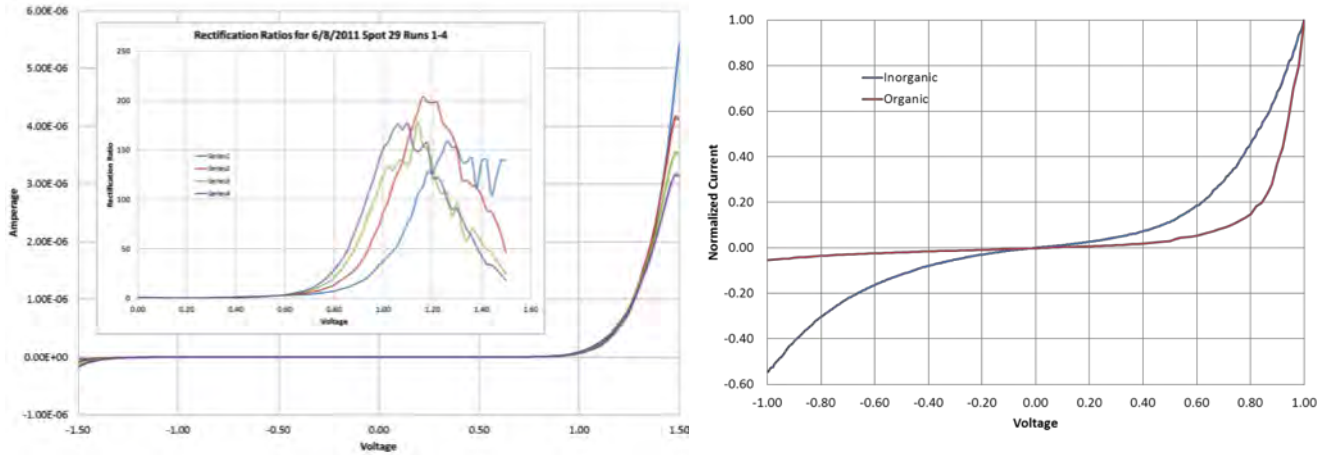
#### 1. Fabrication and Characterization of Self-assembled monolayer based MIM junction

Self-assembled monolayers (SAMs) have been explored for possible use as a dielectric in tunnel junctions for THz rectenna applications. Modeling of device performance was done in MATLAB with a custom modified BDR equation. Automated experimental trace to model fitting successfully deduces barrier heights and tunneling parameters from measured data.



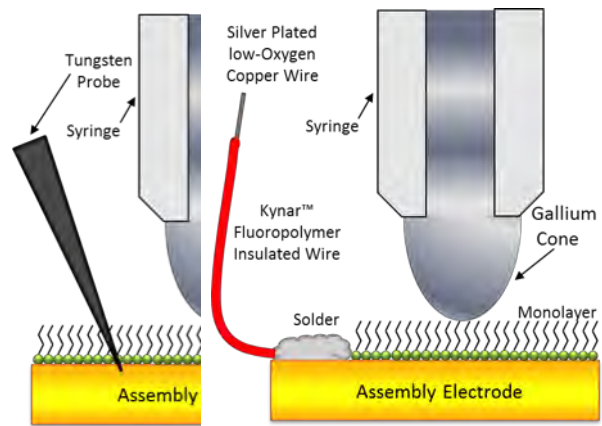
**Figure 1:** Two-inch (50mm) diameter wafer at left holding all test structures fabricated at the Center for Integrated Nanotechnology (CINT). Inset to the right (b) 32-element probe pad diode array, inset (c) detailed SEM of single diode junction, inset (d) process control detail of junction area.

A focus on fabrication of evaporation test structure resulted in a wafer scale integrated test structure. Fabrication was performed at the Center for Integrated Nanotechnology (CINT) in Albuquerque, NM. The device contains thousands of junctions of varying sizes and contact styles down to 0.5  $\mu\text{m}$  features (Figure 1).



**Figure 2:** (a) I-V plot showing of hybrid SAM-Gallium Oxide tunnel junction. Inset, high rectification ratios for aforementioned IV traces reaching up to 200:1. (b) Comparison of Inorganic and Organic tunnel diode performance by normalized current response.

Selection of appropriate SAMs for optimum rectification performance was assisted by a liquid metal test setup employing a Gallium (or Mercury) filled syringe, goniometer stage, and Keithley 2400 source meter. Using this setup, DC performance was studied through a number of SAMs. High performance was seen using Gallium as a top metal and 1H,1H,2H,2H-Perfluorodecanethiol (Figure 2a). Comparing these results to similarly constructed Ni-NiOx-Cr, inorganic tunnel diodes, organic-based devices demonstrate superior performance (Figure 2b). Following these experiments, improvement of the test setup was done to improve noise and minimize complications in the AC domain yet to be tested (Figure 3). AC testing requires full modeling of parasitics to subtract for accurate test results; the modeling of these parasitics in addition to preliminary measurements has been completed.



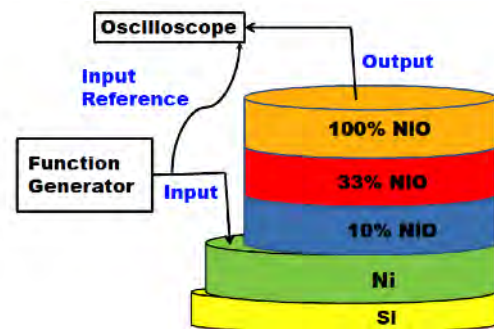
**Figure 3:** Graphic showing improvement of electrical connection with assembly electrode. Tungsten probe contact was a source of noise and inconsistency in measurement and remedied by directly soldering wire to the base.

## 2. Development of inorganic MIM junction using metal-oxide gradient film

Trilayer gradient NiO stack was done by sputtering Ni on 500nm thick SiO<sub>2</sub> on a Silicon substrate followed by sputter deposition of the NiO layers with oxygen concentrations of 10%, 33% and 100%. The percentage of the O<sub>2</sub> content in NiO was controlled by setting the O<sub>2</sub> to Ar flow ratios such that the partial pressure of O<sub>2</sub> was 10% of the total gas pressure during sputtering for 10% NiO layer. The same procedure was followed when depositing NiO layers having 33% of O<sub>2</sub> (NiO (33%). The depositions of the first two layers of NiO were done at 30W. For the 100% NiO layer (NiO(100%)), plasma was struck using only O<sub>2</sub> gas and was done at 50W since O<sub>2</sub> is lighter than Ar and more power is required for the momentum transfer process. The base pressure was 3 μTorr and the deposition pressure was 3mTorr while depositing Ni and 30mTorr while depositing the NiO layers. Pre-sputtering of the Ni target for 5 min was done while depositing both Ni layer and the NiO layers to avoid any contamination. After the deposition of each NiO layer, a wait period of about 10 min was given so as to allow an interface to form.

Figure 4 shows layout of device and measurement setup that we used to measure AC signal (1Hz to 5 MHz and peak voltage 100mV to 6V) propagation through the thin film stack ({Ni/NiO(10%)/NiO(33%)/NiO(100%)}(A)) where input signal was passing from function

generator through Ni to the film and output signal was collected via tungsten tip to oscilloscope. It was observed that below 20 kHz signal, output signal follows the input signal whereas beyond 20 kHz signal, peak of output signal starts getting clipped symmetrically as shown in figure 5 for 1MHz. For clear visibility of clipping, a plot of input voltage vs output voltage for all frequency mentioned above is shown in figure 6 where the clipping voltage (V<sub>c</sub>) is marked. It was found that V<sub>c</sub> changes with frequency for example at 50 KHz frequency and 1V signal; V<sub>c</sub> is 0.8V, which decreases to 0.65V for 1MHz frequency. Peak voltage dependent clipping properties of the device was also investigated. It was found that at signal voltage below 200mV, the clipping characteristics were not observed for any frequency range. It was also observed that V<sub>c</sub> increases along with the gradual increase of input peak voltage from 200mV to 5V for a particular frequency e.g. 1MHz. Above 5V peak voltage signal, clipping property of the stacks is lost (breakdown); and thereafter, output has same sine wave nature as input. Interestingly, after one and half hour of breakdown, film restarts showing clipping properties.



**Figure 4:** Schematic diagram of measurement setup and device structure for trilayer NiO stack



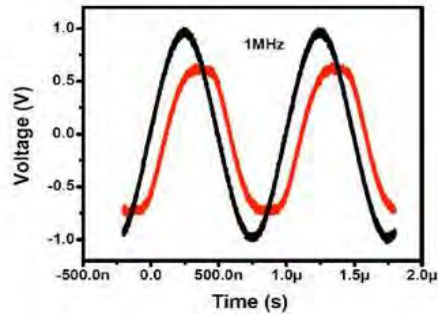


Figure 5: Typical input and output characteristics for 1V signal of frequency 1MHz

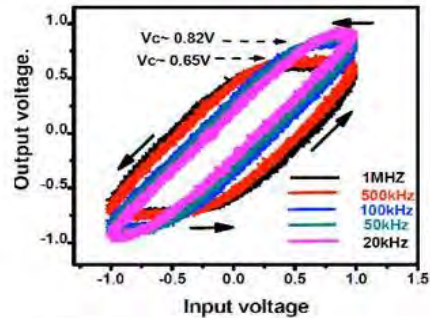


Figure 6: The input voltage vs output voltage. Arrows indicates direction of AC cycle.

To further study the effect of oxide gradient, a new stack  $[\text{Ni}/\text{NiO}(10\%)/\text{NiO}(50\%)/\text{NiO}(100\%)](\text{B})$  was deposited where the middle layer was deposited at 50% oxygen  $[\text{NiO}(50\%)]$  and the remaining two layers were deposited as the same as in stack A. The new stack B also shows clipping characteristics similar to that shown by stack A, except that  $V_c$  at 1MHz and 1V signal changes to 0.6V. Clearly, change of oxide concentration gradient has an effect on  $V_c$ .

A new stack was designed where Ni interlayer was sandwiched between each oxide layer [device structure  $\{\text{Ni}/\text{NiO}(10\%)/\text{Ni}/\text{NiO}(33\%)/\text{Ni}/\text{NiO}(100\%)\}(\text{C})$ ]. The stack C also showed clipping properties under AC signal. Clipping properties were observed for months under constant AC signal. All devices (A, B and C) were measured in ambient condition. This shows the robustness of the device properties. DC measurement of stacked films A, B and C revealed nonlinear, asymmetric, and non-hysteretic current-voltage ( $I-V$ ) characteristics as shown in figure 7. In DC measurement, Ni was bottom contact and tungsten tip as top contact. The analysis to understand clipping properties of NiO gradient stack is underway.

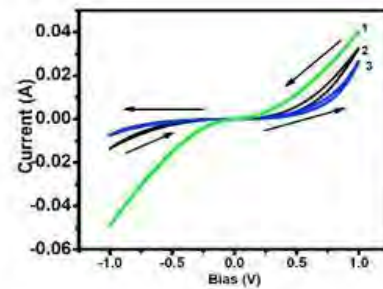
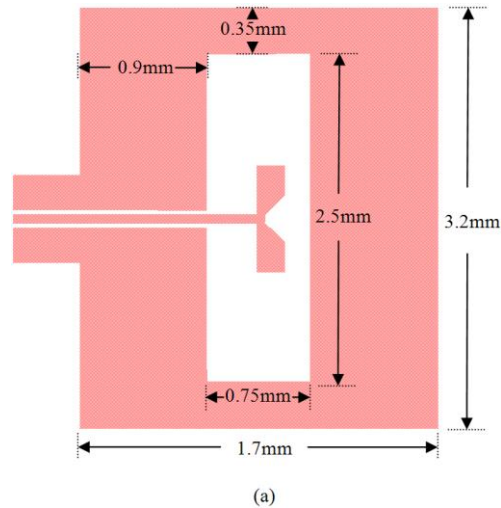


Figure 7: Current-voltage ( $I-V$ ) characterization of samples A, B, C where voltage was cycled.

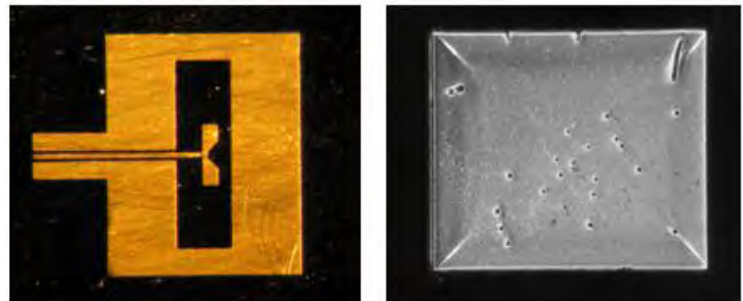
### 3. Modeling and characterization of a high frequency antenna

In this task, we present the design, fabrication and testing of a CPW-fed folded dipole slot antenna supported by a 50  $\mu\text{m}$  silicon membrane, operating at 60 GHz. Silicon was chosen due to its easy integration abilities with traditional fabrication technologies. The folded dipole antenna included in the slot, provides wide bandwidth performances with multi-frequency band operations. This antenna structure is also scalable and can be integrated with current commercial devices. The layout of the folded dipole slot antenna is shown in Figure 8. The design and simulation of the antenna structure was performed using Agilent's Momentum Electromagnetic Simulator, which combines full-wave and quasi-static electromagnetic solvers for antenna modeling. A high resistive silicon substrate with infinite surface area was assumed for simulation purpose.



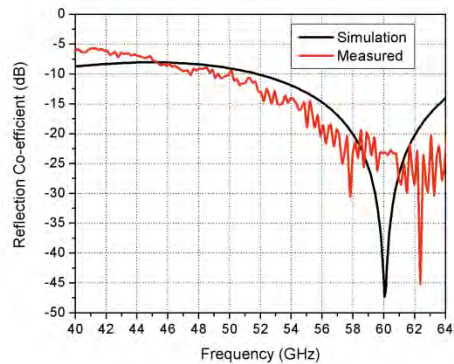
**Figure 8:** Momentum layout of 60 GHz slot antenna with folded dipole

The folded dipole slot antennas were realized on a 4" and 250  $\mu\text{m}$  thick silicon substrate. Initially, silicon substrate was thermally oxidized to grow a 1  $\mu\text{m}$  thick  $\text{SiO}_2$  layer. Since the oxidation layer was required only on the membrane etch side, the oxide layer was chemically etched on the other side. While the oxidized side provided as an etch protectant layer during the micromachining process, the un-oxidized side served as the ground plane for the antenna. Following the oxide etch process, a photolithography step was performed to pattern the antenna and CPW configuration pads on the substrate. Then, a thin layer of chromium (Cr) and gold (Au) were deposited on the substrate. Cr was deposited with a thickness of  $\sim 30$  nm and acted as an adhesion layer for the top Au ( $\sim 300$  nm) layer. After the contact pads were made, photolithography was performed on the backside of the substrate and windows were opened underneath the devices. The substrate was then subjected to a dry etching process, to micromachine the backside from 250  $\mu\text{m}$  to 50  $\mu\text{m}$ . Figure 9 (a) and (b) shows the microscopic image of the fabricated antenna and the membranes etched beneath the antenna in silicon, respectively.



**Figure 9:** An Optical micrograph of fabricated 60 GHz folded dipole slot antenna on silicon

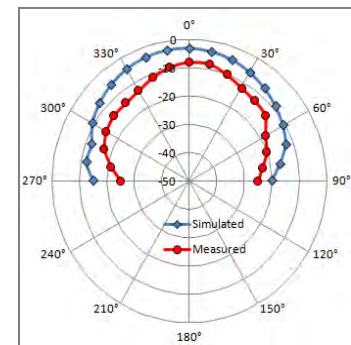
The simulated vs. measured reflection coefficient data of the antenna is illustrated in Figure 10. The



**Figure 10:** Measured vs. simulated reflection coefficient of the folded dipole slot antenna

figure shows that at 62 GHz, the antenna is well matched to  $50\Omega$  with a reflection coefficient of -45 dB. An additional resonance appeared at 55 GHz, which is contributed, to the antenna structure achieving multi-band operations. By minimizing the membrane thickness, additional surface waves were reduced and the antenna achieved a bandwidth of 25% at  $S_{11} < -10$  dB; improving the performance of previous silicon micromachined antennas. The antenna operates over a wideband from 50 to 65 GHz, proving its ability to be used in WLAN and V-band frequency applications. The discrepancy between data can be contributed to a variance in membrane thickness and losses caused by surface waves present during measuring.

Results obtained during the radiation pattern measurement are shown in Figure 11. The measured results are in good agreement with those achieved during simulation. The maximum co-polarization magnitude achieved was -8 dB at  $0^\circ$  with a gain of 4.1 dBi. This is the case because the pattern achieves maximum radiation at right angles to the dipole and drops off to zero on the antenna's axis. However, the slight difference in magnitudes of the measured vs. simulated patterns is due to inaccuracies during the measuring setup which requires precise positioning of the receiving antenna and stability in the angle guiding structure.



**Figure 11:** Measured vs. Simulated Co-Polarized E-plane radiation pattern (dB) of the 60 GHz antenna.

### Journal and Conference publications:

1. R.Ratnadurai, S.Krishnan, E. Stefanakos, Y. Goswami, S. Bhansali, "Rectification properties of inorganic MIM Tunnel Junctions: A Review," *Advanced Energy Materials*, 2011. (Under Review)
2. S. Krishnan, J. Boone, S. Bhansali, "Membrane Supported 94 GHz Slot Antenna for Wideband Applications," *IEEE Journal of Antennas and Propagation*, 2011. (Under Review)
3. J. Boone, S. Krishnan, S. Bhansali, "CPW-fed Folded Dipole-Slot Antenna for WLAN Applications," *IET Microwaves, Antenna and Propagation*, 2011. (Under Review)
4. M. Celestin, S. Krishnan, E. Stefanakos, Y. Goswami, S. Bhansali, "Advances in SAM based MIM Tunnel Junctions," *Chemical Review*, 2011. (Under Review)
5. R.Ratnadurai, S. Koiry, S. Krishnan, S. Bhansali, E. Stfanakos, Y. Goswami, "NiO based thin film Clipper devices," *FESC Summit, Gainesville, Sept 27-28, 2011.*
6. M. Celestin, S. Krishnan, S, Bhansali, E. Stefanakos, Y. Goswami, "Current Trends in Micro and Nanotechnology based Energy Harvesting," *NanoFL, Miami, Sept 30- Oct 1, 2011.*
7. J. Boone, S. Krishnan, S. Bhansali, T. Weller, "Micromachined Vertical Coaxial Probes for Nanoscale Device Characterization," *NanoFL, Miami, Sept 30- Oct 1, 2011.*



8. S.P. Koiry, S. Krishnan, R. Ratnadurai, D.Y. Goswami, S. Bhansali, “Controlled ex-situ doping of electrochemically polymerized 5,10,15,20 tetrakis (4-hydroxyphenyl)-porphyrin (THPP) for hybrid switching circuits,” ECS 220<sup>th</sup> meeting, Boston, Oct 9-14, 2011.
9. M. Celestin, S. Krishnan, D.Y. Goswami, E. Stefanakos, S. Bhansali, “ Organic Tunnel Diodes Fabricated for Rectenna based IR Sensing Applications,” Advances in Applied Physics and Materials Science Congress, Antalya, Turkey, May 12 -15, 2011.
10. M. Celestin, S. Krishnan, D.Y. Goswami, E. Stefanakos, S. Bhansali, “ Fabrication and Modeling of Organic Tunnel Diodes,” 3<sup>rd</sup> Annual USF Research Day, Tampa, FL, Oct 2010.
11. R. Ratnadurai, S.Krishnan, E. Stefanakos, D.Y. Goswami, S. Bhansali, “Design Analysis of MIM tunnel junctions,” 3<sup>rd</sup> Annual USF Research Day, Tampa, FL, Oct 2010.
12. J. Boone, S.Krishnan, E. Stefanakos, D.Y. Goswami, S. Bhansali, “Design and Simulation of a Scalabe Dipole Fed Slot Antenna,” 3<sup>rd</sup> Annual USF Research Day, Tampa, FL, Oct 2010.

**University of South Florida**  
*Clean Drinking Water using Advanced Solar Energy Technologies*

**PI:** Lee Stefanakos **Co-PIs:** Yogi Goswami, Matthias Batzil, Maya Trotz, Sesha Srinivasan  
**Students:** Chennan Li (PhD), O. Kofi Dalrymple (Ph.D.) Yang Yang (PhD)

**Description:** The availability of fresh water is a big problem facing Florida. In many locations, Florida's water is contaminated from leaky underground tanks and agricultural pesticides. Although salt water desalination is possible, conventional systems are too energy intensive. Solar energy can supply the power, and innovative vacuum and humidification/dehumidification desalination systems can provide adequate fresh water for the state's needs. Another goal is to develop photocatalytic disinfection to remove contaminants and integrate these technologies with solar PV for complete water supply systems. Projects include: Natural Vacuum Solar Flash Desalination: Creating vacuum conditions above liquids increase their evaporation rates. This phenomenon can be integrated into a practical continuous desalination process by repeatedly flashing sea water in vacuumed chambers to produce water vapor that will be condensed producing fresh water. Solar PV Assisted Photocatalysis for Air/Water Disinfection: Improving titanium dioxide photocatalysts for purification and disinfection of water and air contaminated with organic, heavy metal and microbiological species, using solar energy. This can be integrated into a practical continuous desalination process by flashing sea water in vacuum chambers to produce water vapor that will be condensed, producing fresh water.

