Energy Research and Development Division
FINAL PROJECT REPORT

ENERGY INNOVATIONS SMALL GRANT PROGRAM: 2008 INDEPENDENT ASSESSMENT REPORTS

Prepared for: California Energy Commission
Prepared by: San Diego State Research Foundation

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PREFACE

The California Energy Commission Energy Research and Development Division supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable, and reliable energy services and products to the marketplace.

The Energy Research and Development Division conducts public interest research, development, and demonstration (RD&D) projects to benefit California.

The Energy Research and Development Division strives to conduct the most promising public interest energy research by partnering with RD&D entities, including individuals, businesses, utilities, and public or private research institutions.

Energy Research and Development Division funding efforts are focused on the following RD&D program areas:

- Buildings End-Use Energy Efficiency
- Energy Innovations Small Grants
- Energy-Related Environmental Research
- Energy Systems Integration
- Environmentally Preferred Advanced Generation
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy Technologies
- Transportation

Energy Innovations Small Grant Program: 2008 Independent Assessment Reports is the interim report for the Energy Innovations Small Grant Program (contract number 500-98-014) conducted by San Diego State University Research Foundation. The information from this project contributes to all of PIER's RD&D Programs.

For more information about the Energy Research and Development Division, please visit the Energy Commission's website at www.energy.ca.gov/research/ or contact the Energy Commission at 916-327-1551.

ABSTRACT

The California Energy Commission has been conducting the Public Interest Energy Research (PIER) program through competitive solicitations to advance science or technology in each of the seven PIER program areas to benefit California ratepayers since 1997. In addition, the Energy Commission has also funded and managed the Energy Innovations Small Grant (EISG) Program since 1998. The role of the EISG program is to advance research into new and innovative energy concepts and technologies whose feasibility is not yet sufficiently established to meet traditional research and development funding requirements.

The EISG program supports early phase development of promising new energy technology concepts. This category of projects is not covered by PIER general solicitations that focus primarily on development of established concepts. Qualifying EISG projects address one of the defined PIER research, development and demonstration areas. If the feasibility of an innovative energy concept is proven through the EISG project work, traditional research and development funding may become available to further develop the project.

Independent Assessment Reports are written at the completion of every EISG grant project. These reports outline the objectives of the project, discuss the successes and failures, and offer recommendations for potential future work. This report presents a collection of twenty-eight independent assessment reports for EISG grant projects awarded during 2008.

Keywords: Ratepayer, California Energy Commission, Energy Innovations Small Grant, EISG, Independent Assessment Report, IAR, Public Interest Energy Research, PIER RD&D, electricity, natural gas, transportation, research, energy technology concepts, project, market, outcomes, conclusions, benefits

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EXECUTIVE SUMMARY

The Energy Innovations Small Grant (EISG) program is a component of the Public Interest Energy Research (PIER) Program managed by the California Energy Commission. The PIER Program benefits California electric and gas ratepayers by funding energy research, development, and demonstration projects that are not adequately provided for by the competitive and regulated energy markets.

The Energy Commission recognizes the need for a program to support the early development of promising new energy technology concepts that are not mature enough to be covered by PIER general solicitations. The Energy Commission has established the EISG program to meet this need.

This report is a compilation of the Individual Assessment Reports for grant projects that were awarded in 2008 and that have not been previously published.

All data sources for tables and figures are from the author unless otherwise noted.

CHAPTER 1:
Introduction

Table 1: 2008 EISG Projects with IARs Included in this Section

Project	Researcher	EISG Funding
Flexible Zinc And Copper Oxide Based Solar Cells	Rutgers University	$ 95,000
Feasibility Study of a Novel Biochemical Platform for Ethanol Production	University of California	$ 95,000
Micro-Optic Slab Concentrators for Low Cost Solar Panels	University of California San Diego	$ 95,000
Biomimetic Antireflection Coatings for Highly Efficient Solar Cells	University of Florida	$ 95,000
Proportional Time Delay Relay for Air Conditioner Latent Capacity Recovery	Proctor Engineering Group, Ltd.	$91,470
Semiconductor Quantum Dot Based Heterostructures for High Efficiency Photovoltaics	University of California at San Diego	$95,000
Heat Activated Cooler With Two Stage, Multi-Fluid Ejector and Novel Mixing Chamber	ThermAvant Technologies, LLC	$92,630
Transient Operation and Control of Fuel Cell Temperature Variations	National Fuel Cell Research Ctr University of California, Irvine	$50,000
Nitric Oxide Reduction Using Oxy-Combustion in Stationary Power Engines	University of California at San Diego Center for Energy Research	$95,000
Nanowire Thermoelectrics for Industrial Waste Heat Recovery	Nanotron, Inc.	$95,000
Improving High Solids Biomass Conversion Efficiency Using Spray Dried Enzymes	University of California, Davis	$78,826
Developing Ultrahigh Efficiency	University of California, San	$,95000