**Budget:** \$326,756  
**Universities:** USF

## Progress Summary

### Study of thermal desalination process using waste heat

Models were developed to study the thermal desalination process using waste heat, solar thermal energy and geothermal energy. Models were validated by using the experimental data available in the literature. A model was developed for Supercritical Organic Rankine Cycle (SORC) for geothermal application and model of Organic Rankine Cycle (ORC) was developed for solar thermal applications. Further study is needed to find out optimum condition of using thermal desalination system using waste heat.

### Photocatalysis for Air/Water Disinfection and decontamination

Photocatalysis is a promising water treatment technology capable of utilizing solar light. However, the construction of an effective photocatalytic disinfection system for water purification is currently limited by the lack of reliable models to aid in the design and testing of these systems. Simplified models have been proposed, but most are inadequate because they rely on traditional disinfection theories which are not applicable to photocatalysis. Therefore, the major goal of this research is to develop a model for photocatalytic disinfection based on fundamental processes which may then be used to design water treatment systems in the state of Florida.

ZnO and ZnO/Fe nanowires have been synthesized on glass substrate by using conventional

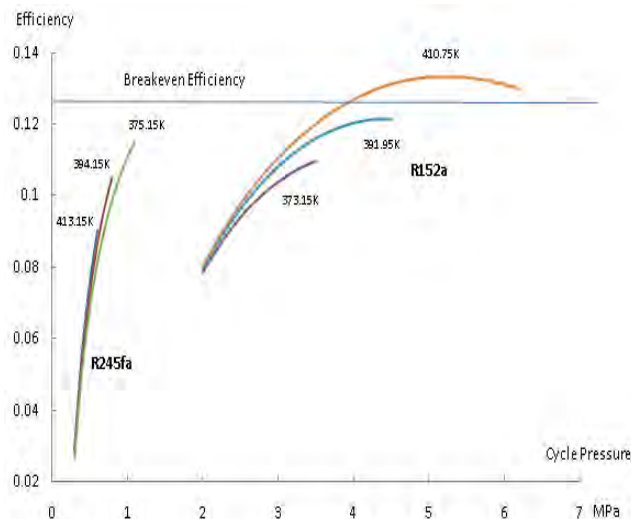
hydrothermal method. The characterizations of nanowires were investigated by using UV-visible spectrometer, SEM, XRD. The photocatalytic activities were studied for decontamination of dichlorobenzene and decolorization of methyl orange in water. The activities also compared with TiO<sub>2</sub> (Degussa P25) film. In decontamination of dichlorobenzene test, ZnO/Fe nanowires showed more activity than P25 under visible light and similar activity with P25 under UV light. In decolorization of methyl orange test, P25 showed more activity than ZnO nanowires.

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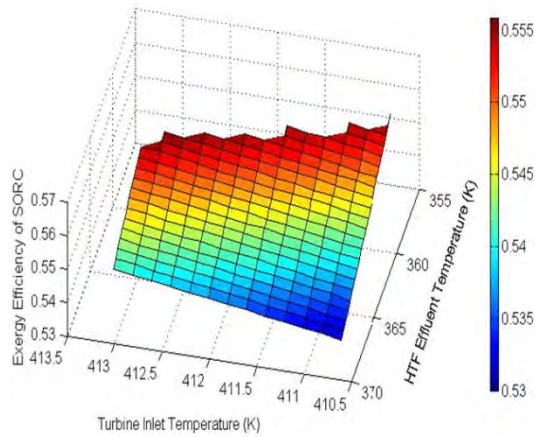
### Supercritical Organic Rankine Cycle Driven Reverse Osmosis Desalination:

A novel idea of a Supercritical Organic Rankine Cycle (SORC) driven seawater reverse osmosis (RO) system (SORC-RO) was proposed. The proposed system is studied using two types of low-grade heat sources with a maximum temperature of 423.15K and compared with the conventional Organic Rankine Cycle driven seawater reverse osmosis system (ORC-RO). The results show that a SORC-RO system is particularly suitable for once-through heat source applications such as geothermal and industrial waste heat as energy sources for desalination. The proposed system using R152a as the working fluid operates at 6.048MPa pressure to directly drive a RO desalination system with a 50% recovery without converting the mechanical energy into electricity. The SORC using R152a has a thermal efficiency higher than 13% whatever the heat source is recirculating or once-through, while conventional ORC using R245fa is only suitable for stable, recirculating heat sources. This study is meaningful due to the facts that once-through heat sources including the geothermal and industrial waste heat sources are more commonly seen than the stable heat sources such as solar collectors. And if the heat source is waste heat, the SORC-RO system could make full use of the heat sources and reduce the thermal pollutions to the environment. A comprehensive list of the working fluids candidates for the SORC-RO using low-grade heat sources less than 423.15K is proposed based on the critical pressure and temperature of the fluids.

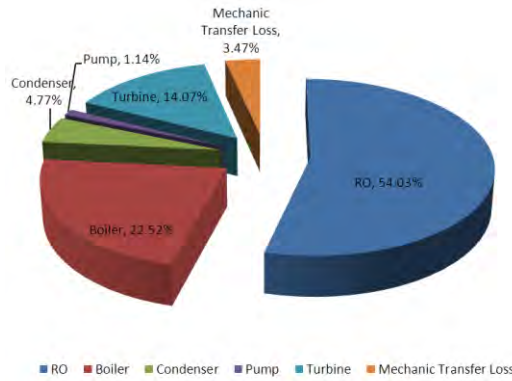
#### 1. Modeled supercritical organic Rankine cycle for geothermal application



Thermal Efficiencies of R152a-based SORC and R245fa-based ORC with once-through heat source (356K-413K)

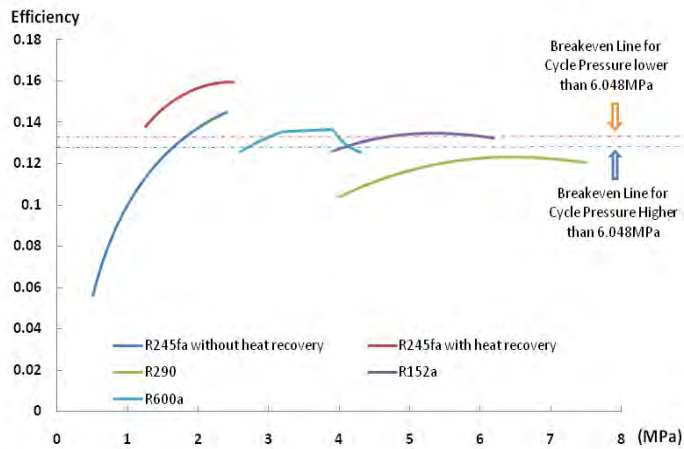


Exergy Efficiencies of SORC using 152a as working fluids



R152a-based SORC-SWRO Exergy destruction breakdown  
(P=6.048MPa, HTF effluent 356.15K, Turbine Inlet 410.75K)

2. Modeled organic Rankine cycle for solar thermal application.



Thermal Efficiencies of R152a-based SORC and R245fa-based ORC with solar thermal heat sources

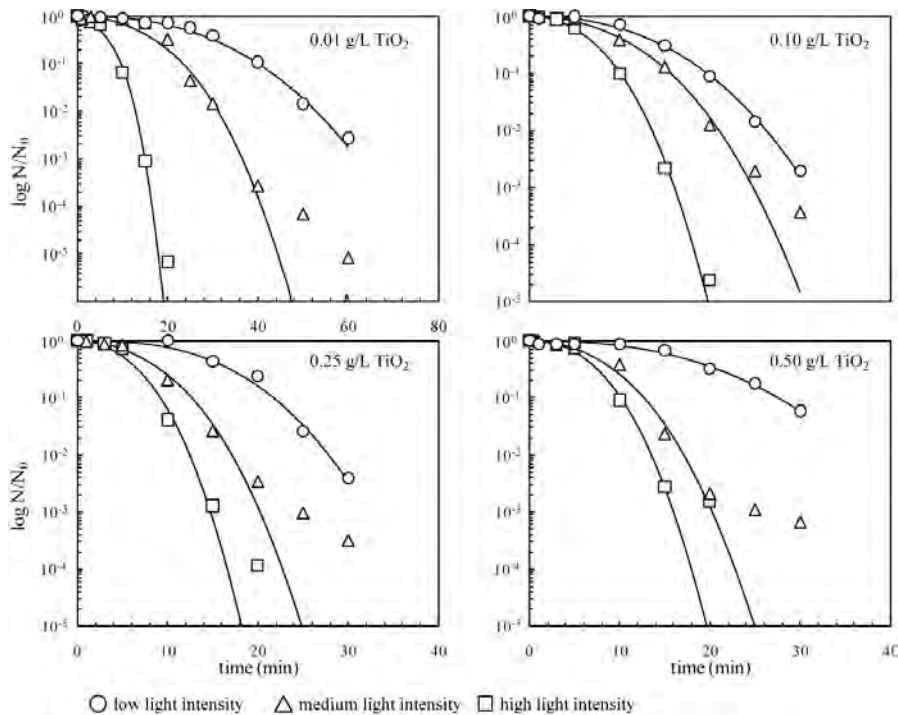


## Photocatalytic Disinfection

A comprehensive mechanistic model for photocatalytic disinfection was developed to optimize the design of the photocatalytic disinfection process. A major benefit of the mechanistic model is the significant cost reduction associated with performing fewer preliminary experiments to determine the effectiveness of various combinations of catalyst concentration and light intensity for a given organism. The model simulates the effect of light intensity and catalyst concentration on the disinfection process and shows good agreement with the experimental data for stable colloidal suspensions, that is, suspensions in which rapid aggregation of cells and  $\text{TiO}_2$  do not occur.

The following summarizes the main findings of the study:

- Most efficient disinfection achieved at high light intensity and lowest catalyst concentration (0.01 g/L)
- Model predicted disinfection rate constants ( $k_{dis}$ ) within 2 orders of magnitude, with less variation at lower  $\text{TiO}_2$  concentration (within an order of magnitude)
- Disinfection has log-linear relationship with light intensity within the range in our research
- Small variation in disinfection efficiency for 0.10-0.50 g  $\text{L}^{-1}$ , especially at low and medium light intensity
- Generation rate per mass of catalyst reduces exponentially with catalyst concentration
- Colloidal interactions play a significant role in the disinfection process
- $\text{TiO}_2$  appears to be strongly and specifically adsorbed to cells
- Model shows disinfection does not vary significantly from pH 6-8



## Photocatalytic Decontamination Results:

### 1. UV-vis absorbance spectrum

The ZnO nanowires show larger enhancement absorption under visible light compare to ZnO nanoparticles. The ZnO/Fe nanowires show more absorption not only under visible light but also under UV light.

### 2. Structural studies

Scanning electron microscopy (SEM) image (Fig.1) showed the diameter of ZnO nanowires were 50-100nm with hexagonal structure. The X-ray diffraction (XRD) patterns showed a dominate diffraction peak for (002), indicating a high degree of orientation with the c-axis vertical to the substrate surface. The XRD results imply that the samples were highly crystallized type.

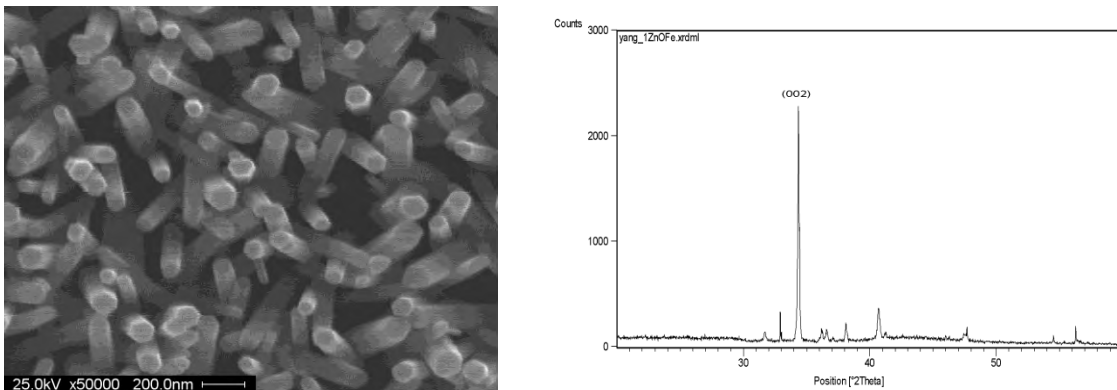


Figure 1: SEM image (left) and XRD pattern (right)

### 3. Photocatalysis studies

Under visible light studies (Fig.2), for dichlorobenzene (DCB) decontamination, ZnO nanowires show a similar photoactivity with P25. However, ZnO/Fe shows a better photoactivity than P25. For methyl orange (MO) decolorization, P25 was better activity than ZnO nanowires.

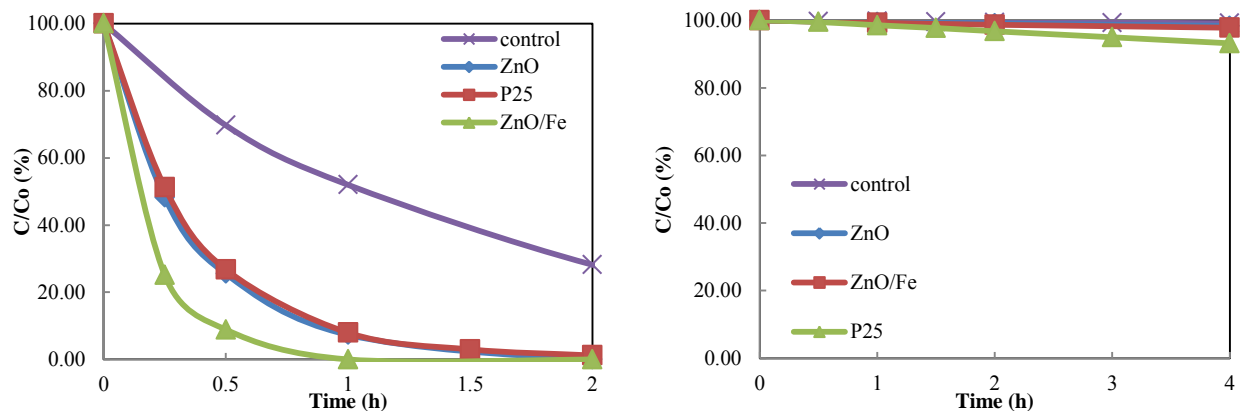


Figure 2: Photocatalysis under visible light test (Left: DCB test. Right: MO test)

Under UV light studies (Fig.3), for DCB decontamination, ZnO nanowires show a less photoactivity than P25 but ZnO/Fe shows a similar photoactivity with P25. For MO decolorization, P25 shows better activity.

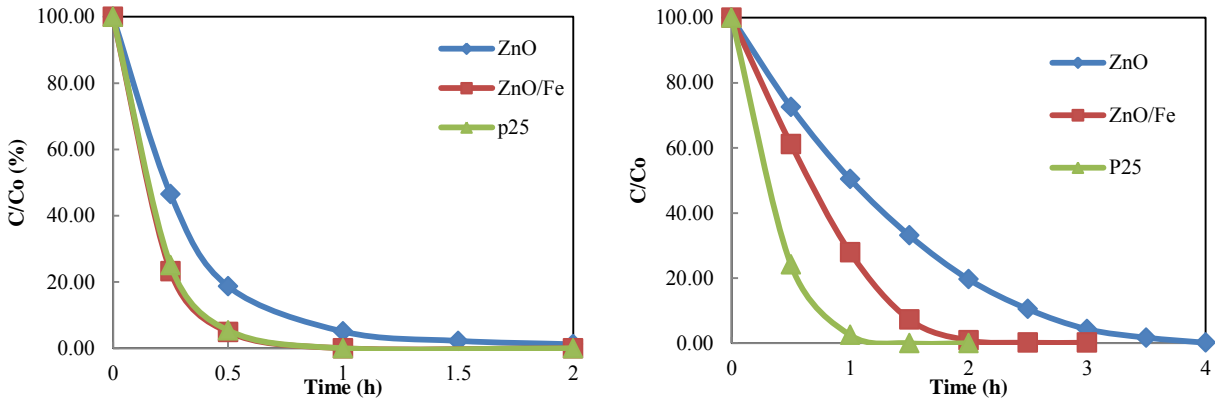


Figure 3: Photocatalysis under UV light (Left: DCB test. Right: MO test)

Compare ZnO nanowires with P25 photoactivity in DCB test. ZnO nanowires showed similar activity with P25 under visible and less activity than P25 under UV light. Thus, ZnO nanowires have less activity under total UV-vis light. However, when compare ZnO/Fe with P25, the activity of ZnO/Fe shows better activity than P25 under visible light and similar activity with P25 under UV light. Therefore, ZnO/Fe nanowires should have more activity than same amount of P25 under total UV-vis light or sun light for decontamination of DCB. For MO decolorization, P25 shows better activity in both under visible light and UV light test.

**University of South Florida**  
*Creation of Carbon Sequestration Data, Technologies and Professional Cohorts for Florida*

**PI:** Mark Stewart   **Co-PIs:** Jeffrey Cunningham, Maya Trotz  
**Students:** Arlin Briley, PhD, Mark Thomas, PhD

**Description:** Rising concerns over increasing levels of greenhouse gases, especially carbon dioxide, have led to suggestions to capture carbon dioxide at fixed sources, such as fossil fuel power plants, and sequester the carbon for millennia by injecting it underground. Florida overlies many thousands of feet of carbonate rocks which may be suitable for geologic sequestration of carbon dioxide. This project is investigating the potential for geologic sequestration of carbon dioxide in Florida, the physical and chemical changes that may occur as a result of injection, assess the potential for escape of injected carbon dioxide, determine the risk, if any, to aquifer systems used for water supplies, develop methodologies for Florida utilities to predict the performance and risks of proposed sequestration projects, and educate a cohort of geologic sequestration professionals to create a carbon sequestration industry in Florida. This project has graduated two PhD students, Tina Roberts-Ashby, US Geological Survey, and Roland Okwen, Illinois State Geological Survey, one post-doctoral student, Anwar Shadab, Missouri University of Science and Technology, and currently supports two PhD students.

**Budget:** \$479,640

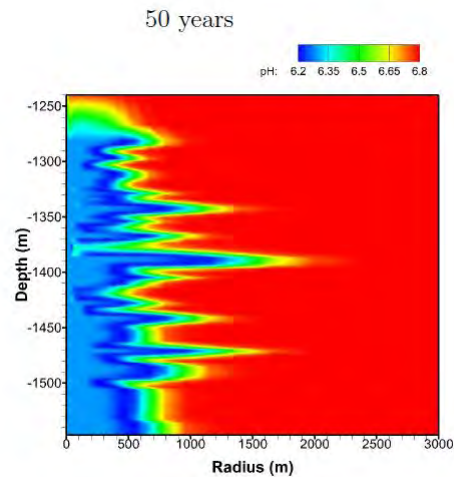
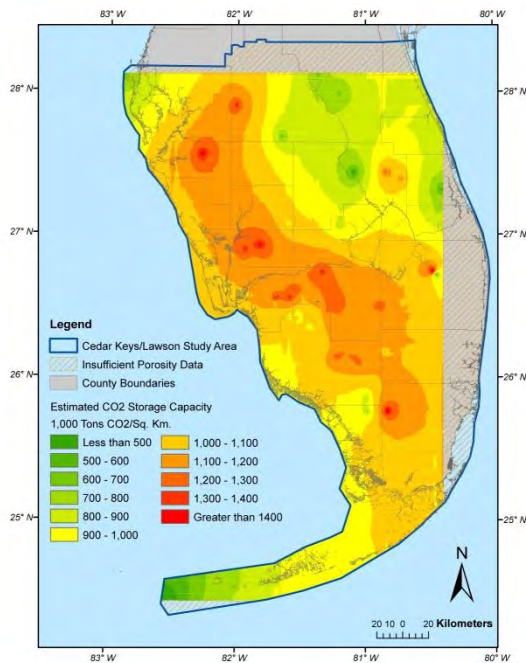
**Universities:** USF

**External Collaborators:** TECO, RTI, ECT, DOE

### Progress Summary

Progress continues on the collaboration with Tampa Electric Co, DOE and RTI on the carbon sequestration and wastewater injection pilot project at the Polk Power Station (PPS). The total DOE funding for this project is \$160 million. USF is responsible for the mathematical modeling of the pilot carbon sequestration and wastewater injection project at the PPS. In conjunction with this project, USF has a continuing grant through Tampa Electric/ECT Inc that currently supports two PhD students. Four refereed publications on carbon sequestration appeared in print in 2011, one is in press, and one is in review. Ten presentations on research results were given at national and regional meetings by faculty members and graduate students. A proposal was submitted to DOE to investigate an innovative and potentially very important conjunctive injection of carbon dioxide and wastewater and is in review. This proposed project would provide a new source of potable water, help municipalities deal with wastewater disposal, increase the efficiency and safety of carbon sequestration, and reduce costs through shared facilities. This proposal would leverage current Federal funding at the PPS project. Two USF GCS PhD students, Tina Roberts-Ashby, USGS, Washington, DC, and Roland Okwen, Illinois State Geological Survey/Univ Illinois, are continuing to collaborate with the USF Carbon Sequestration Group on GCS research. The USF GCS group has achieved international recognition through its refereed publications in international journals and presentations at national meetings. As a result of USF GCS Group work, Florida was selected for one of the few DOE funded carbon sequestration pilot projects in the US. The USF GCS group will continue to attempt to leverage the existing funding at PPS to further funded research and graduate training in carbon sequestration.