Project	Researcher	EISG Funding
Thermal To Electric Energy Conversion Technique	Diego	
Innovative Biogas Hydrogen Sulfide Removal Technology	Iowa State University	$95,000
Printing Low Cost Solar Cells with Ultrasonic Ejection	Alion, Inc	$93,350
High Efficiency Nanowire LEDs for Solid State Lighting	UC San Diego	$94,998
Renewable Energy Through Purification of Low BTU Landfill Gas	Pacific Consolidated Industries LLC	$95,000
Undershot Impulse Jet Hydro-Turbine	K.R. Broome and Associates	$95,000
Fully Printed All Inorganic Nanoparticle-Based Solar Cells	University of California, Santa Cruz	$95,000
Closed Loop Tracking for Solar Thermal Heliostats	Mark Convery	$89,000
Osprey: Ultra Efficient Mass Microalgae Culturing and Harvesting Device	Green Reactions LLC	$95,000
Module Level Power Converters for Parallel Connected Photovoltaic Arrays	Missouri University of Science and Technology	$94,997.53
Low Cost Dye Sensitized Solar Cells	Torrey Hills Technologies LLC	$95,000
High Efficiency, Compact SiC-Based Solar Inverter	Aegis Technology Inc.	$95,000
Direct Solid Oxide Fuel Cells	University of California, San Diego (UCSD)	$95,000
Petcoke Fueled SOFC Power Generator for On-Site Application	Materials and Systems Research Inc	$94,930
Development of High Efficiency and Cost Effective Micro Wind Turbines	Iowa State University	$94,868

Project	Researcher	EISG Funding
Flywheel Hybrid with Switch Mode Continuously Variable Transmission	Worcester Polytechnic Institute	$87,027
Metallic Nanotubes as Low Cost and Durable Fuel Cell Catalysts	University of California Riverside	$95,000

CHAPTER 2:
2008 Independent Assessment Reports

The Energy Innovations Small Grant (EISG) program awards numerous grants for innovative energy research projects every year. Independent Assessment Reports (IARs) highlight the project outcomes for each of the EISG projects. This chapter includes the IARs from grant projects that were awarded in 2008 that have not previously been published.

2.1 Flexible Zinc And Copper Oxide Based Solar Cells

Awardee: Rutgers University

Principal Investigator: Aurelien Du Pasquier

Keywords: transparent conductor, PV, GZO, ZnO, Cu_2O, nanotips, polyimide, dye solar cells, MOCVD

2.1.1 Abstract

The goal of this project was to develop a new flexible conducting window material, Gallium-doped Ga doped transparent conducting Gallium doped Zinc Oxide, coupled with highly ordered zinc oxide nanotip arrays for solar cells. The window material would be a low cost alternative to the industry standard indium tin oxide (ITO). The nanotips are attractive because they combine a large surface area for efficient charge collection with a direct path for charge transfer to the external circuit. These structures have already been grown by metal oxide chemical vapor deposition (MOCVD) at Rutgers University using proprietary techniques. The GZO-ZnO nanotips (or GZO-ntZnO) were investigated here as building blocks for incorporation into one of two different solar cell designs. The first would produce a GZO-ntZnO based Titanium dioxide TiO_2 dye sensitized solar cell (DSSC) on a polyimide substrate. The second approach would employ GZO-ntZnO arrays on glass coupled with a copper oxide (Cu_2O) solid-state absorber to form a ZnO-Cu_2O heterojunction (interface between two layers of dissimilar crystalline semiconductors). The researchers investigated Cu_2O synthesis by several different techniques. For both solar cell design approaches the cost goal for a commercial device was < \$1/W_P.