**Funds leveraged/new partnerships created:** The USF Geological Carbon Sequestration (GCS) group has a continuing collaborative relationship with Tampa Electric and DOE to provide mathematical modeling expertise for the DOE-funded carbon sequestration and wastewater injection project at the Polk Power Station in Polk County, Florida. This collaboration provides research funding and training for two PhD students, Arlin Briley and Mark Thomas. This project was used as leverage for a proposal submitted to DOE in September, 2011, to investigate the conjunctive injection of wastewater from a reverse osmosis plant and CO<sub>2</sub> captured at the Polk Power Station. Municipal wastewater from the City of Lakeland will be treated to potable water standards in a reverse osmosis plant. Ninety percent of the original wastewater will become potable water, and the 10% reject water from the RO plant will be injected in a deep well after CO<sub>2</sub> injection. Preliminary modeling suggests that the waste water injection transfers the CO<sub>2</sub> from a supercritical gas phase to a dissolved phase, safely sequestering it for millennia. This process could provide for efficient wastewater reuse, safe CO<sub>2</sub> sequestration, and lowered costs through shared facilities.

## 2011 Annual Report

Progress continues on the collaboration with Tampa Electric Co, DOE and RTI on the carbon sequestration and wastewater injection pilot project at the Polk Power Station (PPS). The total DOE funding for this project is \$160 million. USF is responsible for the mathematical modeling of the pilot carbon sequestration and wastewater injection project at the PPS. In conjunction with this project, USF has a continuing grant through Tampa Electric/ECT Inc that currently supports two PhD students. Four refereed publications on carbon sequestration appeared in print in 2011, one is in press, and one is in review. Ten presentations on research results were given at national and regional meetings by faculty members and graduate students. A proposal was submitted to DOE to investigate an innovative and

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### **Publications:**

In 2011 four refereed publications appeared in print, one has been accepted, and one is in review. Two articles are in the *International Journal of Greenhouse Gas Control*, and one each in *Transport in Porous Media*, *Computational Geoscience*, *International Journal of Remote Sensing*, and *Chemical Geology*.

Okwen R, Stewart M, Cunningham JA. 2011. Effect of well orientation (vertical vs. horizontal) and well length on the injection of CO<sub>2</sub> in deep saline aquifers. *Transport in Porous Media*, 90(1), 219-232. doi: 10.1007/s11242-010-9686-5.

Okwen R, Stewart M, Cunningham J. 2011. Analytical model for screening potential CO<sub>2</sub> repositories. *Computational Geosciences*, 15(4), 755–770. doi: 10.1007/s10596-011-9246-2

Okwen R, Stewart M, Cunningham J. 2011. Temporal variations in near-wellbore pressures during CO<sub>2</sub> injection in confined aquifers. *International Journal of Greenhouse Gas Control*, 5, 1140–1148. doi: 10.1016/j.ijggc.2011.07.011

Okwen R, Pu R, Cunningham JA. 2011. Remote sensing of temperature variations around major power plants as point sources of heat. *International Journal of Remote Sensing*, 32(13), 3791–3805. doi: 10.1080/01431161003774723.

Roberts-Ashby, Tina, Stewart, M., 2011. Evaluation of the Sunniland Formation of the South Florida Basin for carbon sequestration. *International Journal of Greenhouse Gas Control*, accepted 9/2011, in press.

Thomas MW, Trotz MA, Stewart M, Cunningham JA. Geochemical modeling of CO<sub>2</sub> sequestration in deep, saline, dolomitic-limestone aquifers: 1, Critical evaluation of thermodynamic sub-models. Under review at *Chemical Geology*, submitted July 2011.

### **Presentations:**

Faculty members and students presented 11 papers at national and regional meetings.

Anwar S (presenter), Cunningham JA, Trotz M, Thomas MW, Stewart M. Pore-scale modeling of reactive-multiphase-buoyant flow for carbon capture and storage. Presented at the 2010 Fall Meeting of the American Geophysical Union: December 13-17, San Francisco, California.

Roberts-Ashby, Tina (presenter), Stewart, M, 2010. Evaluation of the Cretaceous-Paleocene Cedar Keys-Lawson injection zone for geological carbon sequestration in Florida. Presented at the 2010 Fall Meeting of the American Geophysical Union: December 13-17, San Francisco, California.

Thomas MW (presenter), Briley A, Trotz M, Stewart M, Cunningham JA. Geochemical modeling of CO<sub>2</sub> sequestration in deep saline aquifers in Florida. Presented at the 2010 Fall Meeting of the American Geophysical Union: December 13-17, San Francisco, California.

Cunningham JA (presenter), Trotz MA, Stewart MA, Goswami DY. , 2011. Potential for carbon capture and sequestration (CCS) in Florida. Presented at the 2011 AEESP Research and Education Conference: July 10-12, Tampa, Florida.

Anwar S (presenter), Cunningham JA, Trotz M, Thomas M, Stewart M., 2011. Pore-scale modeling of reactive multi-phase flow for carbon capture and storage. Presented at the 2011 AEESP Research and Education Conference: July 10-12, Tampa, Florida.

Anwar S, Cunningham J (presenter), Thomas M, Trotz M, Stewart M., 2011. Pore-scale modeling of reactive multi-phase flow for carbon capture and storage. Presented at the 242nd American Chemical Society National Meeting & Exposition: August 28 - September 1, Denver, Colorado.

Thomas MW, Cunningham J (presenter), Briley A, Trotz M, Stewart M., 2011. Geochemical modeling of CO<sub>2</sub> sequestration in carbonate aquifers: Critical evaluation of thermodynamic models used to predict mineral dissolution and precipitation. Presented at the 242nd American Chemical Society National Meeting & Exposition: August 28 - September 1, Denver, Colorado.

Stewart M (presenter), Cunningham J, Trotz M, Okwen R, Thomas M, Briley A, 2011. Geochemical modeling of CO<sub>2</sub> and wastewater injection to maximize sequestration efficiency. 2011 Aquifer Storage and Recovery Conference, American Ground Water Trust, September 12, Orlando FL

Cunningham J (presenter), Goswami DY, Stewart M, Trotz M. , 2011. Carbon capture and sequestration: Opportunities in Florida. Presented at the Florida Energy Systems Consortium (FESC) Summit: September 27-28, Gainesville, Florida.

Okwen R, Thomas M (presenter), Briley A, Stewart M, Trotz M, Cunningham J. , 2011. Simulation of alternating wastewater/CO<sub>2</sub> injection into a deep saline aquifer. Presented at the Florida Energy Systems Consortium (FESC) Summit: September 27-28, Gainesville, Florida.

Briley A (presenter), Thomas M, Trotz M, Cunningham J, Stewart M., 2011. Practical heuristic for selection of geochemical model basis of supersaturated water and mineral precipitation. Presented at the Florida Energy Systems Consortium (FESC) Summit: September 27-28, Gainesville, Florida.

### **Funded research:**

a. **Project:** : Physical and geochemical modeling of geologic sequestration of carbon dioxide and RO reject water at the Polk Power Station (PPS), Polk County.

Principal Investigators: M Stewart (USF), J Cunningham(USF), M Trotz(USF), R Okwen(ISGS)

Students: Arlin Briley (CEE, PhD), Mark Thomas (CEE, PhD)

Grantors and Collaborators: Tampa Electric Company, ECT Inc.

Funding: Funding is provided on a continuing and as needed basis, for specific tasks. Current funding is about \$40,000-\$50,000 per year. Funds provide research support for faculty members Cunningham, Trotz, and Stewart, a sub-contract with Dr Roland Okwen (USF PhD) of the Illinois State Geological Survey, licenses for advanced modeling software, and support for two current PhD students, Arlin Briley and Mark Thomas in CEE.

Description: This project is part of a >\$160,000,000 project funded by DOE and the SWFWMD. SWFWMD funded two deep injection wells at PPS to dispose of reverse osmosis reject water from a RO plant that will process City of Lakeland wastewater. The potable water from the RO plant will replace Floridan Aquifer water currently used by Tampa Electric at the PPS. The existence of a suitable deep injection zone was confirmed by earlier USF research. As a result of the availability of deep injection wells and the integrated coal gasification-combined cycle (IGCC) power plant at PPS, the PPS was selected by DOE for a pilot project for hot-gas clean up, carbon capture, and carbon sequestration. USF is responsible for modeling the physical and chemical behavior of both the injected carbon dioxide that will be captured by the CCS pilot plant and the reject water from the RO plant. This project provides a unique research opportunity, as it is the only CCS project where injection of CO<sub>2</sub> will be followed by wastewater injection. The majority of the refereed publications and meeting presentations of the USF Carbon Sequestration group have been based on research results from this project.

Project lifespan: Carbon sequestration will begin in 2013, and continue for 1 year and the wastewater injection will start in 2014 and continue indefinitely. USF expects to be involved in this project at least through 2015.

**b. Project:** Monitoring of carbon sequestration using InSAR

Principal Investigator: Tim Dixon (USF)

Grantor: DOE

Funding: This part of a larger grant from DOE held by Tim Dixon. Funding on the FESC project is probably about \$50,000

Project description: This project will use the carbon dioxide and wastewater injection projects at the Polk Power Station (PPS) to investigate the use of radar interferometry to monitor the progress of CO<sub>2</sub> injection at CCS sites. Dixon has received permission to include the PPS site as one of the investigative sites for this DOE grant.

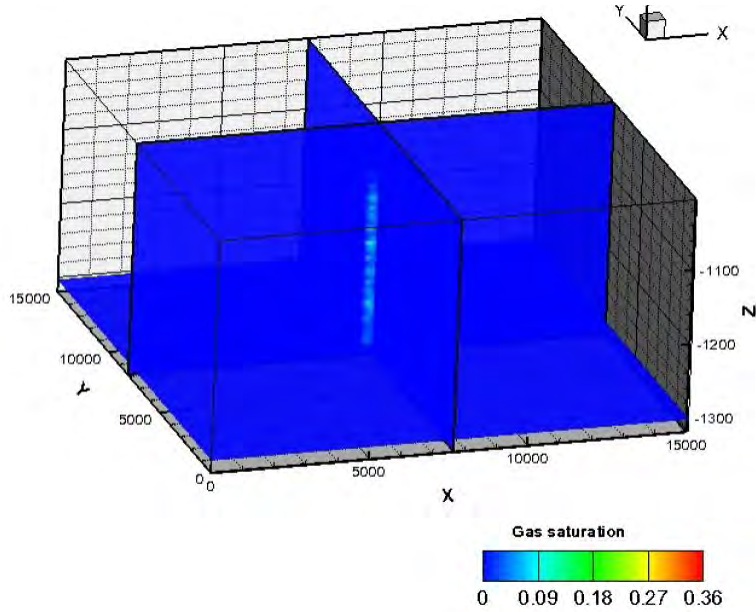
### **Proposals submitted:**

a. Project: The current CCS and wastewater injection project at the Polk Power Station (PPS) provides a unique research opportunity. In 2013 approximately 300,000 tons of carbon dioxide will be injected in the second of two deep injection wells at PPS drilled to 8,000 ft below land surface. As the principal purpose of the deep wells is disposal of RO plant reject water and waste streams from PPS facilities, after CO<sub>2</sub> injection wastewater will be injected into the deep disposal well. Preliminary modeling (see figures below) suggests that the carbon dioxide sequestered as a supercritical gas phase will dissolve in the injected waste water. This will convert the CO<sub>2</sub> from a very buoyant supercritical gas to a more dense dissolved phase. This nearly eliminates the buoyancy effect of sequestered CO<sub>2</sub>, greatly reducing the importance of caprock continuity and sequestering the CO<sub>2</sub> in a chemically stable form. The proposed project will create predictive geochemical models for the conjunctive injection of CO<sub>2</sub> and wastewater, calibrated to monitoring data from the PPS.

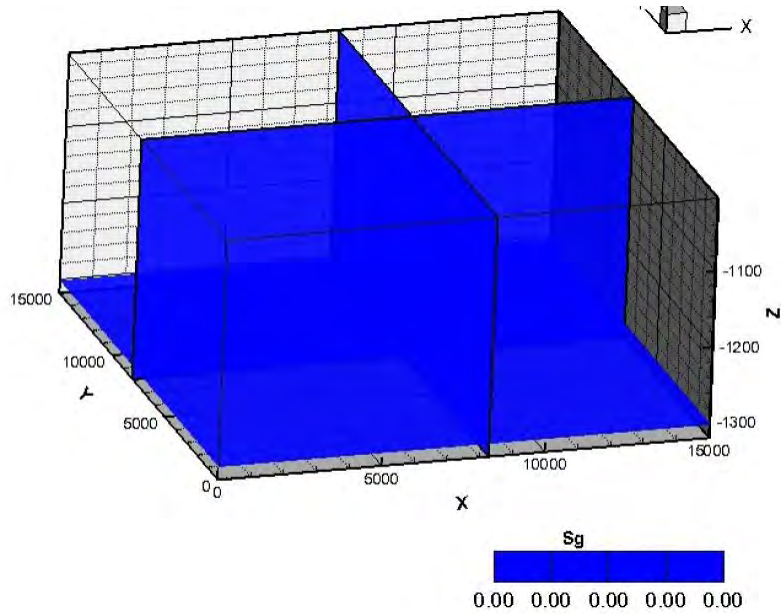
Submission: A pre-proposal was submitted to DOE in September. Funding is expected to be about \$250,000/yr for four years, 2012-2016



CO2 gas phase saturation after 1 year of CO2 injection



CO2 gas phase saturation after 1 year of wastewater injection



b. **Project:** Use of high resolution GPS to monitor CO2 sequestration

**Principal Investigator:** Rocco Malservici (USF)

**Grantor:** DOE

**Funding:** Rocco Malservici submitted a pre-proposal for this project, and has been invited by DOE to submit a full proposal. Expected success rate for full proposals is about 50%.

## UNIVERSITY OF SOUTH FLORIDA

### *Design, Construction and Operation of CSP Solar Thermal Power Plants in Florida*

**PI:** D. Yogi Goswami   **Co-PIs:** Elias Stefanakos, Muhammad M. Rahman, Sunol Aydin, Robert Reedy  
**Students:** Gokmen Demirkaya (Ph.D.); Ricardo Vasquez Padilla (Ph.D.);  
 Huijuan Chen (Ph.D.); Jamie Trahan (Ph.D.)

**Description:**

Florida utilities are mandated to achieve 20% renewable energy contribution to their generation mix by 2020. While technologically feasible with solar energy, the capital costs are high – presently, capital costs range from \$6,000-\$7,000/kW for PV and \$3,500-\$4,000/kW for concentrating solar thermal power. This project targets the development of solar thermal power technology for bulk power and distributed generation, which will diversify energy resources in Florida and reduce greenhouse emissions by utilizing renewable sources. Also, there will be economic impacts with the establishment of new power industry in Florida, which will help the electrical utilities of the state to meet the renewable portfolio standards. The project has three main tasks; the first one is to develop design methodologies and standards for the proven solar thermal power technologies in combination with bio or fossil fuels based on Florida conditions and resources. Secondly, the project aims to set up demonstration and test facilities for these technologies for optimization for Florida conditions, and the final task is to develop and commercialize innovative technologies based on new thermodynamic cycles.

**Budget:** \$882,000

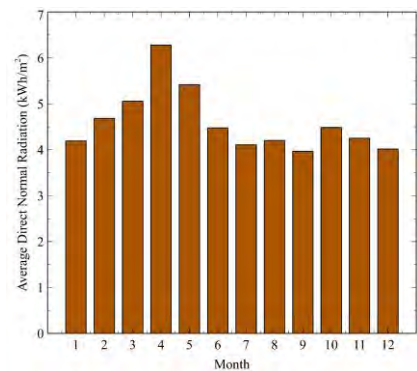
**Universities:** USF, UF, UCF

### Progress Summary

**Research Objectives for Current Reporting Period:** The main research objectives for the current reporting period include the development of a test facility and pilot demonstration systems based on parabolic trough technology.

**Progress Made Toward Objectives during Reporting Period**

Daily integration (DI) approach was used to obtain the average direct normal solar radiation for the location of the pilot demonstration solar plant (USF, Tampa, FL). The direct normal solar radiation obtained for Tampa is shown in Fig. 1. The annual average for this location is 4.6 kWh/m<sup>2</sup>-day. These solar radiation values and the solar shading analysis for solar collector rows were used for the solar field calculation. The solar field layout proposed for 50 kW<sub>e</sub> is shown in Fig. 2. The Soponova 4.0 (Sopogy Inc.) parabolic trough collectors will be used in the solar field for providing 430 W/m<sup>2</sup> of thermal energy after losses. The solar field is being designed to work in conjunction with a thermal energy storage system which will use phase change material (PCM) as a storage material.



**FIG. 1:** Direct Normal Radiation For Tampa, FL

The remaining thermal energy will be provided by a natural gas boiler, which will work in series with the solar field and supply thermal energy to the power block when the solar energy is not available.

The power block that will convert the thermal energy to electricity is based on Organic Rankine Cycle. This power block will have a nominal capacity of 120 kW<sub>e</sub>. A preliminary study on condensation methods for solar thermal plants is also conducted and more research will be devoted to the development of cost effective dry cooling technology.

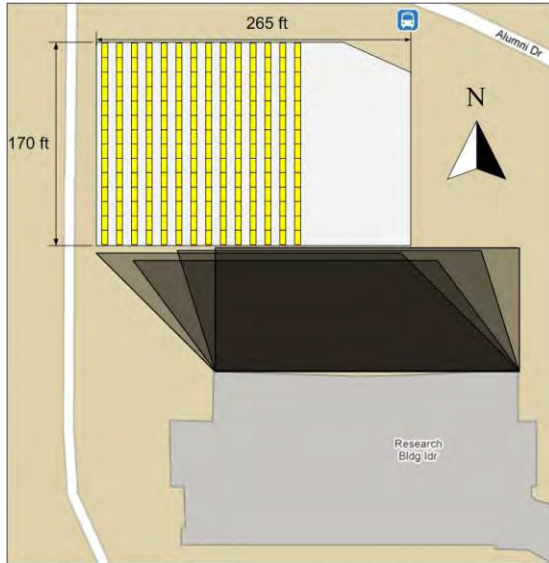


Fig 2: Proposed Solar Field Layout

Research activities for the next reporting period will focus on the modeling of heat transfer losses through the solar receiver and field piping, pressure drops and pumping requirement and thermal energy storage system design.

## 2011 Annual Progress Report

### Task 1: Development of simulation and design methodology for parabolic trough and parabolic dish

The objective of the task one is to develop a simulation and design methodology for the parabolic trough and parabolic dish based technologies for Florida conditions. Solar radiation, solar collector and thermal storage topics are the subtasks, and following progresses have been made during the period.