Researchers in this project achieved successful deposition of GZO-ntZnO transparent windows and nanotip arrays by metal organic chemical vapor deposition (MOCVD). However, investigation into the use of GZO coated polyimide for making dye sensitized solar cells did not show any promise. Researchers demonstrated a new low temperature chemical growth method for Cu_2O by solution treatment of metallic copper. This technique seems promising for further investigation of Cu_2O heterojunctions. However cost analysis of the MOCVD window deposition approach revealed that, because of the high cost of the metallo-organic precursor chemicals, the technique was too costly by at least a factor of 30 to be practical in a commercial device. The researchers concluded it is necessary to identify less costly chemicals for MOCVD or to find a different synthesis technique for GZO-ntZnO transparent windows and nanotip arrays.

2.1.2 Introduction

California bill AB32 requires the State to reduce its greenhouse gas emissions (GHG) to 1990 levels by the year 2020, roughly a 25 percent reduction.[1] Solar photovoltaic (PV) systems can provide an important contribution to meeting this requirement. Worldwide, 59 percent of PV systems are tied to the grid.[2] The high cost of grid- tied PV systems has limited their ability to compete with low cost grid based electricity. For example, a residential PV system has cost $8000 to $12000 per kW_P (peak kW) installed, yielding electricity costs of about $0.30 per kWh in sunny locations. This can be compared to an electricity tariff (cost to the consumer) of about $0.10 per kWh.[2] Thus an installed residential system cost would have to drop to about $\$3/W_P$ to compete with grid electricity.[2] Depending on the nature of the application, the PV module represents 40—60 percent of the total installed cost of a PV system.[2,3] The current (September 2010) average retail price of a single PV module has dropped to about $\$4/W_P$. However the lowest retail price for a multi-crystalline silicon solar module is $1.99 per watt, and the lowest retail price for a mono-crystalline silicon module is $2.17 per watt.[3] The lowest thin film module retail price is $1.07 per watt.[3] Taking into account difference in quality, warranty, quantity, etc., the large difference between average retail price and lowest available retail price points to the existence of a supply issue for the lowest price modules. One of the most cost effective techniques for large-scale manufacturing is reel-to-reel (RTR) processing of thin film or tape articles. However RTR for PV requires that all components including transparent window, anode, cathode, absorber, and substrate be flexible to allow for bending on the reel. The dominant transparent conductor for PV cells, indium tin oxide (ITO), causes problems for RTR fabrication. It is costly, brittle, and carcinogenic in the workplace.[4,5] The issue of brittleness is a serious limitation since ITO cracks under bending. A new transparent conducting film technology that is compatible with high volume reel-to-reel manufacturing would bring large rewards by bringing down PV production costs.

Reductions in manufacturing costs would offer potential benefits to California ratepayers from increased solar penetration into the energy market place. These include lower greenhouse gas emissions, greater price stability in the future, and reduced necessity for new expensive central generating plants and long distance transmission line expansion. Highlighting these benefits, "The California Solar Energy Industries Association (CALSEIA) released a study on Feed in Tariff (FIT) pricing showing that the value of renewable generation is between 5 and 12 cents per kWh over the wholesale price of electricity from natural gas…"[6] This additional value was based on the environmental, transmission, and reliability values of adding renewable

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1 http://gov.ca.gov/index.php?/press-release/4111/

2 http://www.solarbuzz.com/StatsCosts.htm

3 http://www.solarbuzz.com/ModulePrices.htm

4 http://www.nanotopblog.com/index.cfm/2009/4/8/Transparent-Conductor-Markets-ITO-Remains-Dominant

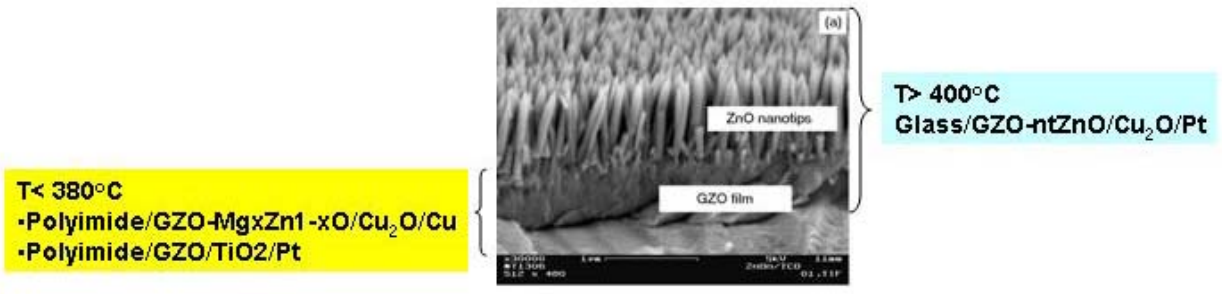
5 http://ntp.niehs.nih.gov/ntp/About_NTP/BSC/2009/July/Draft_ResConcept/ITO.pdf

6 http://calseia.org/?option=com_directory&page=viewListing&lid=324&Itemid=70

generation to California's electricity supply. What has limited the realization of these benefits until recently has been the low fraction of the energy market of solar derived electricity. Today, however, the US photovoltaics market is accelerating and grew by 36 percent in 2009.[7] In the United States, California now plays a lead role in the base load state market. California has accounted for 53 percent of United States PV on-grid installations and is expected to maintain its strong position in 2010. Overall the United States solar market, led by California, is forecast to grow tenfold by 2014. High demand for lower price PV systems will reward the development of a low cost, high volume, reel-to-reel technology.

The advancement of science or technology proposed in this project was the development of low cost solar cells based on a new flexible conducting window material, Ga doped transparent conducting ZnO (GZO), coupled with highly ordered zinc oxide nanotip arrays. The nanotips are attractive because they combine a large surface area for efficient charge collection with a direct path for charge transfer to the external circuit. These structures have been grown by metal oxide chemical vapor deposition (MOCVD) at Rutgers University using proprietary techniques and are shown in Figure 1. The GZO-ZnO nanotips (or GZO-ntZnO) are regarded in this project as building blocks for incorporation into one of two different solar cell design approaches. The first would produce a GZO-ntZnO based TiO_2 dye sensitized solar cell (DSSC) on a polyimide substrate. The power conversion efficiency goal of the DSSC approach is > 8 percent. The second approach would employ GZO-ntZnO arrays on glass coupled with a copper oxide (Cu_2O) absorber grown by several techniques. In this approach the power conversion efficiency goal is > 2 percent, an efficiency that has never been achieved with this otherwise promising material. For both approaches the cost goal is < $1/$W_P$.

Figure 1: Summary of Proposed Photovoltaic Devices



2.1.3 Objectives

The goal of this project was to determine the feasibility of integrating Ga-doped zinc oxide (GZO) transparent conducting windows and zinc oxide nanotip arrays in dye sensitized solar cells and in solid-state solar cells using Cu_2O light absorber. The efficiency objectives were 8 percent for the dye solar cell and 2 percent for the ZnO/Cu_2O solar cell. The researchers established the following project objectives:

7 http://www.electroiq.com/index/display/photovoltaics-article-display/0967278919/articles/Photovoltaics-World/industry-news/2010/july/us-solar_market led.html

1. Optimize MCOVD growth of GZO on polyimide substrates. Obtain sheet resistance < 20 ohm.sq^{-1}.

2. Optimize TiO_2 photoanodes on fluorine-doped tin oxide (FTO) substrates. Fabricate DSSC prototypes with mixtures of TiO_2 nanoparticles and nanocrystals that are annealed at 380^{o} C. Demonstrate solar conversion efficiency > 8 percent in 1 sun AM 1.5 conditions.

3. Demonstrate TiO_2 dye solar cells on polyimide prototypes with η > 8 percent and fabrication cost lower than \$1/W_P.

4. Test aging and efficiency with gel electrolyte. Demonstrate solar conversion efficiency > 5 percent in 1 sun AM 1.5 conditions. Demonstrate that the device can retain 80 percent of initial efficiency after 1000h.

5. Optimize MCOVD growth of GZO-$Mg_xZn_{1-x}O$ nanotips on glass. Characterize by scanning electron microscopy, x-ray diffraction, optical transmission, and photoluminescence.

6. Develop a growth method for Cu_2O. Confirm depositions of Cu_2O phase by x-ray diffraction. Verify correct morphology by field emission scanning electron microscopy.

7. Build GZO-ZnO/Cu_2O solar cells. Demonstrate solar conversion efficiency > 2 percent in 1 sun AM 1.5 conditions. Demonstrate fabrication cost is less than \$1/W_P.