Parabolic trough solar systems are currently one of the most mature and prominent applications of solar

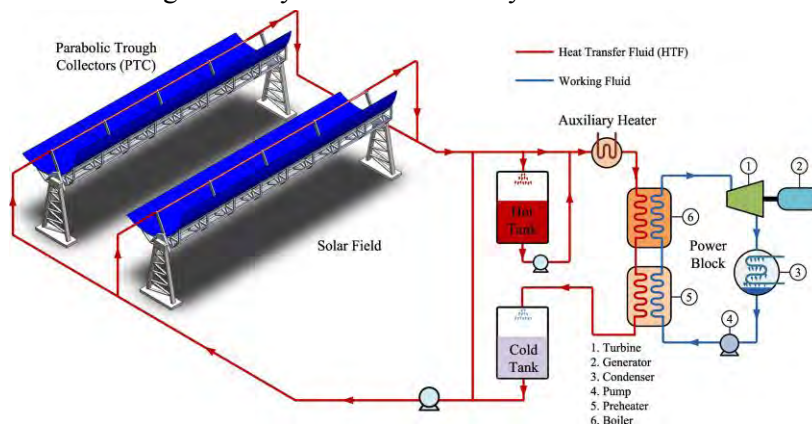


Fig. 3: Parabolic Trough Power Plant

energy for production of electricity. Compared to conventional power plants, parabolic trough solar power plants produce significantly lower levels of emissions and carbon dioxide. Thermal simulations and cost analysis of the system are used to evaluate the economic feasibility. Complex models and components are integrated to emulate real operating conditions, such as: Solar

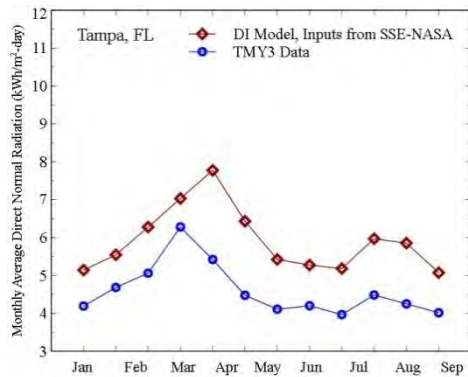


Fig. 4: Comparison of Two Models

Radiation Model, Solar Thermal Collector, Thermal Energy Storage, Solar Field Piping, Power Block, Cost Analysis, and Integration of all Systems. This progress report presents a preliminary design method to calculate solar radiation data and thermal collector efficiency which are used to determine the size and the cost of solar field.

An hourly solar radiation model is necessary to calculate the energy input that come from the sun, since the solar collector performance changes during the whole day. The inputs for the hourly solar radiation model are the long term average values of total horizontal and diffuse radiation, which can be obtained by ground or satellite measurements. Satellite data provide information about solar radiation and meteorological conditions in locations where ground measurement data are not available. Gueymard developed a Daily integration approach model to predict the monthly-average hourly global irradiation by using a large dataset of 135 stations with diverse geographic locations (82.58N to 67.68S) and climates. The results showed that the daily integration model is most accurate than previous hourly models.

The second part of this report is about the numerical heat transfer model. The receiver consists of an absorber surrounded by a glass envelope. The absorber is typically stainless steel tube with a selective absorber surface. The glass envelope is an antireflective evacuated glass tube which protects the absorber from degradation and reduces heat losses. The Solar receiver uses conventional glass to metal seals and bellows to achieve the necessary vacuum enclosure and for thermal expansion.

The heat transfer model is based on an energy balance between the heat transfer fluid and the surroundings (atmosphere and sky). A comprehensive radiation model between the absorber and the envelope is included in this study. The results showed that the new model has lower RMSE than the NREL Model (0.985% and 1.382% respectively). The numerical heat transfer model integrated with the solar radiation model can be used for evaluating the performance of solar collectors for any location.

## Task 2: Development of a test facility and pilot demonstration

The second task targets the development of a test facility and pilot demonstration systems based on parabolic trough and dish technologies. The experimental combined power and cooling setup will be used as a preliminary study of the demonstration system that will be developed.

### **PERFORMANCE ANALYSIS OF A RANKINE-GOSWAMI COMBINED CYCLE**

Improving the efficiency of thermodynamic cycles plays a fundamental role for the development of solar power plants. These plants work normally with Rankine cycles which present some disadvantages due to the thermodynamic behavior of steam at low pressures. These disadvantages can be reduced by introducing alternatives such as combined cycles which combine the best features of each cycle. In the present study a combined Rankine-Goswami cycle is proposed and a thermodynamic analysis is conducted. The Goswami cycle, used as a bottoming cycle, uses ammonia-water mixture as the working fluid and produces power and refrigeration while power is the primary goal. Figure 5 shows a schematic of the Rankine-Goswami cycle.



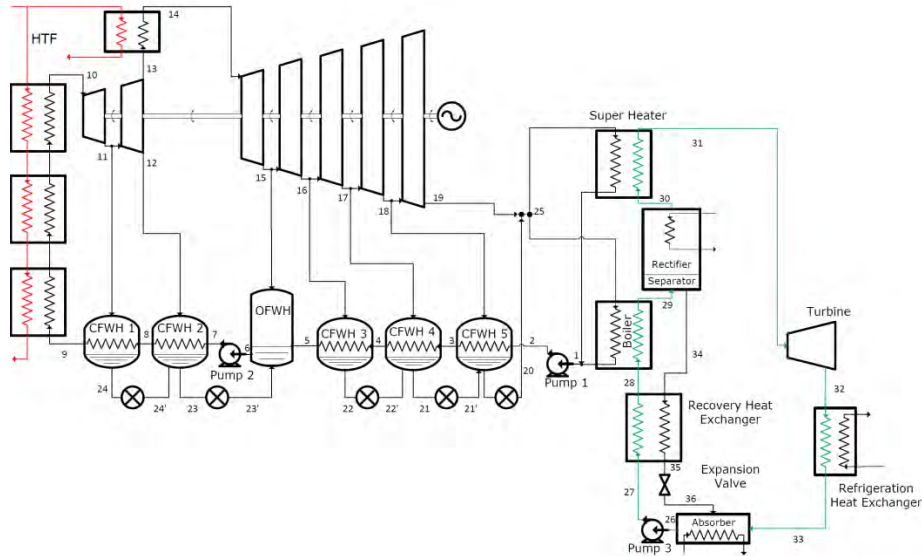


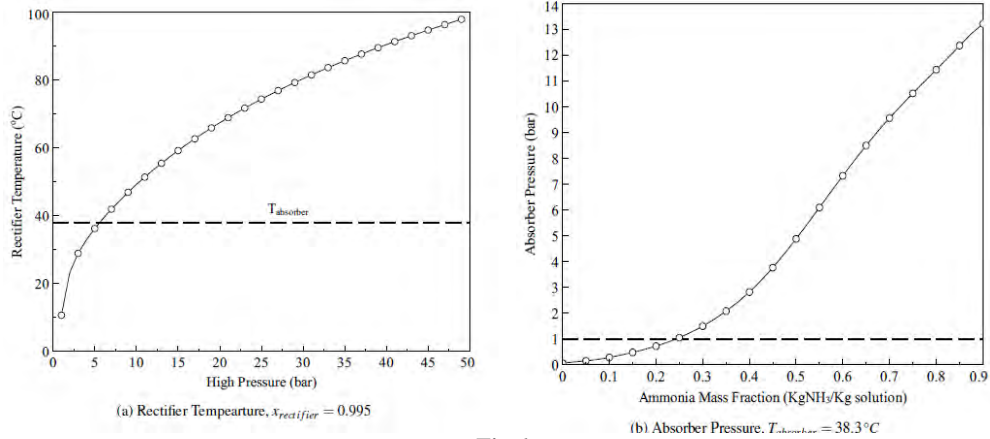
Fig.5

The detailed explanation about the parameters that were used for simulation is given in the paper. Different cases were also considered for parametric studies which are shown below.

Case	Rectifier	Superheater	Controlled Parameter
R	Yes	No	$x_{rectifier} = 0.995$ $T_{superheater} = T_{rectifier}$
R+S	Yes	Yes	$x_{rectifier} = 0.98$ $T_{superheater} = T_{boiler}$
B (Base)	No	No	Saturated vapor condition at the boiler exit

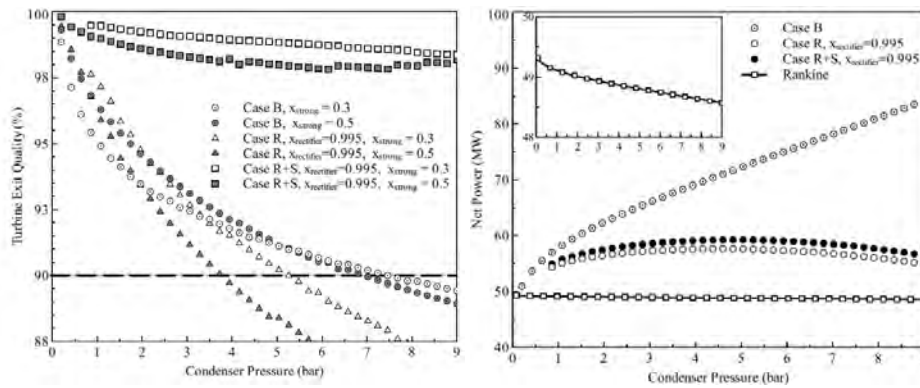
The thermodynamic properties of water and steam were implemented in Python 2.6 by using the international-standard IAPWS-IF97 steam tables. For the Goswami cycle, the properties of ammonia were obtained from a Gibbs free energy formulation given by Xu and Goswami. In this study the amount of the electric work obtained from the topping cycle was held constant at 50 MWe while for the bottoming cycle the turbine work was considered as an output parameter. Figure 6 shows the effect of the high pressure side on the rectifier temperature and absorber concentration, In this case, the ammonia concentration range was selected such as the absorber was kept at least under atmospheric pressure.



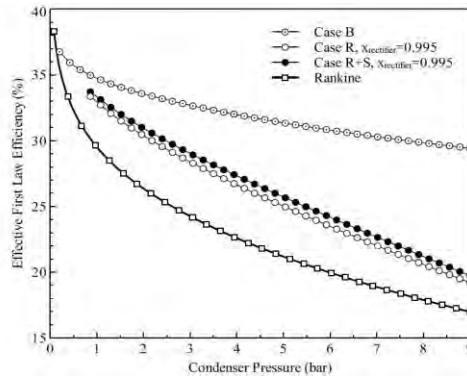


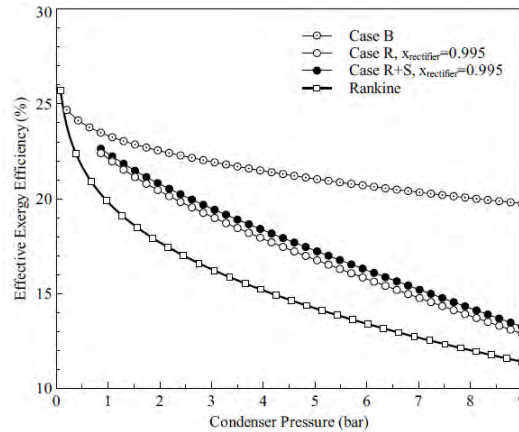
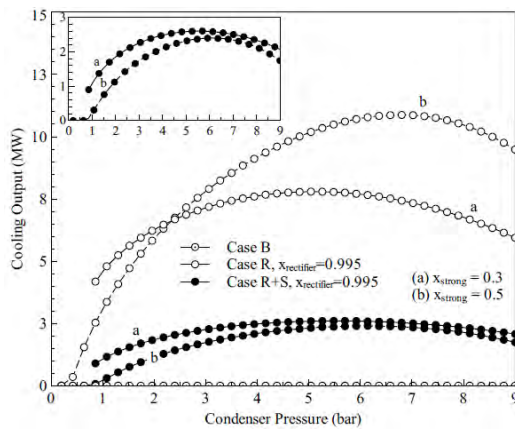
**Fig 6**

Figure 7 shows the effect of the condenser pressure on the Goswami bottoming cycle exit quality for different cases and ammonia mass fraction. Moreover, Figure 8 shows the effect of the variations of the net-work with the condenser pressure for ammonia mass concentration of 0.3, in all the studied cases.



The effect of condenser pressure on the effective First Law efficiency is also illustrated in Figure 9 while the cooling capacity of the Goswami bottoming cycle is presented in Figure 10. The effective exergy efficiency in the cycle as a function of the condenser pressure and ammonia mass fraction is also presented in Fig.11.





### Task 3. Installation and Operation of 50kWe Solar Power Plant

Sopogy Inc. Honolulu Hawaii is the main contractor for installation and operation of 50kWe Solar Power Plant at USF. SunQuest Energy at Clearwater FL is the sub-contractor of Sopogy. They are currently in final stage for preparing the complete engineering drawing of the Solar Power system in order to get the permit for the construction of solar power plant. It is expected that by the mid November permits should be in place so that Sopogy will be able to ship the material to USF. We are hoping that Sopogy will be able to start the construction of power plant sometime in the month of December 2011. Power block for generating electricity will be supplied by GulfCoast Green Energy. Power block is a Green Machine Elite 4000 manufactured by Electratherm. This machine will produce about 50kWh electricity from the thermal energy produces by solar field that will have 199 Soponova 4.0 parabolic concentrators from Sopogy Inc.

### Task 4: Thermal Energy Storage

We are currently working on the development of low cost thermal energy storage (TES) systems for Concentrating Solar Power (CSP). The objective is to research and develop a thermal energy storage system (operating range  $300^{\circ}\text{C} - 450^{\circ}\text{C}$ ) based on encapsulated phase change materials (PCM). The system will be able to meet the utility-scale base-load concentrated solar power plant requirements at much lower system costs compared to the existing TES concepts. This project is developing a TES system concept that will allow for an increase of the capacity factor of the present CSP technologies to 75% or greater and reduce the cost to less than  $\$10/\text{kWh}_t$  as compared to the present cost of about  $\$40/\text{kWh}_t$ .

We have successfully prepared porous pellets of phase change materials that will allow for the volumetric expansion during PCM melting and hence impose less stress on the encapsulating material. We have developed the encapsulation techniques and selected the low cost encapsulating materials that will be used to encapsulate the PCM. Currently we are optimizing the process for encapsulating the PCM so that it can undergo at-least one thousand charge and discharge cycles without any deterioration of the encapsulation. We are also working on the development of numerical model that will help to design the thermal energy storage systems.

## University of South Florida *Energy Delivery Infrastructures*

**PI:** Lee Stefanakos **Co-PIs:** Zhixin Miao

**Students:** L. Piyasinghe (Ph.D.), L. Xu (Ph.D.), A. Balter (Master), M. Alhaider (Ph.D.)

**Description:** The proposed project is to simulate the effects of a renewable energy generation system in a microgrid context to the distribution grid system. The proposed project is to simulate the combination of renewable distributed generation and a battery system to assess the effects during critical conditions such as power system peak.

A research opportunity is to investigate how existing tools can be applied to properly representing dynamic and transient behaviors of microgrids. Therefore, in this project we propose using simulation tools to model a microgrid and investigate how well we can reproduce its measured behavior in the field.

**Budget:** \$485,184

**Universities:** USF

### Project Summary

This project report summarizes three on-going tasks: 1) Microgrid power management scheme analysis; 2) Control and operation of a battery system in a microgrid; 3) Impacts of pulse power loads on a microgrid.

Microgrid power management scheme analysis: With the increasing use of renewable energy resources and energy storage devices, inverter-based distributed energy resources (DERs) become the important components in microgrids. As diesel generators with direct ac connections are the current most cost effective and reliable power sources, the stability investigation of microgrids should include both types of DERs. In this project, dynamics of diesel generation are included and the interaction of the diesel generators and the inverter-based DERs will be investigated using eigenvalue analysis and time-domain simulations. The significant contributions of this research project include: 1) identification of the stability problem in microgrids with inverter-based DERs and conventional generators and 2) investigation of the interaction problem of inverter-based DERs and conventional generators in islanded microgrids.

Control and operation of a battery system in a microgrid: the objective of this task is to investigate the control strategies of a Li-Ion battery group with a PV array within a microgrid. At the grid-connected mode, the battery and the PV array operate at power control mode, while at the autonomous mode the battery provides voltage and frequency control instead. The contributions of this work include: (i) a detailed model of battery including state of charge (SOC) modeling, short-time and long-time transient characteristics and a detailed model of PV array have been built; and (ii) effective control strategies for a battery with the PV array system to operate at both the grid-connected and the autonomous modes have been developed. A test microgrid consisting of a voltage source converter (VSC) interfaced battery, a PV array, passive loads and an induction machine is built in PSCAD/EMTDC. Simulations are carried out and demonstrate the proposed control strategies could coordinate independent distributed generation effectively.

Impacts of pulse power loads on a microgrid: the objective is to investigate the pulse power load (PPL) impact on the stability of a microgrid with power electronic converters. The PPLs are largely employed in areas of high power radars, lasers, high energy physics experiments and weapon systems such as rail guns. The peak power of a pulse load can vary from several hundred kilowatts to several hundred megawatts and the time duration is typically from microseconds to seconds. Hence for the proposed work, a microgrid with Voltage Source Converter (VSC) based inverters and synchronous generators are considered in order to provide better approach towards the smart grid. The study is conducted in PSCAD/EMTDC and Matlab/SimPowersystems.

## 2011 Annual Progress Report

### Microgrid power management scheme analysis

Stability analysis of a microgrid is carried out in [1]. The system consists of diesel generators with direct ac connections, which are the current most cost effective and reliable power sources, and VSC converter interfaced DERs. Those DERs could be fuel cells. Stability investigation for the hybrid systems has not been addressed in the previous literature. The research work models the dynamics of diesel generation and converter control loops in a dq reference frame. The interaction of the diesel generators and the inverter-based DERs is investigated using eigenvalue analysis and time-domain simulations. The significant contributions of [1] include: (i) identification of the stability problem in microgrids with both inverter-based DERs and conventional generators and (ii) investigation of the interaction problem of inverter-based DERs and conventional generators in islanded microgrids.

The study system is shown in Fig. 1. The system is built based on the benchmark system of IEEE standard 399-1997. Two diesel engine generators and two converter-interfaced DERs form a microgrid. Under islanded conditions, the breaker connected to the utility is open.

### Effect of f-P droop on dominating system modes

The root locus of a changing  $f - P$  droop gain in one of the inverter-based DERs is shown in Fig. 2. From the root locus diagram in Fig. 2, it is found that the gain of the  $f - P$  droops in the inverter-based DERs do not impact the system stability significantly. Rather, the gain of the  $f - P$  droop in the diesel engine impacts system stability significantly. A larger gain means more participation in load sharing. In Fig. 2, it is noted that the larger the gain, or the more the diesel engines participate into load sharing, the more unstable the microgrid becomes. Therefore, the diesel generators should have a limited gain. This results in an insignificant participation in load sharing. Fig. 3 shows the dynamic response of the four DERs due to a load change. The simulation results corroborates with the analysis.

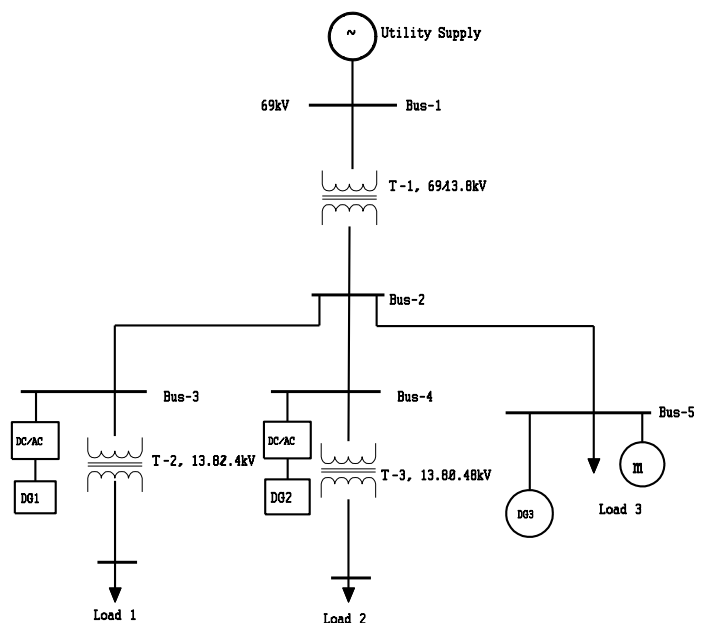
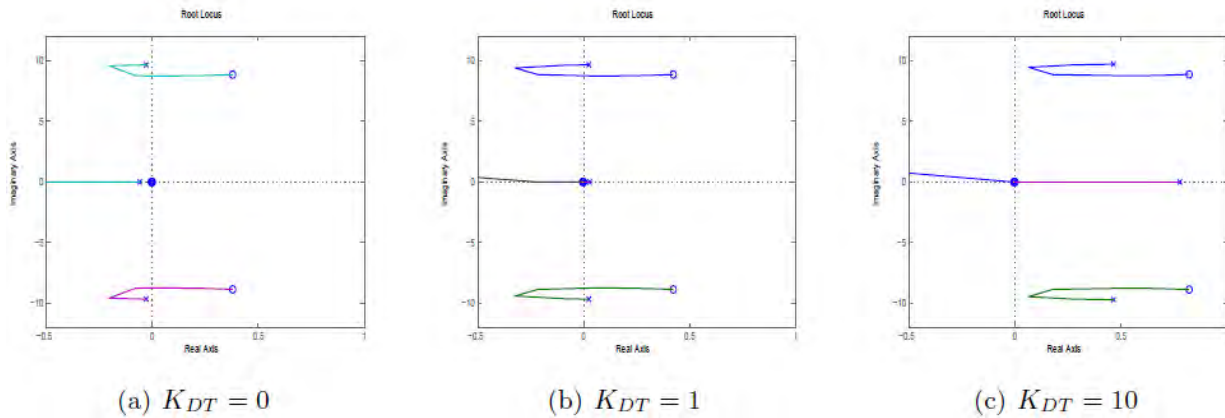
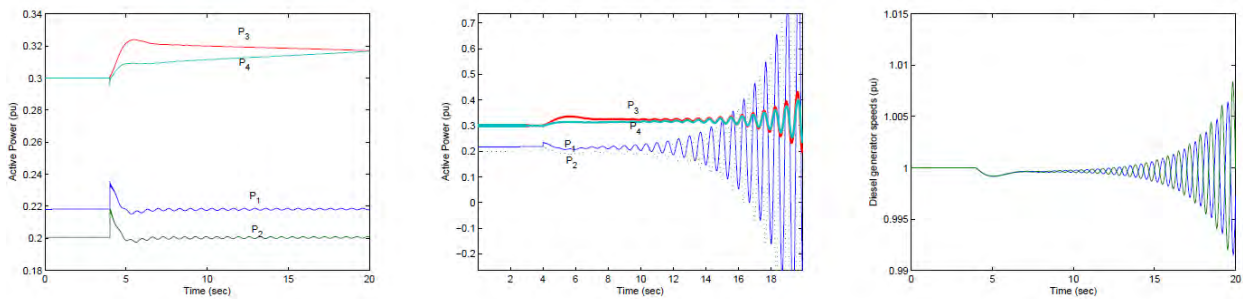


Fig. 1: Study system



**Fig. 2:** Root locus diagrams with a changing f-P droop gain in DER3.



**Fig. 3:** Dynamic performance of the four DERs due to a load change.

Publications & Conferences

1. Z. Miao, A. Domijan, and L. Fan, "Investigation of Microgrids with Both Inverter Interfaced and Direct AC Connected Distributed Energy Resources," *IEEE Trans. Power Delivery*, vol. 26, no. 3, pp. 1634-1642, July 2011.
2. L. Xu, Z. Miao and L. Fan, "Control of a back-to-back VSC system from grid-connected to islanded mode in microgrids," in *Proc. Of IEEE EnergyTech*, May 2011
3. Z. Miao, A. Domijan, and L. Fan, "Negative Sequence Compensation for Unbalance in Distributed Energy Resources Interfacing Inverters," *International Journal of Power and Energy Systems* (accepted)
4. L. Fan, Z. Miao, and A. Domijan, "Impact of Unbalanced Grid Conditions on PV Systems," *IEEE Power & Energy Society General Meeting* 2010.