2.1.4 Outcomes

1. The researchers successfully applied MCOVD to growth of GZO on polyimide substrates. The lowest sheet resistance measured was 58.4 ohm sq^{-1}.

2. The researchers fabricated TiO_2 photoanodes on FTO substrates. The highest solar conversion efficiency measured was 5.66 percent under AM 1.5 conditions.

3. The researchers attempted to fabricate TiO_2 dye solar cells on polyimide prototypes. The test cells on polyimide displayed no observable photo response. The researchers observed poor adhesion of the TiO_2 to the GZO/polyimide film.

4. Since the TiO_2 dye solar cells could not be fabricated in Objective 3, testing with a gel electrolyte was not possible. The researchers replaced the photoactive medium with Cu_2O semiconductor and gel electrolyte. However, water in the aqueous electrolyte dissolved the CuO_2.

5. The researchers successfully applied MCOVD to grow GZO-$Mg_xZn_{1-x}O$ nanotips on glass. The samples were characterized by field emission scanning electron microscopy and optical transmission.

6. The researchers developed a new low temperature (90^{0} C) chemical growth method for photovoltaic grade Cu_2O. The researchers did not report morphology results by field emission scanning electron microscopy.

7. The researchers fabricated GZO-ZnO/Cu_2O solar cells. The best cells demonstrated diode rectification and a low degree of photo response. The researchers did not report

solar conversion efficiency. They analyzed fabrication costs from the cost of the various metallo-organic precursors for MOCVD. Assuming a device with 10 percent solar conversion efficiency could eventually be built, the solar cell would cost \$27.19/W_p for the GZO-ZnO layer only.

2.1.5 Conclusions

1. The researchers did not meet this goal. The sheet resistance of MCOVD grown GZO on polyimide substrates did not meet the goal of sheet resistance < 20 ohm.sq^{-1}.

2. The researches partially met this goal. They successfully fabricated TiO_2 photoanodes on FTO substrates. The highest measured solar conversion efficiency was 5.66 percent under AM 1.5 conditions. This did not meet the goal of 8 percent.

3. The researchers did not meet this goal. They stated that the transmission spectrum of the GZO/polyimide films had a poor overlap with absorption spectrum of the N179 dye used in the cells, allowing only photons beyond 600 nm into the dye to generate photocurrent. This explanation seems unlikely since Figure 1 of the proposal shows that GZO has excellent transmissivity from 400 nm to at least 800 nm and polyimide is widely used successfully in other solar cell applications. It would appear that the real problem was not identified. Secondly, there were unsolved problems with adhesion of the TiO_2 to the GZO/polyimide film.

4. The researchers did not meet this goal. Since the TiO_2 dye solar cells could not be fabricated, it was not possible to test with a gel electrolyte. Therefore the researchers replaced the photoactive medium with Cu_2O semiconductor and gel electrolyte. The Cu_2O displayed some photo response indicating some degree of photovoltaic quality. However water in the aqueous electrolyte dissolved the CuO_2.

5. The researchers partially met this goal. They successfully applied MCOVD to grow GZO-$Mg_xZn_{1-x}O$ nanotips on glass. The samples were characterized by field emission scanning electron microscopy and optical transmission. However the researchers did not report x-ray diffraction and photoluminescence characterization data.

6. The researchers partially met this goal. They developed a new low temperature (90^0 C) chemical growth method for Cu_2O and high temperature oxidation (~800^0 C). X-ray diffraction revealed depositions of Cu_2O phase. The researchers did not report morphology results by field emission scanning electron microscopy, however.

7. The researchers did not meet this goal. The best GZO-ZnO/Cu_2O cells fabricated demonstrated only diode rectification and a low degree of photo response. The researchers did not report solar conversion efficiency. They analyzed solar cell fabrication costs assuming a future 10 percent efficiency. Due to the high cost of the various metallo-organic precursors for MOCVD, the solar cell cost \$27.19/W_p for the GZO-ZnO layer alone. Thus the goal of fabrication cost less than \$1/W_p was not met.

While the researchers made some progress, they did not achieve the main goal of this project to determine the feasibility of integrating Ga-doped zinc oxide (GZO) transparent conducting windows and zinc oxide nanotip arrays in dye sensitized solar cells and in solid-state solar cells using Cu_2O light absorber.

2.1.6 Recommendations

There were three main components to this research program:

1. The deposition by MOCVD of GZO transparent windows and ZnO nanotip arrays (GZO-ntZnO) as building blocks for solar cells.
2. The incorporation of the GZO-ntZnO developed into a TiO_2 dye sensitized solar cell (DSSC) on a polyimide substrate.
3. The deposition of the GZO-ntZnO developed on glass and incorporated into a solar cell

The researchers achieved successful MOCVD deposition of GZO-ntZnO transparent windows and nanotip arrays by MOCVD. However the researchers' cost analysis revealed that because of the high cost of the metallo-organic precursor chemicals, the technique was too costly by at least a factor of 30 for commercial applications, calling into question the approach. Therefore it is necessary to identify less costly chemicals for MOCVD or to find an entirely new synthesis technique for GZO-ntZnO.

The researchers reported that the use of GZO coated polyimide for making dye sensitized solar cells did not show any promise. They therefore recommended not pursuing this area of research. This conclusion seems to be correct given the evidence on hand.

The researchers developed a new low temperature chemical growth method for Cu_2O by solution treatment of metallic copper. This technique seems promising for further investigation. With the cost issue in mind, it seems useful to consider this absorber material in solar cells with other types of contacts. Before spending too much effort on development of Cu_2O based heterojunction solar cells, it would be useful to estimate their maximum efficiency based on the known properties of Cu_2O.

2.1.7 Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the ratepayer from this research is reduced environmental impacts of the California electricity supply or transmission or distribution system. The potential benefits to California from increased solar penetration into the energy market place are several, including lower greenhouse gas emissions, greater price stability in the future, and reduced need for central generating plant and for long distance transmission line expansion. Highlighting these benefits, the California Solar Energy Industries Association (CALSEIA) released a study on Feed in Tariff (FIT) pricing showing that the value of renewable generation is between 5 and 12 cents per kWh over the wholesale price of electricity from natural gas, a fossil fuel. This

additional value is based on the environmental, transmission, and reliability values of adding renewable generation to California's electricity supply. What has limited the realization of these benefits until recently has been the low fraction of the energy market of solar derived electricity. However the United States photovoltaics market is accelerating and grew by 36 percent in 2009. California now plays a lead role in the base load state market for the United States. The State has accounted for 53 percent of US PV on-grid installations and is expected to maintain its strong position in 2010. The United States solar market, led by California, is forecast to grow tenfold by 2014. Higher demand for lower priced PV systems could reward the successful development of a low cost, high volume, reel-to-reel technology.

2.1.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

The researchers had not performed a market analysis by the end of this project. They were preparing technical papers for publication.

Engineering/Technical

The researchers planned to continue the work started in this project. They estimated two additional years to complete product development and demonstration.

Legal/Contractual

The researchers submitted two patent applications that grew out of this work. They received a $42,000 subcontract from a local business working under a DOE STTR grant for related research.

Environmental, Safety, Risk Assessments/ Quality Plans

It is premature at this point to address environmental, safety, and risk assessments/quality plans.

Production Readiness/Commercialization

Commercialization processes are premature until basic feasibility questions are answered.

2.2 Feasibility Study of a Novel Biochemical Platform for Ethanol Production

Awardee: University of California

Principal Investigator: Zhiliang Fan

2.2.1 Abstract

The goal of this project was to prove the feasibility of a new method of producing ethanol from cellulosic biomass. The researchers postulated that cellulose can be directed to cellobionic acid production by reducing β-glucosidase (bgl) production and by enhancing cellobiose dehydrogenase (CDH) production and that cellobionic acid can be utilized as carbon source for

ethanol production. The researchers created a mutant Neurospora crassa strain with six of the seven bgl genes knocked down to enhance cellobionate production. Addition of CDH further enhanced production. They then used cellobionate in the production of ethanol. The researchers were able to produce approximately 90 percent of the theoretical yield of ethanol and acetic acid using the proposed biochemical process.

Keywords: Cellobionate, new platform, ethanol, acetic acid

2.2.2 Introduction

Political turmoil, increasing costs of foreign oil, and a relatively recent focus on environmental awareness necessitate a search for sustainable, environmentally friendly, and cost effective fuel alternatives both locally and nationally. Ethanol is a renewable, clean, high performance fuel or fuel additive that is readily usable by most cars in the United States. Bio ethanol has historically been produced from feedstocks such as sugar cane, corn, and potato. However this production leads to concerns regarding increased food prices and shortages. Recent developments have focused on cellulosic ethanol production, which uses cellulose fibers from forestry residues, municipal solid waste, or industrial waste streams that do not impact food supplies.