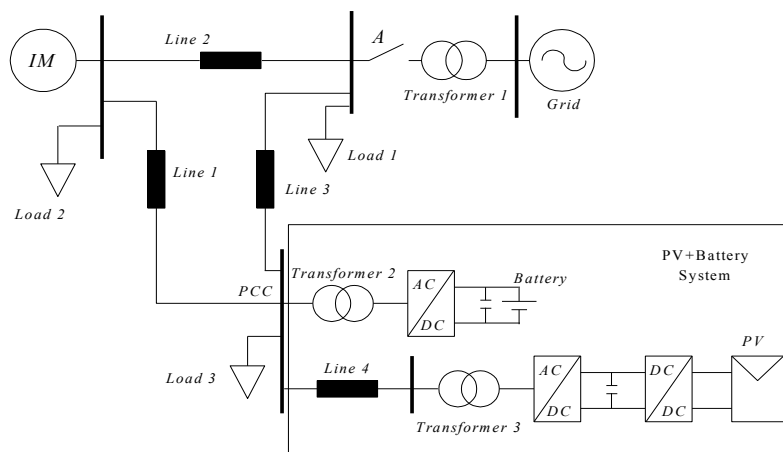


### Control and operation of a battery system in a microgrid

The objective of this research is to study the control strategies for a microgrid with both a battery group and a PV array. The study approach is detailed model based simulation. Detailed battery models have been developed both by mathematic equations and electrical circuits. A Li-ion battery model is using electrical components, which was validated through experiments. PV model has been investigated thoroughly in the literature. The current source and anti-parallel diode model has been proved to be able to simulate the V-I characteristics of a solar cell accurately. For the PV and battery combined systems, a power management mechanism that could optimize the power flow. Utilize batteries to reduce the fluctuations of PV output. The power within PV and battery system can be scheduled from the power system's point of view. Besides the PV and battery combined system, PV and capacitor combined system is also examined by other researchers. Capacitors are also could be used to reduce the power fluctuation of PV, or participate in frequency control.

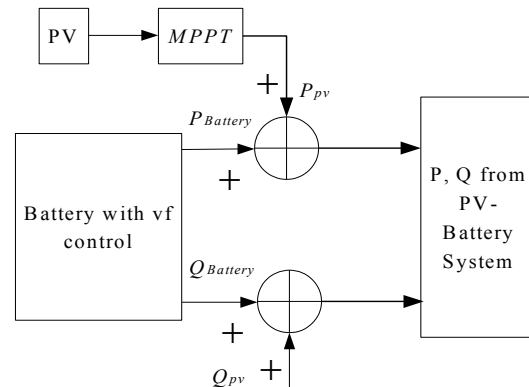
The focus of this task is control strategies at the autonomous mode. We have conducted research on developing battery operating strategies based on a detailed battery model at both the grid-connected and the autonomous mode. The research is expanded to include a PV array in the microgrid. Coordination among different DERs will be taken into consideration.

The microgrid studied in this paper consists of three distributed energy resources (DERs). An induction machine driven by a diesel engine works at the generating mode. It supplies active power to the loads within microgrid. A PV array is connected to the microgrid and supports the loads as well. A VSC interfaced battery station is included to store excess energy from the PV array or inject energy when there is a need. Fig. 4 shows the topology of the investigated microgrid where three distribution lines are used to connect each component. The topology complies with the IEEE Standard 399-1997.



**Figure 4:** Study System of Task 2

Fig. 5 shows the power coordination mechanism of the PV and the battery system. AC grid voltage and frequency are the variables to be controlled. The output real power and reactive power of the battery system are dependent on the measured frequency error and voltage error. The total output power from the PV and the battery should meet the requirement of the microgrid.



**Figure 5:** Coordinated control strategy of PV and battery system at autonomous mode in Task 2.

### Publications & Conferences

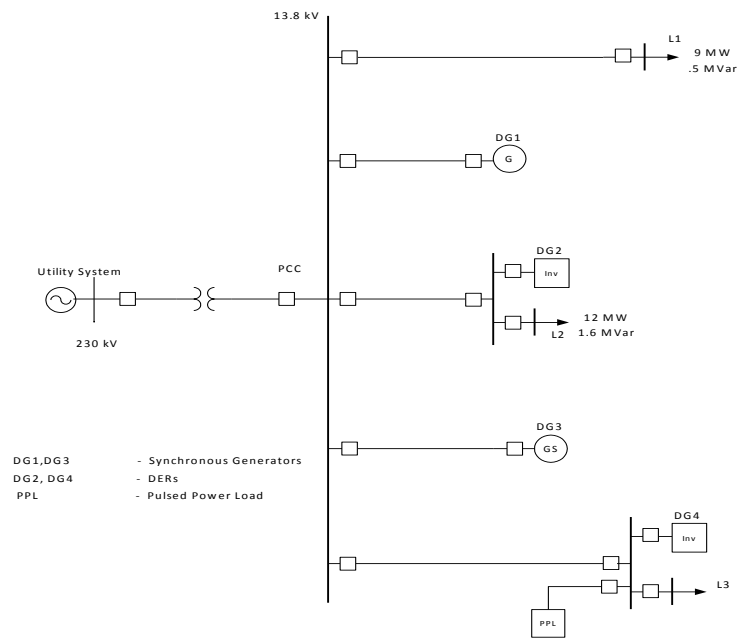
L. Xu, Z. Miao and L. Fan, “Control of a battery system to improve operation of a microgrid,” submitted to IEEE Trans. Sustainable Energy.

L. Xu, Z. Miao and L. Fan, “Coordinated Control of a Solar and Battery System in a Microgrid,” submitted to IEEE T&D meeting 2012.

### **Impacts of pulse power loads on a microgrid**

The objective is to investigate the pulse power load (PPL) impact on the stability of a microgrid with power electronic converters. The PPLs are largely employed in areas of high power radars, lasers, high energy physics experiments and weapon systems such as rail guns. The peak power of a pulse load can vary from several hundred kilowatts to several hundred megawatts and the time duration is typically from microseconds to seconds. Hence for the proposed work, a microgrid with Voltage Source Converter (VSC) based inverters and synchronous generators are considered in order to provide better approach towards the smart grid. The study is conducted in PSCAD/EMTDC and Matlab/SimPowersystems.

The work done in references considers the impact of a PPL load on system voltage profile only. But for the proposed task 3 here, the impact on both voltage and the frequency of the microgrid system is considered. The study microgrid system to evaluate the impacts of PPL is shown in Figure 6.



**Figure 6:** Study Microgrid System in Task 3

PPL can be connected to a microgrid either directly or through storage element. For the proposed work PPL connected through a capacitor is considered since the system is unable to provide peak load of the PPL without losing the stability of the system. PPL model here consists of a three phase rectifier, filter circuit and buck converter.

Publications & Conferences

L. Piyasinghe, Z. Miao and L. Fan, “Investigate the Microgrid Operation with Pulsed Power Loads,” to be submitted to IEEE PES general meeting 20

**University of South Florida**  
*Energy Efficient Technologies and the Zero Energy Home Learning Center*

**PI:** Stanley Russell    **Co-PI:** Yogi Goswami

**Students:** Mario Rodriguez (MA), Sean Smith (MA), Jon Brannon (MA), Jean Frederic Monod (MA)

**Description:** The project is to create and evaluate an affordable residential scale Zero Energy building that will function as an exhibition of energy efficiency and Zero Energy Home [ZEH] technology on the University of South Florida campus. The project will feature the most cost-effective combination of renewable solar energy with high levels of building energy efficiency. The building will incorporate a carefully chosen package of the latest energy efficiency technologies and renewable energy systems to achieve the most successful and reliable results.

The building will utilize Photovoltaic solar electricity and solar domestic hot water heating systems using the grid as an energy storage system, producing more energy than needed during the day and relying on the grid at night. Plug-in hybrid automobile technology offers a promising means of providing distributed energy storage for such homes. Using a systems approach to couple zero energy home technology with PHEVs we will explore opportunities to develop marketable products that meet Florida's energy and environmental goals.

**Budget:** \$344,600

**Universities:**

USF-School of architecture, College of Engineering, College of Mass Communications, School of Business

FSU-College of Engineering

UF- Department of Interior Design

UF-Rinker School of Building Construction

UCF-Florida Solar Energy Center

**External Collaborators:**

Palm Harbor Homes

Beck Construction

Hees and Associates Structural Engineers

## Progress Summary

Design Development was completed in November of 2010. The 889 square foot Zero Energy House Learning Center is a flexible, modular, pre-fabricated, net zero energy prototype that can adapt easily to different site situations and client needs. The key factor shaping the design approach is Florida's mild climate and an indoor outdoor lifestyle. FLeX House combines the wisdom of vernacular Florida houses, ZEH research, with cutting edge technologies to make a holistic system engineering based, zero energy building package. The project will feature the most cost-effective combination of energy-efficiency technologies and renewable energy systems. The ZEHLC will serve as a teaching and learning tool on campus while promoting the use of ZEH technologies throughout the southeastern US.

The prefabrication process maximizes efficiency and quality control and reduces waste when compared to the site built counterpart. Once fabricated, the main body of the house can be shipped to the site on a single truck minimizing transportation costs. The main body contains sliding modules that are deployed from the main body to complete setup at the site quickly with a minimum use of equipment and labor. The modular system is easily expandable and reconfigurable according to the wants and needs of the client and the site situation.

The plan is laid out on the east west axis to maximize shading and natural ventilation and minimize direct solar gain. Because of the hot climate, the living spaces focus on the cooler, north side of the site. The entire north wall, composed of sliding glass panels can be opened combining the interior living spaces, the exterior deck and the garden into one continuous indoor/outdoor space. The interior space can be left open with a continuous flow from the kitchen to the master suite/office area, or it can be partitioned to separate the living and bedroom areas for privacy and to create two separate thermal zones for energy conservation.

As a net zero energy house FLeX House utilizes Photovoltaic panels for site based, clean renewable energy generation. The grid tied 5 kW array will send electricity back to the municipal electric utility grid during peak hours of generation and FLeX House will take electricity from the grid in the evening or on cloudy days. Over the course of a year the net consumption from the grid will equal zero.

Flex House is equipped with low flow fixtures to conserve water. Rain water is diverted from the roof into a cistern where it is stored and used for irrigating the organic vegetable garden. To keep energy consumption to a minimum FLeX House includes high efficiency energy star rated appliances. To reduce the amount of energy required for lighting, FLeX House was designed to make the best use of natural day light for its interior spaces with large glazed areas on the north and south facades and light colored interior finishes that reflect the light and brighten the interior spaces.

The HVAC system consists of a heat pump and solar thermal panels that circulate refrigerant or heated water to two interior fan coils to cool or heat the house. The energy recovery ventilator [ERV], by precooling the outside supply air, allows the chilled water system to run more efficiently. The ERV combined with a liquid desiccant dehumidifying system allows the fan coil temperatures to exceed the dew point while still maintaining good indoor air quality.

Flex house is designed to meet Florida's demanding hurricane code. All exterior finish materials have been tested for impact in hurricane winds and have obtained the required Florida product approvals. The building skin is durable, galvanized corrugated metal and the wood louvers are made from cypress which has a natural resistance to rotting and intrusion from insects. In the off season the bedroom and entry modules can be slid back into the main body of the house and the entire exterior can be shuttered to protect the house from the weather and vandalism.

Construction Documents were completed in March and a contract between Beck Construction and USF was finalized. After delays in the contract process, construction began in mid-May, 2 months behind the original schedule. Construction continued through the summer and was completed in early September. The house was disassembled and shipped to Washington DC on September 12<sup>th</sup>. FLeX House was successfully reassembled in West Potomac Park in DC and was exhibited in the 2011 Solar Decathlon. Tens of thousands flocked to the popular house which was second in total attendance among the 19 houses on display. The house was disassembled and shipped back to Tampa where it is scheduled to arrive in the morning of 10/14. Once reassembled in its permanent location on campus the house will begin its life as the ZEHLC.



**Funds leveraged/new partnerships created**

<b>New collaborations</b>		
Florida Power and Light	Sponsor	\$10,000
TECO	Sponsor	\$10,000
OUC	Sponsor	\$10,000
Progress Energy	Sponsor	\$10,000
USF COE	Sponsor	\$20,000
UCF	Sponsor	\$16,000
Wells Fargo	Sponsor	\$15,000
CSI	Sponsor	\$500
Solar World	Sponsor	Gift in Kind
Bosch	Sponsor	Gift in Kind
Sothern Cypress Manufacturers	Sponsor	Gift in Kind
Simpson Strongtie	Sponsor	Gift in Kind
Kohler	Sponsor	Gift in Kind
Dupont	Sponsor	Gift in Kind
Pella, CWS	Sponsor	Gift in Kind
Lithonia	Sponsor	Gift in Kind
Beck Construction	Industry Partner	

<b>Proposals</b>						
Title	Agency	Reference Number	PI, Co-investigators and collaborators	Funding requested	Project time frame	Date submitted
2011 Solar Decathlon	DOE		Stanley Russell	\$100,000	8/2010	12/2011
Technology Fee Grant	USF		Stanley Russell Mark Weston Yogi Goswami	\$223,462	1 year	3/15/2011

<b>Grants Awarded</b>						
Title	Agency	Reference Number	PI, Co-investigators and collaborators	Period of Performance	Funding awarded	
2011 Solar Decathlon	DOE		Stanley Russell	16 months	\$100,000	

Before beginning design on the ZEH Learning Center we studied vernacular precedents and more recent building and research projects that have aimed at zero energy or near zero energy status. We looked at Vernacular Florida architecture as precedent for passive cooling, heating and daylighting. Building design in Florida changed considerably with advancements in mechanical systems in the mid- 20<sup>th</sup> century. Up until that time houses typically had wide overhangs to shade the walls and windows, wide covered porches for outdoor living and high ceilings with crawlspaces under the floor to induce natural ventilation. After air conditioning became popular houses were built to close out the heat with smaller windows, compartmentalized interiors, and low flat ceilings. Passive solar design was experimented with during the energy crisis of the 1970s and although it was mostly applied to cold climates, many of the lessons learned during that period are once again relevant in the current movement toward zero energy buildings.

Because the thermal comfort range of the average American has changed since the proliferation of air conditioning, it would be difficult for most to live in a passively cooled home especially in Southern Florida. Regardless, the principles of vernacular buildings and passive solar design can complement advances in highly efficient mechanical systems to greatly reduce the energy consumption of buildings. There is also evidence that comfort levels can be gradually altered when standards are placed on heating and cooling levels in buildings. South Korea for example, has set a standard of not less than 26c [79f] in the summer for air conditioning and not more than 20c [68f] in the winter for heating in public buildings. In Japan, air conditioning in public buildings is mandated at not less than 28 [82f] degrees in the summer season.

Many of the examples of near zero and zero energy houses in Florida are projects implemented by The Florida Solar Energy Center® (FSEC), a research institute of the University of Central Florida. Since 1998 with funding from the department of energy's building America program FSEC has built and monitored several zero energy and near zero energy houses in the State of Florida. Data gathered from monitoring the performance of these houses is a valuable resource for ZEH research. The FSEC projects made it clear that combining energy efficiency in building design and appliances with PV and solar thermal systems for clean renewable energy generation can result in affordable zero energy houses.

The *Off Grid Zero Energy Building* [OGZEB] at Florida state university is an off grid zero energy test house which is just beginning to yield data. In addition to Photovoltaic panels, the OGZEB incorporates hydrogen fuel cells for storage and production of electric power. The *Florida House Learning Center* in Sarasota Florida, like the proposed ZEH Learning Center, was established to showcase sustainable building technologies to builders and the general public. The Florida House contains exhibits of various green building products and the building itself has explanatory text in various locations to describe the technologies at use. I traveled to Japan in June and met with engineers at two of Japan's largest housing manufacturers Misawa Homes and Sekisui Haimu. Misawa Homes produced its first Zero Energy House Model in 1998 and since then has sold thousands throughout Japan. Both companies take a systems approach to life cycle cost, energy use and CO<sub>2</sub> emissions with their highly efficient manufacturing processes. The experience in Japan made the advantages of factory built homes evident and led us to pursue a housing manufacturer as an industry partner.

In addition to documenting what has already been accomplished in the field of building energy efficiency we also feel that it is important to know about the emerging technologies that will transform Zero Energy Building design in the near future. Some of these are already beyond the testing stage and in commercial production but are expensive compared to more conventional alternatives. This is often a function of supply and demand and in many cases it can be assumed that an increased demand for these products will lead to lower prices. We think that raising public awareness to increase demand for quality products is

one important function of the Zero Energy House Learning Center. Technologies like Aerogel insulation, vacuumed insulated glass, electro-chromic glass, building integrated photovoltaic materials and OLED lighting will revolutionize building design and construction when they reach an affordable level. Liquid desiccant cooling and dehumidification show promise for the next generation ZEH in the hot and humid southeast. Liquid Desiccant solar cooling systems developed as part of the Department of Energy's SBIR program convert hot water from solar thermal panels into cooling and dehumidification.

We are also interested in the interface between the ZEHLC and other related systems. The key to energy efficiency in the future will undoubtedly lie in smart grids that will regulate the flow of electricity to and from buildings according to peak and low demand periods. The plug-in hybrid electric vehicles, soon to be released by several auto makers, will be key elements in regulating this flow and storing energy for the grid and will be considered as an integral part of the ZEHLC design.

The Solar Decathlon is an event held every other year on the Mall in Washington DC to showcase the latest advances and emerging technologies for energy efficient buildings. 20 Teams are chosen from an international pool of applicants to design and build energy efficient buildings on the Mall. In answer to the RFP for the 2011 Solar Decathlon I assembled a team of experts from FSU, UF, UCF and USF in the fall of 2009 to make a proposal. Our proposal was deemed competitive in January 2010 and we were asked to submit a schematic design proposal by March of 2010. Based on the strength of our submission, Team Florida was chosen as one of 20 teams to compete in the 2011 Solar Decathlon. Participation in the 2011 Solar Decathlon expands the potential of the ZEHLC as a learning tool and facilitates additional funding and input from experts across the state.

Based on our research from the first year we began looking at architectural and engineering innovations that could improve on current ZEH technology and construction practices. The closed nature of recent Florida houses and early attempts at ZEH was identified as a problem that we wanted to address with the ZEHLC. We maintain that contemporary Florida houses can significantly reduce their annual energy consumption by incorporating the same passive solar strategies that were commonly used in Florida homes before the advent of air conditioning. A building envelope that is well sealed and insulated and can be opened during the cooler/dryer months of the year and closed when temperature and humidity levels are too high, can have a more open feeling and save energy at the same time. Furthermore, studies at FSEC have shown that the majority of heat gain comes through the roof of Florida homes and attic spaces reach extremely high temperatures in the range of 140<sup>0</sup>. We considered the use of a shading device that would cover the entire roof and east and west walls of the house to significantly reduce or eliminate direct solar radiation coming in contact with the building envelope. A ventilated space between the shading device and the house would prevent the buildup of hot air that commonly occurs in the attic space of Florida houses. According to a life cycle assessment of energy use, we looked at a modular, factory built house to minimize construction waste and maximize efficiency in labor and energy use during the construction process. Innovative mechanical systems including a liquid desiccant system for controlling humidity levels and reducing latent heat load; a solar thermal system that takes advantage of a high thermal conversion of solar radiation and uses it for a variety of energy end uses and a heat pump tied to the solar thermal system to increase efficiency in both systems.

To test the effectiveness of different building envelope alternatives, we built 3- 8'x8'x8' structural insulated panel modules, each with a different envelope system. Module 1, the control case, had no additional treatment of the envelope. Module 2 had a 3/4" ventilated airspace on the exterior skin of the roof and walls. Module 3 had a shading device covering the roof and east and west walls.



Fig. 1: module construction



Fig. 2: module 2 complete



Fig. 3: testing module 3

The 3 modules were monitored under identical conditions simultaneously over an 8 hour period with a Campbell Scientific PS100 Data logger and 3 temperature and relative humidity sensors attached to determine the most efficient and economical configuration of the building envelope. The results confirmed that the module with the shading device had the lowest interior temperature at the end of the 10 hour period. The temperature difference within the modules continued to grow as the hours passed and the insolation continued to raise the temperature disproportionately in the unprotected module 1.

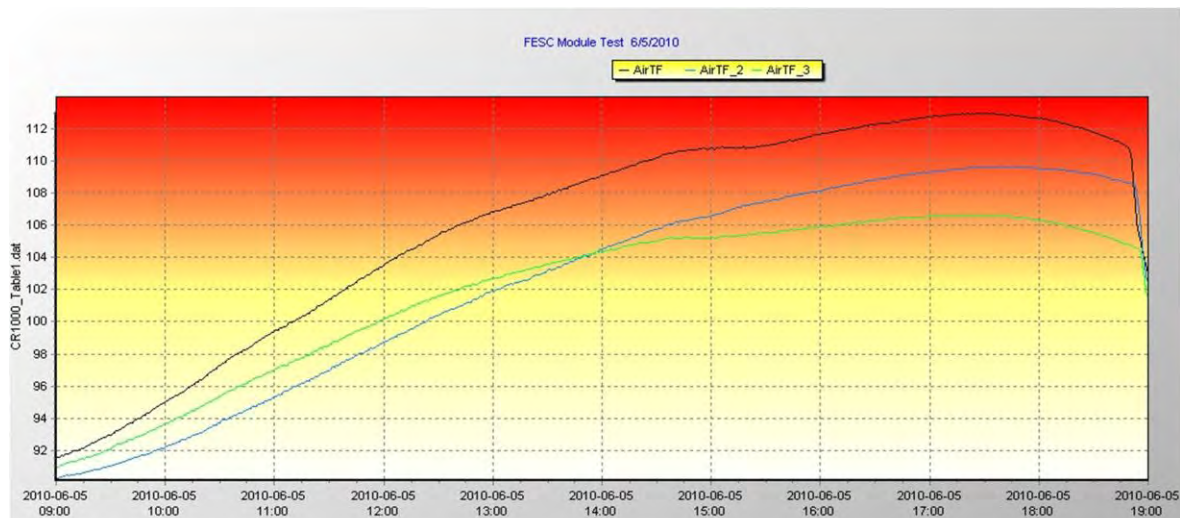


Fig.4: black line is module 1, blue line is module 2, green line is module 3

We applied our research from the first 11/2 years of the grant period to our schematic design concept. Based on our research we were convinced that contemporary houses can significantly reduce their annual energy consumption by incorporating passive solar strategies. We decided on a hybrid approach to the building envelope combining current thinking in ZEH technology with vernacular wisdom with an envelope that can be opened during the cooler/dryer months of the year and naturally ventilated and closed and mechanically cooled when the outdoor temperature and humidity levels are too high to achieve an acceptable comfort range by natural ventilation.



The entire north elevation is sliding glass panels that can be opened to the garden to allow natural ventilation and a sense of connection with the landscape promoting a healthy and energy efficient indoor/outdoor Florida lifestyle. On the south elevation all of the glass is shaded by louvers to eliminate insolation during most of the year. During winter when the sun is lowest in the sky there are typically several cold days when afternoon temperatures are low enough to require space heating. Louvers on the south side of the building will be adjustable so that the sun can be allowed to penetrate the space on cold days but can also shade the sun on warm winter afternoons.

A shading structure made of steel tubing and wood louvers will completely shade the roof and east and west walls of the house stopping the hot solar rays from radiating through the building envelope. An 18” space separating the shading device and the building will allow air to pass through freely and prevent the buildup of hot air between the two. The umbrella will also support the PV array and solar thermal panels making them easily accessible without disturbing the building envelope. The house is designed for pre fabrication to minimize construction waste and maximize efficiency in labor and energy use during the construction process. Since we plan to ship the house in one piece the exterior dimensions are limited by shipping restrictions. Portions of the building that go beyond the prescribed shipping width are designed to telescope out from the main building envelope making the house economical to ship and quickly deployable at the site. A 5 KW PV array will provide electric power to the house; a liquid desiccant system will control humidity levels and reduce latent heat load; a solar thermal system that takes advantage of Florida’s high thermal conversion of solar radiation will be used for space heating, hot water and to regenerate the liquid desiccants. Hot and chilled water will be circulated around the house to fan coil units in 3 zones for localized control of temperatures and reduced temperature fluctuations when compared to forced air systems.

Design Development was completed in November of 2010 complete with a BIM model of the building a detailed half inch scale model and a digital animated walk thru. The scale models were exhibited at the International builder’s show in Orlando in January 2011. A 70 page set of Construction Documents was completed in March of 2011 and a contract between Beck Construction and USF was finalized for the construction of FLeX House. After delays in the contract process, construction began in mid-May, 2 months behind the original schedule. Construction continued through the summer and was completed in early September. The house was disassembled and shipped to Washington DC where it was successfully reassembled in West Potomac Park and exhibited in the 2011 Solar Decathlon. Tens of thousands flocked to the popular house which was second in total attendance among the 19 houses on display. The Solar Decathlon gave students the opportunity to tour the other 18 houses and exchange ideas with their peers as well as explain their ideas to the thousands of visitors to the house. The 3 week event was an exceptionally intense and rich learning experience for the students involved. The house was disassembled and shipped back to Tampa where it is scheduled to arrive on the morning of 10/14. Once reassembled in its permanent location on campus the house will begin its life as the ZEHLC and become an exhibition of energy efficient technologies as well as a living laboratory for energy efficiency research.

ZEHLC research has been presented at the following conferences and meetings:

Russell S.R., *Reaching Zero Energy in Florida’s Hot Humid Climate*, ARCC 2011 CONSIDERING RESEARCH: Reflecting upon current themes in Architectural Research, Detroit MI, spring 2011,

Russell S.R., Weston M., Goswami Y., Doll M. *Flex House*, ASME 2011 5th International Conference on Energy Sustainability & 9th Fuel Cell Science, Engineering and Technology Conference, Washington D.C. Summer 2011



Russell S.R. *Energy Efficiency and the Zero Energy Home Learning Center*, ACSA National Conference, RE.building, New Orleans Louisiana, Spring 2010

Russell S.R. *Evolution of the American Zero Energy House*, Eco-Architecture 2010, La Coruna Spain, Spring 2010

Russell S.R. *Evolution of the American Zero Energy House*, International Conference On Building Science And Engineering, Johor Bahru, Malaysia, December 2009

Eco House Symposium- Kanagawa University, Kanagawa Japan- summer 2011

AIA Florida Annual Conference- Naples Florida- summer 2011

ASME Tampa Bay Annual Meeting- FLeX House- summer 2011

AIA Tampa Bay Designer's Luncheon Lecture Series- fall 2010- 2011 Solar Decathlon - FLeX House

CSI Luncheon - FLeX House- spring 2011

ZEHLC research has been published in the following journals:

Russell S.R. *Hybrid ZEH for Florida's Hot Humid Climate*, The International Journal of Design & Nature and Ecodynamics, WIT Press.

The ZEHLC design model has been exhibited at the following venues:

Title- *U.S. Department of Energy Solar Decathlon 2011 Finalists: A Special Presentation*,

Venue- National Building Museum, Washington DC

Date- 5/ 1- 7/25, 2010

Title- *U.S. Department of Energy Solar Decathlon*

Venue- Orange County Convention Center

Date- 1/12-1/15, 2011

Title- *U.S. Department of Energy Solar Decathlon*

Venue- McCormick Place Chicago IL.

Date- 1/12-1/15, 2011

Title- *U.S. Department of Energy Solar Decathlon 2011 Finalists*

Venue- Portland Downtown Marriot Waterfront, Portland, Oregon

Date- 8/11-8/14, 2010

Title- *U.S. Department of Energy Solar Decathlon 2011 Finalists*

Venue- National Renewable Energy Laboratory Visitor Center

Date- April 2010

Title- *Zero Energy House Learning Center*

Venue- ASCA National Conference Poster Session, Montreal, Canada

Date- 3/ 2011

We applied for and received a \$100,000 from the DOE for the 2011 Solar Decathlon.

Our team raised \$55,000 in cash donations and an additional \$75,000 in gifts in kind.

**University of South Florida**  
***Feasibility, Sustainability and Economic Analysis of Solar Assisted Biomass Conversion***

**PI:** B. Joseph **Co-PI:** Q. Zhang

**Students:** Matt Wetherington (BSChE), Maria Pinilla (MS, Civil and Environmental Engineering),  
Chita Yang (PhD in Chem. Engg.)

**Description:** The main deterrent for commercialization of biomass conversion processes is the cost of conversion; particularly the need to sacrifice as much as 30% of the energy content in the biomass for the thermo chemical conversion step. We want to research and develop the concept to use solar thermal energy from concentrating units to provide energy for the biomass gasification step. We also propose to evaluate the sustainability of such a process.

**Overall Objective:** The overall objective is to conduct a theoretical analysis of solar assisted thermo chemical conversion of biomass from the point of view of energy efficiency, economic feasibility, environmental impact, and long term sustainability of renewable energy production.

**Budget:** \$45,238

**Universities:** USF

### **Progress Summary**

The overall objective for this FESC project was to conduct a theoretical analysis of solar assisted thermochemical conversion of biomass from the point of view of energy efficiency, economic feasibility, environmental impact, and long term sustainability of renewable energy production.

We completed a comparative study of the solar assisted biomass conversion versus unassisted conversion to liquid fuels. A feasibility study by NREL for converting biomass to alcohol fuels served as a basis for these calculations, though we focused more on the production of drop in fuels such as gasoline, diesel and jet fuel. Our study using computer generated mass and energy balance models combined with economic evaluation and profitability analysis showed that while solar assisted biomass conversion provided advantages in terms of carbon emissions, the capital cost of installing a solar thermal energy station made the process less attractive when compared to the conventional process. Life cycle analysis of the processes are currently in progress.

**Funds leveraged/new partnerships created:** We have submitted a number of proposals following up on this work, but none has been funded yet.

## 2011 Annual Report

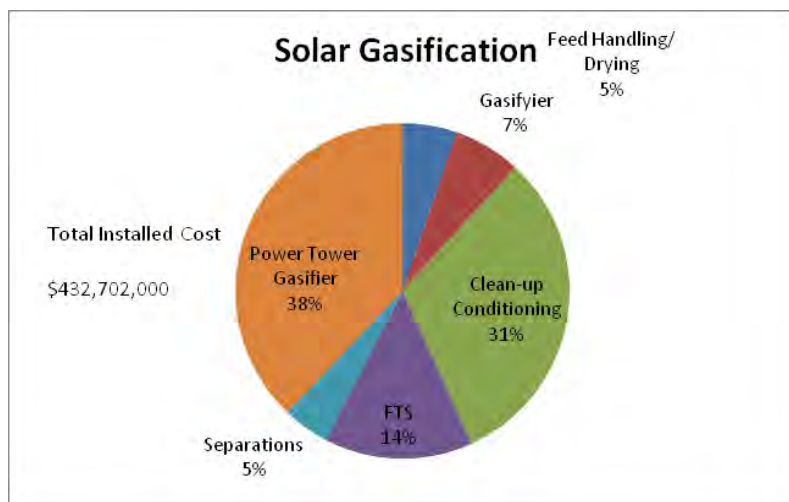
The project is motivated by the following factors:

- ▶ Increasing global demand for fossil fuels
- ▶ Global political instability
- ▶ Increasing fossil fuel prices
- ▶ Potential fossil fuel shortage in the future
- ▶ Increasing environmental impacts associated to fossil fuels
- ▶ The U.S. should be able to sustainably displace around 30% of the country's current petroleum consumption by 2030.

The overall objective for this FESC project was to conduct a theoretical analysis of solar assisted thermochemical conversion of biomass from the point of view of energy efficiency, economic feasibility, environmental impact, and long term sustainability of renewable energy production. The specific objectives for our group are to evaluate the design, economic feasibility and environmental impacts and long term sustainability of solar assisted biomass conversion and identify the opportunities for technological improvement.

To achieve the above objectives, two different systems were compared: (1) biomass conversion without solar unit and (2) solar assisted biomass conversion. The two processes were compared using a computer simulation and economic analysis model developed using CHEMCAD process simulation package. We have completed a life cycle assessment (LCA) that will assess the environmental impacts associated with the system (1) using the data from the NREL report. A comparative LCA will be performed for the system (2) using the technical data from our simulations.

A process design using the NREL report as a basis indicate that the solar assisted conversion costs more based on the current estimates of the costs of solar concentrating units. As the costs of the parabolic troughs used for solar energy conversion is reduced ( mass production will lower costs) the use of solar energy to assist the gasification step will become more economical. The following figure shows the capital cost breakdown for a solar assisted plant.



To date, the life cycle assessment (LCA) for the biomass conversion process described in the NREL report has been completed. The overall process input into GaBi – a LCA software has been completed. The life cycle assessment for the second system is currently under development in GaBi. The results from two systems will be compared to evaluate the benefits of solar assisted biomass conversion from environmental perspective.

**Publications resulting from the project:**

1. *Matt Wetherington and Babu Joseph* . Cost Models for a Biomass Based Transportation Fuels Plant. Florida Energy Systems Consortium Annual Summit. University of Central Florida, Orlando, Sept 2010.
2. M. Pinilla, Q. Zhang, B. Joseph. LCA: Mixed Alcohol Synthesis via Indirect Liquefaction of Biomass, Paper presented at AEEESP distinguished lecture series Symposium, USF, Feb 2011.
3. M. Pinilla, Qiong Zhang, and Babu Joseph, “ Comparative Life Cycle Assessment of Biofuels and Electricity Production from Algal Biomass, 2011 FESC Summit, University of Florida, Gainesville, Florida, Sept 27-28, 2011.
4. M. Pinilla, Qiong Zhang, and Babu Joseph, “Comparative Life Cycle Assessment of Lignocellulosic Biomass Conversion into Different Energy Products”, 2011 FESC Summit, University of Florida, Gainesville, Florida, Sept 27-28, 2011.

**University of South Florida**  
***Power Generation Expansion Portfolio Planning to Satisfy Florida's Growing  
Electricity Demands***

**PI:** Tapas K. Das    **Co-PIs:** Ralph Fehr  
**Students:** Patricio Rocha (Ph.D. graduated August 2011), Felipe Feijoo (Ph.D.)

**Description:** The objectives of the proposed research are to 1) develop a comprehensive generation technology based portfolio optimization (GTPO) model and its solution algorithm, and 2) develop educational resources to enhance training of scientific workforce for the state of Florida. The research will directly address three major challenges: fulfillment of the growing power demand, meeting the emissions targets, and supply of technology workforce. The potential economic impact of the proposed research on the State of Florida is expected to be very high, since an energy-secure environment is a basic necessity to support the current trend of explosive growth both in industry and human resources.

**Budget:** \$ 71,906

**Universities:** USF

**External Collaborators:** Argonne National Laboratory (not funded by this project)

### **Progress Summary**

#### **CO2 cap-and-trade revenue redistribution strategy to spur green generation technology growth**

During the initial phase of the project, our efforts were focused on developing a generation capacity expansion model that incorporates the implications of the implementation of a CO2 cap-and-trade program in the U.S. A CO2 cap-and-trade program will change the way generators make capacity expansion decisions, especially if the allowances (or pollution permits) created with the program are distributed via auction (as opposed to be given away for free based on historical emissions). In fact, the profitability of a particular expansion plan is measured by adding the profits obtained by the generator in the allowance and electricity markets. Furthermore, the generators' bids and profits in the electricity market are directly impacted by the additional cost generators incur in purchasing allowances.

This year, we have continued our investigation of the issue of optimal redistribution of the revenue collected from the CO2 allowances. It is anticipated that the implementation of a CO2 emissions control scheme, either a cap-and-trade program with auctioned permits or a carbon tax, will provide the government with an important new source of revenue. Economists advocate for the redistribution of this carbon revenue i.e., for the emissions control schemes to be revenue neutral. We have developed an optimization model to obtain redistribution strategies of the carbon revenue collected by an electricity-sector emissions control scheme. We consider two types of subsidies through which the redistribution is accomplished: i) bid subsidies for low-emission generators, which are directed at lowering locational marginal prices throughout the power network, and ii) R & D subsidies, whose purpose is to improve the competitiveness of low-emission generators against fossil-fuel generators. We use empirical curves found in the literature to model the potential effect of R & D subsidies on the cost reduction of low-emission technologies. The optimization model that we have developed attempts to strike a balance between the allocations of these two types of subsidies for a given planning horizon. In addition, by considering the OPF as the basis for our formulation, we intend to address some of the regional (locational) equity



issues that may arise if an equal per capita revenue redistribution rule (as proposed in the literature) is implemented.

We demonstrated the use of the mathematical model via a 4-node sample problem. We are currently analyzing the results from the sample problem and also expanding the model relaxing some of the strong assumptions involved in the original formulation, e.g., a fixed limit for each green generator for subsidy. We expect to have a more realistic model developed and analyzed to yield useful guidelines for a revenue redistribution strategy.

We contributed an invited research paper titled “Finding Joint Bidding Strategies for Day-Ahead Electricity and Related Markets.” *Handbook of Networks in Power Systems* edited by Rebennack, S., Pardalos, P. M., Pereira, M. V. F., Iliadis, N. A. and Zheng, O. P. (In press)

**Funds leveraged/new partnerships created:** Proposal submitted to DOE for a DOE-IAC (Industrial Assessment Center) on August 2011. Project team: Tapas Das (PI), Yogi Goswami, Lee Stefanakos, Bo Zeng, Lingling Fan, Kwabena Gyimay-Brempong, Ralph Fehr. Amount requested \$1.5 million. (Not funded)

## 2011 Annual Report

### Carbon Revenue Redistribution Strategies in Deregulated Electricity Markets

#### Abstract

The implementation of a CO<sub>2</sub> emissions control scheme, either a cap-and-trade program with auctioned permits or a carbon tax, will provide the government with an important new source of revenue. Several economists advocate for the redistribution of this carbon revenue i.e., for the emissions control schemes to be revenue neutral. In this paper, we present an optimization model to obtain redistribution strategies of the carbon revenue collected by an electricity-sector emissions control scheme. We consider two types of subsidies through which the redistribution is accomplished: i) bid subsidies for low-emission generators, which are directed at lowering locational marginal prices throughout the power network, and ii) R & D subsidies, whose purpose is to improve the competitiveness of low-emission generators against fossil-fuel generators. We use empirical curves found in the literature to model the potential effect of R & D subsidies on the cost reduction of low-emission technologies. The use of the optimization model is demonstrated in a sample problem. Discriminatory and non-discriminatory subsidies scenarios are compared.

#### Introduction

In recent years the U.S. and other countries have reduced or at least have started to debate about reducing greenhouse gas emissions, CO<sub>2</sub> dominant among them. There is agreement as to the market-based nature of the approach that should be taken, a cap-and-trade program or a carbon tax, as opposed to direct intervention by the government. However, the disagreements are vast with regards to which approach is better suited to achieve emissions reductions at a reduced cost for the economy and what design features must be considered in the selected approach (the latter is particularly true for the cap-and-trade approach).

A design feature that is common to both market-based emissions control scheme, is the possibility of returning to the market participants the revenue raised by selling allowances (in the cap-and-trade case) or by collecting the tax (in the carbon tax case). This paper is concerned with developing strategies to redistribute this carbon revenue.

The amount of revenue collected by CO<sub>2</sub> emissions control schemes can be significant. Metcalf et al. in [1] compile estimates of the potential revenue that could be collected through several carbon tax bills proposed in the U.S. Congress. The estimates range from \$69 billion to \$126 billion in the first period of a carbon tax program, gradually increasing throughout the years. Paltsev et al. in [2] estimates that the revenue collected by auctioning allowances in some cap-and-trade proposals for the U.S. range from \$130 to \$366 billion during the first period of implementation. It may be noted that the revenue collected in a cap-and-trade program depends on the number of allowances that are auctioned (in some designs, such as the initial stage of the European Union Emission Trading System, all allowances can be given away for free and no revenue is collected). The only CO<sub>2</sub> cap-and-trade program currently functioning in the U.S., the Regional Greenhouse Gas Initiative (RGGI), has collected proceeds that range from \$38 million to \$117 million in the auctions run so far [3]. Several economists [4, 5, 11] are in favor of redistributing (recycling) the carbon revenue, in other words, of developing emissions control schemes that are revenue neutral. The market participants that are most often mentioned as the potential recipients for the revenue are households and low-emission companies. Some of the means to achieve the redistribution of revenue include lump-sum distribution to households [4], reducing labor or capital taxes, and spending the funds for other purposes such as R & D in low-carbon technologies and energy efficiency [5]. The case for redistributing carbon revenue back to households is based on the assumption that electricity companies will pass on to the consumers the cost of allowances or carbon tax, therefore increasing the electricity prices. In [4], it is estimated that households will spend an additional \$1,158 to \$4,119 annually (in 1999 dollars) if a carbon tax is implemented. The case for redistributing part of the revenue to low-emission companies, on the other hand, is based on the need to increase the market share of low-emission generation. The European Union, for instance, have set targets for renewable-based generation (21 %) for the next decade [6]. This will demand a great deal of innovation from renewable-based generation companies which could potentially be achieved through R & D investment (according to [7], emissions pricing alone might not be enough to improve renewable technologies). In this paper, we present a mathematical model to develop revenue redistribution strategies for a cap-and-trade or a carbon tax program among market participants in a power market. The model is a multi-year version of the DC-based Optimal Power Flow (OPF) problem modified to accommodate carbon revenue constraints and subsidies. We focus on deregulated electricity markets that are subjected to emissions control schemes, similar to the case of several existing markets under the Regional Greenhouse Gas Initiative (RGGI) [8].

## Background

The implementation of a carbon tax or a cap-and-trade program that considers the auction of allowances will represent an important new source of revenue for the government. Economists have argued for the use of this revenue to mitigate some of the distributional impacts of such programs, in particular, the fact that low-income households will be hit harder in terms of percentage of total expenditures by the new carbon charges. However, there are disagreements with regards to the best way of redistributing the revenue. Two are the most discussed approaches: lump-sum redistribution and reduction of distortionary taxes (in labor and capital markets). In a lump-sum redistribution scenario, the revenues will be directly redistributed to consumers via rebates. Barnes and Breslow [4] suggest a trust fund, the "Sky Trust", that would be in charge of collecting and administering the revenue for current and future citizens. Each individual would receive the same annual payout from the trust. Lump-sum redistribution to households was found to have the most progressive distributional effect in a study by the Congressional Budget Office [9] (the study considers a cap-and-trade program with all allowances auctioned). Dinan and Rogers in [10] conclude that lump-sum redistribution would be more helpful for low-income households though the cost for the economy would be greater than if the government would use the revenue to reduce pre-existing distortionary taxes. Using carbon revenue to reduce pre-existing distortionary taxes is espoused by several authors in the literature due to the possibility of obtaining a double dividend i.e. achieving environmental benefits and at the same time reducing the economic costs of the tax system [11]. The

double dividend hypothesis has been widely discussed in the literature. Goulder in [12] identifies different versions of the hypothesis (weak, intermediate, and strong) and concludes that the weak version (returning revenues through cuts in distortionary taxes leads to cost savings in comparison with lump sum redistribution) is easily defended on theoretical grounds whereas this is not the case for the strong version (returning tax revenues through cuts in distortionary taxes leads to negative gross costs).

Parry et al. in [11] argue that a strong double dividend can be obtained for a 2 scenario where part of consumer spending is deductible from labor taxes. Other papers dealing with the double dividend hypothesis include [13, 14, 15]. In this paper, we consider two types of subsidies through which the carbon revenue redistribution is accomplished: bid subsidies for low-emission generators and R & D subsidies for low-emission generators. Since the supply bids of fossil-fuel generators are increased due to the price put on carbon emissions, the purpose of the first type of subsidy (bid subsidies) is to lower the LMPs throughout the network. This would allow customers to pay lower prices for electricity (in comparison with the case where no bid subsidies are allocated) and have more money at their disposal for other activities. In this regard, the effect of the bid subsidies is comparable to that achieved through the lump-sum redistribution via rebates. Simultaneously, the bid subsidies accomplish the objective of increasing the market share of low-emission generators. The second type of subsidy that we consider, subsidies for R & D of low-emission generators, have a more lasting effect on reducing production costs than the bid subsidies, which only increase production during the year they are allocated. Subsidies for R & D are common in several parts of the world with major programs implemented in the United States, the United Kingdom, Denmark, Ireland, Germany, Japan, and The Netherlands [7]. Subsidies for R& D, as part of carbon revenue redistribution strategies, have been included in recent emission control bills introduced in the U.S. Congress. In [16], for example, a portion of the 25% of revenue collected in the allowance auction is targeted for investments in clean energy. The only implemented cap-and-trade program in the U.S., the Regional Greenhouse Gas Initiative, also includes provisions for investment of allowance auction proceeds in R & D. For instance, Connecticut, one of the states members of RGGI, assign 23 % of proceeds to support renewable energy programs administered by the Connecticut Clean Energy Fund (CCEF) [17]. In Europe, Denmark recycles part of the carbon revenue to industry through energy efficiency incentives [18].

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## University of South Florida

### *Production of Liquid Fuels Biomass via Thermo-Chemical Conversion Processes*

**PI:** Babu Joseph **Co-PIs:** Yogi Goswami, Venkat Bhethanabotla, John Wolan, Vinay Gupta

**Students:** Ali Gardezi (PhD), Nianthrini Balakrishnan(PhD), Bijith Mankidy(PhD),  
Justin Stottlemeyer (BS in ChE), Matt Wetherington (BS in ChE)

**Description:** The objective of this project is to develop technology for the economical thermo-chemical conversion of lingo-cellulosic biomass (non-food grade biomass such as agricultural waste, bagasse from sugar mills, citrus peels, switch grass, municipal green waste, etc.) to clean burning liquid fuels. Five of the major advantages of this process over a biochemical route to production of ethanol are: (i) it does not utilize food-grade feed stocks and therefore complements and does not compete with the agricultural food production in the state, (ii) the fuel produced is similar to those derived from petroleum unlike ethanol derived fuels which have at least a 25% lower energy content, (iii) the conversion is accomplished in using fast chemical reactions unlike the slow biological reactions for fermenting alcohol, (iv) the process does not require large amounts of water and associated energy costs of separating the water from the fuel as in bioethanol processes, (v) it can utilize a wide variety of biomass sources unlike the biochemical route which cannot work with high lignin containing biomass.

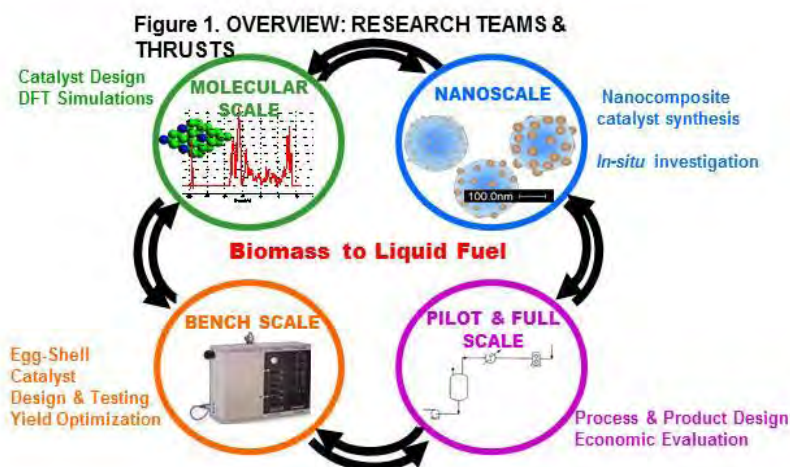
**Budget:** \$554,447

**Universities:** USF

**External Collaborators:** Prado & Associates

### Progress Summary

During the past year, we made progress on four fronts: catalyst design using density functional theory (DFT) simulations in the molecular scale, nanocomposite catalyst synthesis in the nano-level, bench scale reactor testing for the synthesis of liquid fuels from bio gas and biomass conversion process design in the pilot and full scale.





Our research focus is primarily based on cobalt catalysts since they represent the optimal choice for low temperature FTS processes because of higher stability, higher conversion (up to 60–70%), higher productivity, and relatively smaller negative effect of water on conversion. However, fundamental knowledge on reaction mechanisms and development of an economic technology to convert biomass to liquid fuels via FTS process is still not known. Our approach is to study FTS processes at these four different levels to achieve our objective.

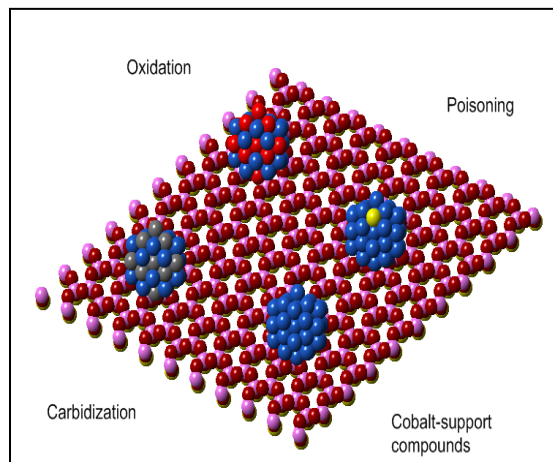
In the past year, at the molecular level, we have performed DFT simulations to understand the role of promoters in the reduction of cobalt oxide which is one of the key steps required in this process for a cobalt catalyst. In the nanoscale level, we have prepared novel composite colloids such as silica supports surface decorated with cobalt nanoparticles as a model FT catalyst. This method allows control over the Co size and its aggregation on the support material. Our bench scale testing of egg-shell catalysts using our fixed bed reactor setup was successful. We were able to produce high grade liquid fuels from both mixtures of CO and H<sub>2</sub> as well as Biosyngas produced from poplar wood. In the area of process design, we have been evaluating alternative strategies to combine the energy intensive biomass gasification step with the energy producing Fisher-Tropsch synthesis of clean liquid fuels from syngas produced in the gasification step.

**Funds leveraged/partnerships:** We have started discussion with QNRF to continue the research in collaboration with Texas A & M University in Qatar. A proposal is under preparation for submission in Jan, 2012. We continue discussions with local industry as well as venture capitalists regarding the construction of a pilot plant using biomass feedstocks. Negotiations are underway between USF and a company regarding the licensing of our egg shell catalyst.

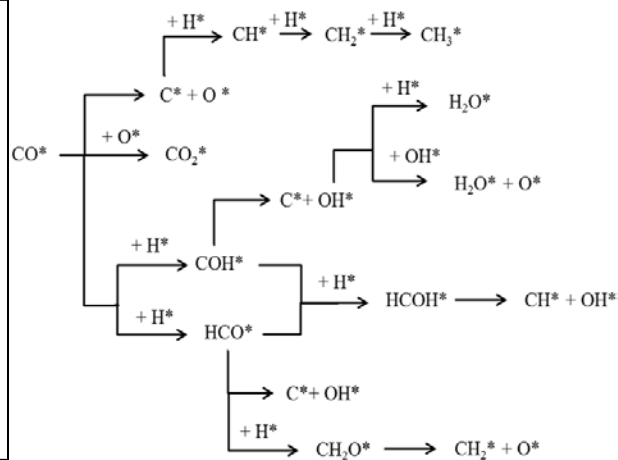
**DFT studies:** The main objective of this research is to study the effect of promoters on the catalyst performance using Density Functional Theory (DFT). Understanding the effect of promoters in the molecular scale would help in tailoring catalysts with higher activity and desired selectivity. Promoters have different functions such as increasing the reducibility, dispersion, activity or extending the life of a catalyst by reducing the deactivation rate. Catalysts are often modified by adding promoters to obtain these desirable properties. The commonly used promoters are transition metals (Zr, Mn, Re, Ru, Rh, Ir, Ni, Pd, Pt, Cu, Ag and Au), and alkali metals (e.g. Li, K, Na, Cs).

The effect of Pt promoter on the reduction of cobalt oxides to metallic cobalt was studied on both flat and stepped surfaces using surface alloy models where the promoter metal was dispersed on the top surface of the catalyst. We found that the activation barrier on promoted catalyst was reduced compared to that on the unpromoted catalyst by about 0.3 eV. We also found that on the promoted catalyst CO dissociation was difficult. A kinetic model was developed and the reaction rate for the promoted catalyst was higher than that for the unpromoted catalyst.

Determining the chain-growth pathway is very important to understand the FTS mechanism. Different mechanisms were proposed for FTS but still there is no clear consensus on the actual mechanism. FTS consists of the following steps: CO activation, hydrogenation and O removal, chain growth and termination. Activation barriers for various primary reactions will be found on Pt promoted and unpromoted Co catalyst to determine the CO initiation pathway that a promoted Co catalyst would follow. The calculations show that the reaction barriers are reduced for most of the reactions in the pathway.



**Figure 2 :** Schematic of deactivation of catalyst



**Figure 3:** Reaction pathways considered

**Eggshell Catalyst Performance Assessment in Biomass Derived Syngas:** The biomass gas derived from pine chips was supplied from Pearson and Associates. Its constituents were analyzed using an Agilent 5975C Mass Spectrometer hooked up with a 6890 N GC. HP-5 MS (5% phenyl)-methylpolysiloxane column provided the initial separation before injection into MS. The results shown in Figure 4 indicate the presence of syngas mixture ( $\text{H}_2$  and  $\text{CO}$ ), hydrocarbons and tar components (benzene, toluene). It was not possible to detect the moisture with mass spectrometer. For moisture detection, the biomass derived syngas was analyzed in a BIO-RAD Excalibur FTS 3000 FTIR equipped with an aligned gas cell. Figure 5 represents the FTIR spectra; the presence of moisture is evident at around  $3400\text{ cm}^{-1}$ . Both the tar constituents and moisture presents problems for downstream unit process (reactor). The presence of higher  $\text{H}_2\text{O}$  content has been shown to favor  $\text{CO}_2$  formation in a fixed bed reactor operation, downgrading one of the advantages of cobalt as Fischer Tropsch catalyst. Additionally, under the normal FTS process conditions i.e. 473-483 K and 20 bar, the system is very close to the saturation temperature of water (i.e. 486 K). Increment in temperature for activity improvement will result in the steam formation accompanied with thermal expansion. This expansion can damage spherical pellet resulting in dust formation inside the reactor. On the other hand, tar can condense in the downstream piping or can accumulate on the catalyst. Although our research group has not come across any literature dealing with the effect of aromatic and poly-aromatic compounds on FTS catalysts, our research experience has shown that the presence of these ring compounds lead to the loss of catalytic activity. However, this needs further investigation which is in progress.

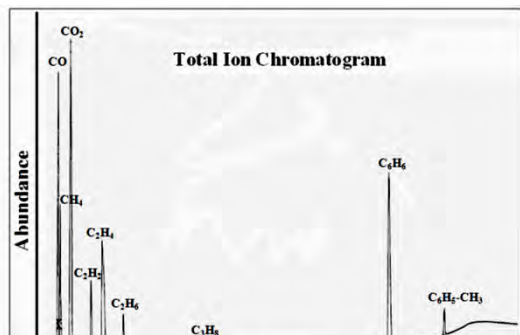


Figure 4: Total ion chromatogram of biomass derived syngas.

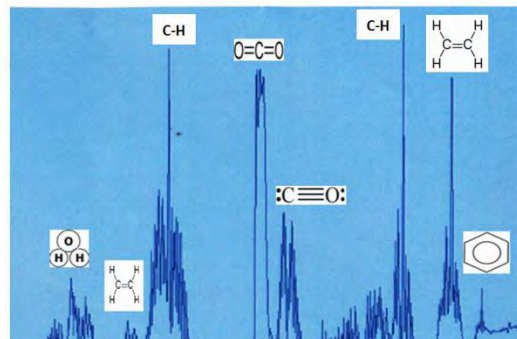


Figure 5: FTIR gas cell analysis of biomass derived syngas.

**Cleansing of Syngas to Remove Moisture and Tar:** Conditioning of biomass derived syngas is a challenging aspect as it needs to be continuous and multistep for successful integration with the downstream operation. As stated earlier, removal of both moisture and aromatics is essential as they can be detrimental for catalyst performance. For this purpose, two inline filters have been installed, consisting of a combination of silica gel beads (Sobead orange, Sorbead WS), molecular sieve for moisture removal and GC C-40 activated carbon pellets for physical adsorption of aromatics. An inline shaw “Moisture meter” is used for to monitor the moisture level going to the reactor. This setup (shown in Figure 6) has successfully cleansed the gas as can be seen by the MS analysis of the gas at the outlet of the filtration system as can be seen in the attached mass spectrometer analysis.

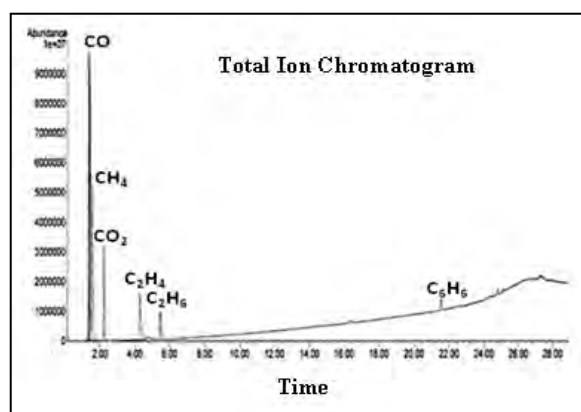


Figure 6: (left) Multistep filtrations setup (right) Total ion chromatogram of biomass derived syngas after cleansing.

**Preliminary Performance Assessment Using Biomass Syngas:** The optimized eggshell catalyst was tested in a fixed bed reactor using cleansed biomass syngas under conventional FTS conditions. The overall material balance shown in Figure revealed a CO conversion of around 52%. This conversion was relatively lower than that reported in previous literatures (for cobalt catalyst) and in comparison to the performance (of same catalyst) on pure gaseous feed (reported earlier). Some of the possible reasons include, transitional nature of the FTS run, the process had to be stopped after 48 hours, due to filtration issues resulting in benzene breakthrough. Later investigations revealed that the activated carbon being used for aromatics removal was surface impregnated with phosphoric acid resulting in pore blockage and diminished physic-sorption activity and regenerability. This filter has thus been replaced. Similarly, the presence of other components lowers partial pressure of carbon monoxide causing the reduced activity. We are planning to perform the next run above 20 bar to bring the partial pressures to the desired level. Other contaminants e.g. CO<sub>2</sub> can be removed from the system using appropriate traps. All these strategies will be implemented to enhance the performance of the liquefaction process.

- Co/SiO<sub>2</sub> Nanocomposite analysis using *in situ* FTIR:** In the previous reports, we have shown that we synthesized cobalt based FTS catalysts with precise cobalt nanoparticle size control (1-14nm). The nanocomposite catalysts were prepared by self-assembly of cobalt nanoparticles on SiO<sub>2</sub> colloids. The immobilization of cobalt nanoparticles on SiO<sub>2</sub> was achieved by surface modification of SiO<sub>2</sub> surface. The nanocomposites thus prepared were next analyzed using an *in situ* AABSPEC FTIR reactor to study the dependency of Co nanoparticle size on catalytic activity. CO gas is one of the primary reactants in FTS. Therefore, we studied the interaction of CO on cobalt surface to understand the effect of cobalt nanoparticle size on CO reaction kinetics. From X-ray diffraction spectroscopy as shown in Figure 7, we identified the cobalt crystal structure as CoO. Then, AABSPEC reactor was used to study an elementary reaction such as CO oxidation on Co-oxide nanoparticle surface to study the dynamics of CO adsorption and CO<sub>2</sub> formation by using infrared spectroscopy. A schematic of CO oxidation on CoO is shown in Figure 8. Based on CO adsorption peak and CO<sub>2</sub> peak profiles obtained from IR, activation energies for step 1 and step 2 were estimated.

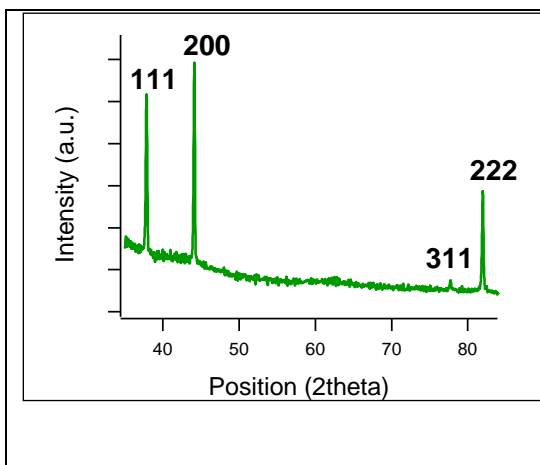


Figure 7: XRD of CoO nanoparticles

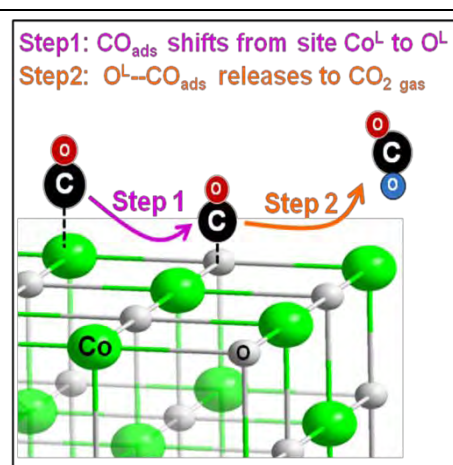


Figure 8: Schematic of CO oxidation reaction

- **Process & Plant Design:** We are now developing a dynamic model of the FTS fixed bed reactor. This model would be useful for plant design and scale up. We are also developing a full process design for the combined gasification/liquefaction process starting with biomass and ending with liquid fuels. This model would be used for economic analysis of such processes.

### Publications resulting from the work so far:

1. S. A. Gardezi, L. Landrigan, B. Joseph, J. T. Wolan, "Synthesis of Tailored Eggshell Cobalt Catalysts for Fischer-Tropsch Synthesis Using Wet Chemistry Techniques", *Submitted to Industrial & Engineering Chemistry* (2011).
2. S. A. Gardezi, B. Joseph, Y. D. Goswami, J. T. Wolan, "Modeling the Start up Phase of Fischer Tropsch Synthesis in a Fixed Bed Reactor: Effect of Pore Filling and Heat Transfer Through the Catalyst Bed", AICHE 2011 Spring Meeting & 7th Global Congress on Process Safety, Mar-2011
3. B. D. Mankidy, C. A. Coutinho, and V. K. Gupta\*, "Probing the Interplay of Size, Shape, and Solution Environment on Macromolecular Diffusion using a Simple Refraction Experiment", *Journal of Chemical Education* 87(5), 515-518 (2010)
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## University of South Florida

### *Solar Photovoltaic Manufacturing Facility to Enable a Significant Manufacturing Enterprise within the State and Provide Clean Renewable Energy*

**PI:** Don L. Morel **Co-PI:** Chris Ferekides, Lee Stefanakos

**Students:** K. Jayadevan (MS), S. Bendapudi (MS 5/11), R. Anders (PhD), Y. Wang (PhD)

**Description:** The primary goal of this project is to enable the establishment and success of local solar photovoltaic manufacturing companies to produce clean energy products for use within the state and beyond and to generate jobs and the skilled workforce needed for them. Thin film technologies have shown record efficiencies of 20%, and present tremendous opportunities for new Florida start-up companies. USF, UCF, and UF are collaborating to develop a pilot line facility for thin film solar technologies, which will serve as a test bed for making ongoing improvements in productivity and performance of solar modules, develop advanced manufacturing protocols, and help train a skilled workforce to ensure the success of new companies.

**Budget:** \$1.6M

**Universities:** USF, UCF, UF

**External Collaborators:** Mustang Solar, a Division of Mustang Vacuum Systems

### Progress Summary

During the reporting period we continued progress in both thrust areas of the project. Development of the thin Film Pilot line is awaiting completion and delivery of the deposition system. The components are being assembled at Mustang Solar, and delivery is expected by June 1. Meanwhile we have been conducting extensive laboratory experiments as part of our preparations for the pilot line. These experiments address both near-term and long term issues. Since the line will be processing CIGS technology, main emphasis is in that direction.

We are using our 25 year processing experience with CIGS to develop new pathways for processing. These pathways are a compromise between those that produce the best laboratory cells and those that are necessary for commercial success. The process that we are developing is termed 2SSS, "2 Step Solid State" processing. The advantages are that the process uses solid Se as the Se source instead of the highly poisonous gas  $H_2Se$ , and simultaneous control of multiple deposition sources is relaxed. Our primary focus initially is in controlling the material composition with the new process. A particular concern from a manufacturing perspective is the effective utilization of source materials. We discovered an interrelationship between the selenization of the metal layers and the loss of Ga. This issue was observed in applying the 2SSS process to the first step of the two step process that we are developing. In this step we form a Cu-rich CuGaSe layer which provides a larger grain platform for growth of the second step layer containing all four elements. For the simplified 2SSS process we found that in order to achieve full selenization Ga was being lost from the precursor layer. This led to development of a modified 2SSS process that overcame this difficulty. Through further development of the process we demonstrated that the film composition using this process is the same as that produced by the highly controlled co-deposition process that produces 20% cells. This new approach is now being utilized in both steps of the 2 step process and initial results are indicating that we can produce the same film quality as with co-deposition while keeping the process time the same. We also have reduced Group III loss to the same level as co-deposition.

An important longer term issue for CIGS technology is the potential for scarce and expensive In. Efforts are underway in many labs to find a solution to this problem. A new material,  $\text{Cu}_2\text{ZnSnSe}_4$  holds promise. In is replaced by the Zn/Sn couple and both are earth abundant. The new material structure (kesterite) is similar to CIGS, but adds additional complications. There is ongoing debate as to what the bandgap is, and cell efficiencies are only about 5%. We have developed a new fabrication pathway for the material that may lead to improved performance. By judicious tuning of the kinetics and thermodynamics of film growth we are able to produce films with the same properties as those produced under more tightly controlled deposition conditions. This is again an attempt to find a manufacturable pathway for this material. Our results are also contributing important insights to the structure of the material and its ensuing electronic properties. If these can be understood and controlled, the material could replace CIGS as a more sustainable material for large scale application.

**Funds leveraged/partnerships:** A new collaboration has been initiated with a small company, Teleos Solar. A pre-proposal has been submitted to the DOE Innovative Manufacturing Initiative FOA.

## 2011 Annual Report

### Thin Film Pilot Line

#### Deposition System

As has been discussed in previous reports we have formed a partnership with a local company, Mustang Solar (MVS), to build and develop the thin film deposition system that is the key piece of equipment in the thin film pilot line. The machine is currently being assembled at Mustang and is scheduled for delivery by June 1. A description of the machine and the approach that we are taking was provided in our last report. Because the design of the machine is based upon USF proprietary processing information and upon MVS proprietary hardware details about the machine cannot be provided in these reports. However, once the machine is operational, we will be providing results on its performance. Meanwhile, we are conducting ongoing laboratory experiments that are directed toward defining the processes that will be transferred to the pilot line machine. Results from these experiments are provided in the next section.

### Lab Scale Experiments

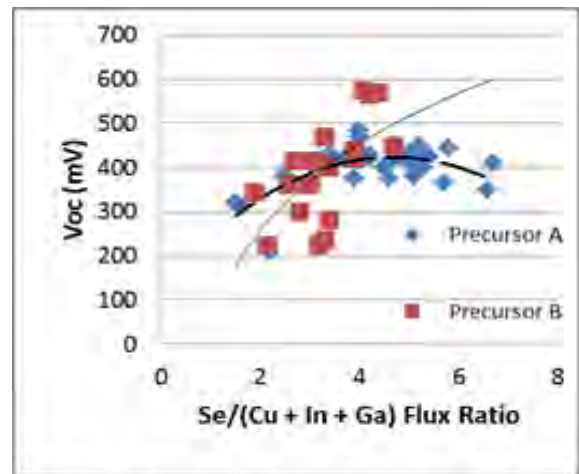
To support the design of the pilot line deposition system we are conducting ongoing experiments at the laboratory scale. These experiments address both near term and long term issues. The pilot line will be processing CIGS, and thus near term experiments are directed toward CIGS processing. Taking a longer view there is concern that at very high production levels the availability and cost of In may cause difficulties. To address this concern modifications of the basic CIGS design are being pursued. In particular we are endeavoring to replace In in CIGS with a combination of Zn and Sn, both of which are more sustainable than In. Further details are provided below.

### CIGS

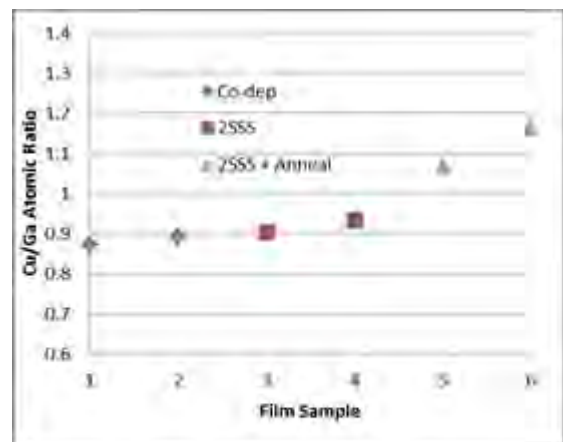
Commercial manufacture of CIGS technology has not yet met with success for a number of reasons. Among these are selection and use of the best deposition methodology. The world record 20% laboratory cells are made with a complex multi-step process that requires simultaneous tight control of three to four deposition sources. Scaling this up to a successful manufacturing level has been a daunting task. We have pursued deposition methodologies that are more amenable to manufacture while admittedly not being able

to produce the level of performance of complex processing. As we approached the institution of a pilot scale system it was apparent that we had to combine the best of these approaches to optimize performance within the demands imposed by commercial manufacturing. To this end we have taken our processes and modified them move toward more complex processing. In doing so we hope to find a manufacturing pathway that others have not pursued and that will be more successful. This has required changes to our processing hardware and recipes and the need to go up a different learning curve. However, we hope to shorten the time it takes by utilizing what we have learned over twenty years of CIGS studies. We use the acronym 2SSS for the new process. It stands for “2-Step Solid State” processing. Before moving on to more difficult device fabrication we first focus on developing processes that produce desired material properties. However, we are guided in this endeavor by device results from our current processing pathways.

Previously we reported results (Fig. 1) that showed different profiles of Voc dependence on Se flux for different precursors (1). To understand the underlying mechanisms we investigated the effect of Se flux on material properties and found interdependence between Ga and Se. Since Voc is largely driven by Ga, this mechanism is in part responsible for the profiles of Fig. 1. However, it is also the case that Ga introduces defects, and this also affects Voc(2). Here our concern was to understand this mechanism so that we could control it and thereby maximize performance while minimizing Ga and Se waste. The 2SSS process can be structured to mimic the 2-step and 3-step processes used with co-deposition. Here we focus on the 2-step process which we will then designate as 2S-2SSS. In this process the first step is to produce a Cu-rich CGS film (which may include some In) with large grain size. In Fig. 2 we show the Cu/Ga ratio for two samples of each type for this first layer produced by 2SSS and by co-deposition. In this case the 2SSS film was produced using the same deposition time and Se flux as the co-deposition film. While it has the same Cu/Ga ratio, its selenization level is only 27% compared with full selenization for the co-dep film. The 2SSS film can be fully selenized with a further anneal at 300° C for 30 minutes in Se flux, and this brings its Cu/Ga ratio to the desired level of about 1.1. However, this has required additional processing time and Se flux as well as the loss of Ga which is why the Cu/Ga ratio increases. The cause of this loss is that in order for Se to fully selenize a precursor layer it has to penetrate through the layers as they form. This gives rise to conditions that foster the formation of volatile Ga<sub>x</sub>Se<sub>y</sub> species. We have developed a modified 2SSS process that overcomes this problem. Fig. 3 shows a comparison of the selenization profile for films made by the standard and modified 2SSS process with that of co-dep films. The selenization profile is determined from the EDS peak amplitudes as a function of beam voltage.



**Figure 1. Voc dependence on Se/metal flux ratio for two different precursors.**



**Figure 2. Cu/Ga ratio for CGS films produced by 2SSS and co-deposition.**



The EDS signal is made to sample increasing depths of the samples by increasing the beam voltage from 15 to 25 kV. Only the low voltage peaks are used for these ratios to accommodate the lowest beam voltage of 15 kV. The data is plotted as Se/(Cu+Ga) ratio in Fig.3. The co-dep film indicates, as expected, a ratio independent of beam voltage indicating uniform selenization of the entire sample. The standard 2SSS film, however, shows increasing Se content with decreasing beam voltage. As the beam voltage increases the selenization level decreases indicating that the top of the film is selenized more than the regions further in, an indication of the difficulty of Se penetrating the upper layers of the forming film. When this sample is subjected to a further anneal at 300 °C for 30 minutes in Se flux, as can be seen the selenization content increases and the profile becomes flatter. With further anneals the film can be made to rise further to match the profile of the co-dep film. However, of greater importance is the behavior of the film deposited with the modified 2SSS process. As can be seen, its selenization profile matches that of the co-dep film. It is also important to note that this film was made using the same deposition time and Se flux as the co-dep film. SEM images and XRD data also indicate comparable grain size and phase purity as co-dep films. Thus in terms of composition and structure these films are equivalent to co-dep films, and they incur minimal Ga loss.

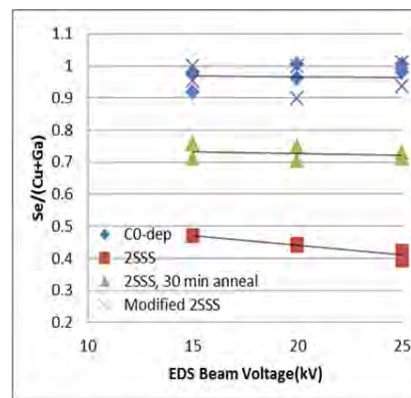


Figure 3. Se/metal ratio as a function of EDS beam voltage for CIGS films made by co-deposition, 2SSS and modified 2SSS processes.

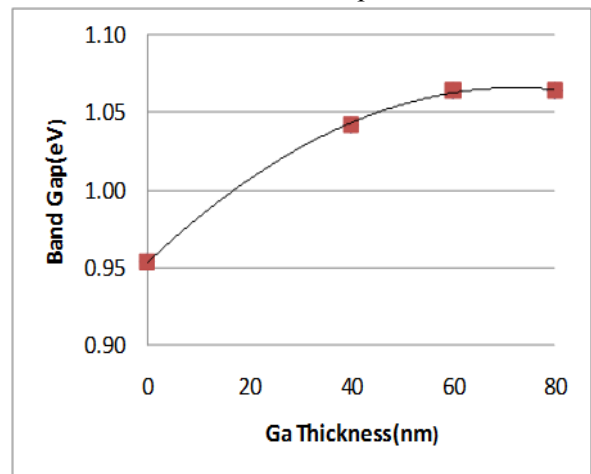
### Kesterite Solar Cells

A new material option that is being pursued is  $\text{Cu}_2\text{ZnSnSe}_4$ . Interest in this material stems from the potential shortage of In and that the Zn/Sn combination satisfies the valency requirements as a replacement for In. The structure that is formed is similar to that of CIGS and is termed “kesterite”. Thus far literature efficiencies are only at the 5% levels as it becomes increasingly clear that this is a complex material. We have turned to our extensive understanding of Ga incorporation in CIS to guide our efforts with this new material. Our first concern again is to understand and control the material properties before proceeding to devices.

We have developed considerable understanding and expertise in the development of CIGS solar cells that is guiding our development of kesterite –based solar cells. Because of the advantages at the manufacturing level discussed above our favored deposition process is 2-step processing using Se vapor, again designated as 2SSS. In using this approach to advance understanding and determine optimum deposition pathways the range we cover goes from co-deposition to selenization of individually deposited metal layers. Results attained thus far for kesterite solar cells are encouraging, but suggest that there are important fundamental issues that must be resolved if competitive performance with CIGS is to be attained. Although present focus is on demonstrating high efficiency, it is also important to build a basis for confidence in the stability of these compounds. Though the similarities to CIGS are many, there are important differences. For example, it seems that at higher temperatures anti-site occupancy is not at play for the sulfur based kesterites, but movement of the sulfur anion drives the phase transition from tetragonal to cubic(2). Although the phase transition is not completed until about 865 ° C, movement of the anion occurs at lower formation temperatures and suggests that the film properties will be a continuous function of processing temperature. This can be a problem with regard to stability, but it can also be an opportunity for optimization, if the controlling mechanisms can be understood. To this end the initial focus of our efforts is on understanding these mechanisms that drive materials properties.

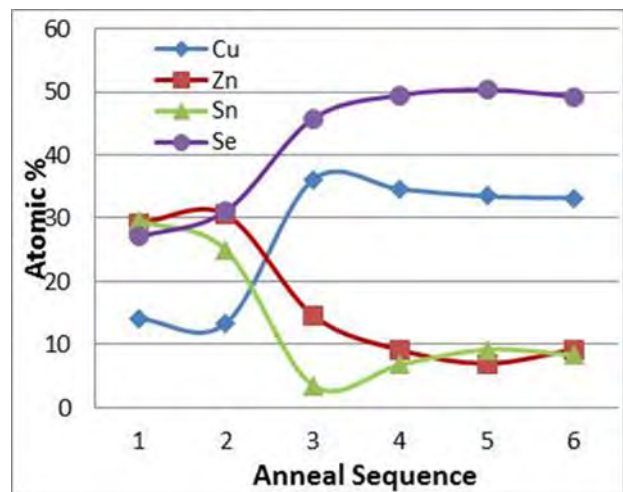


The literature suggests that the band gap of these materials has a range rather than a unique value. This is likely due in part to S migration, but the ability of the Cu and Zn cations to exchange locations is also a consideration(2). It is important then to understand the structural options that the material has, the dependence of electronic properties on those, and most importantly, to use that understanding to control film formation to effect optimum performance. We are applying our extensive experience with the I-III-VI<sub>2</sub> materials and devices to bring this about. A relevant issue that we have had success with is the proper incorporation of Ga. Ga is smaller and more electronegative than In and thus can easily incorporate into an In lattice site. This is the case for co-deposition in which the constituent atoms are all provided to the growth surface at the same time. In 2SSS processing the constituents are deposited in layers and must migrate together to form CIGS. In doing so they can also create an environment in which unfavorable secondary phases can form. In addition, we have also found it difficult for Ga to incorporate at all unless conditions are proper. If we deposit sequential layers of Cu and Ga on a Mo substrate followed by co-deposition of In and Se, we get a band gap of 0.95 eV which is that of CIS. The Ga has a tendency to migrate to the rear of the device where it forms high Ga content CIGS that is not in the space charge layer. By reversing the deposition order and depositing the In<sub>x</sub>Se<sub>y</sub> layer first followed by Cu/Ga we are able to effect Ga incorporation. The dependence of the band gap on the thickness of the Ga layer is shown in Fig. 4. As can be seen, there is a monotonic increase in bandgap with the Ga layer thickness up to about 55 – 60 nm. Voc also increases over this range, but with a slope less than that of the band gap. The implication is that incorporation of the Ga was not effective. Some of the incorporated Ga was creating defects that were competing with the band gap increase and holding Voc down.



**Figure 4. Dependence of CIGS bandgap on Ga layer thickness.**

Before addressing the effect of defects it is first important to understand and control the overall film formation process. The value of the bandgap itself has been the subject of ongoing debate. A recent paper by Ahn et al. (4) suggests that the bandgap of Cu<sub>2</sub>ZnSnSe<sub>4</sub>(CZTSe) is about the same as CIS if the material is made at a temperature of 320 °C. At higher temperatures there is phase separation of ZnSe. These findings suggest a phase instability which is worrisome. We have also addressed this same problem with CZTSe, but using 2SSS processing compared with co-deposition used by Ahn. In 2SSS processing diffusion plays an important role, and as we will show, can be used advantageously to control or limit secondary phase formation. In Fig. 5 we show the compositional dependence of the top layer of a 2SSS film on the anneal time at 400°C. The total film thickness is about three μm, and the composition is determined



**Figure 5. Film composition as a function of the number of anneal times for 40 minutes at 400 C.**

by EDS which just sees the top 0.5  $\mu\text{m}$ . In this case the Cu was deposited first and thus has to diffuse to the top. As can be seen, the Cu is initially low and then climbs to just over 30%. At the same time the Sn and Zn levels are adjusting from their initial values to a 1/1 stoichiometry. This suggests that in a proper environment Zn and Sn may collaborate rather than compete for lattice sites an important advantage to simplify processing.

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