The researchers proposed to significantly reduce the cost of producing ethanol by combining the three most expensive steps into a single biological step. Pretreatment, cellulose production, and enzymatic hydrolysis constitute the bulk of the production expense in the conventional process (Figure 2). The proposed technology (Figure 3) used an aerobic treatment process. In this process microorganisms secrete enzymes needed to hydrolyze cellulose and hemicellulose to the resulting sugars, which are then oxidized to sugar aldonates. The sugar aldonates serve as the reactive intermediates to produce ethanol. Microorganism selection and mutation to knock down copies of β-glucosidase (bgl) was required to increase cellobionate production.

The researchers anticipated two copies of the bgl gene at the proposal phase of the project when the genome sequence of Trichoderma reesei was unknown. However, the discovery of seven copies of the bgl gene through a subsequently published genome sequence led the researchers to select an alternate microorganism, Neurospora crassa. They selected Neurpsppra crassa due to its similarity to the originally proposed microorganism and the availability of single bgl knockouts from the Fungal Genetic Stock Center. They created multiple knockout strains using this stock, including one strain with six of the seven bgl genes knocked down. The researchers were unable to knock down all seven bgl genes. However the addition of exogenous cellobiose dehydrogenase (CDH) was successful in enhancing cellobionate production, which can be used as the carbon source in ethanol production. The researchers found that the yield of cellobionate from cellulose was about 5 percent, and the yield of ethanol and acetic acid from gluconate was about 90 percent of the theoretical yield.

In 2007 the California Biomass Collaborative estimated that the State of California produced 22.6 million dry tons of cellulosic materials which could be used in the production of ethanol. This material could provide an annual production of about 2.9 billion gallons of ethanol.

Figure 2: Conventional Biochemical Platform for Bio Fuels Production

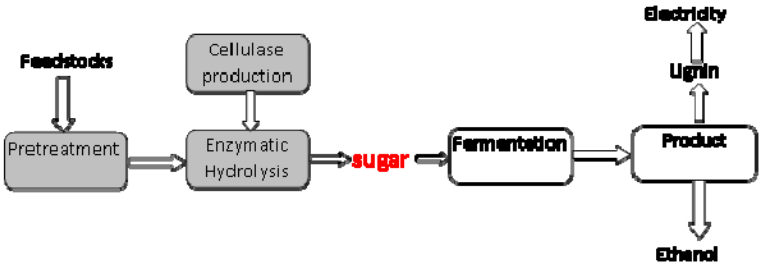
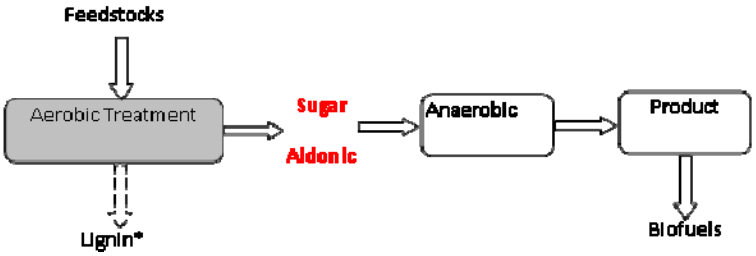


Figure 3: Proposed Biochemical Platform for Bio Fuels Production



The proposed technology is too new to precisely quantify the benefits to California. However, the researchers estimated that the technology could reduce the cost of producing ethanol by approximately $0.02 per gallon. This results in a potential savings of $58 billion per year over current production costs.

2.2.3 Objectives

The goal of this project was to prove the feasibility of a new method of producing ethanol from cellulosic biomass. The researchers postulated that cellulose can be directed to cellobionic acid production by reducing β-glucosidase (bgl) production and by enhancing cellobiose dehydrogenase (CDH) production and that cellobionic acid can be utilized as carbon source for ethanol production. The researchers established the following project objectives:

1. Construct mutant of cellulolytic fungus Trichoderma reesei that is deficient in bgl1 and bgl2 gene products. Verify that no intracellular and extracellular β-glucosidase activities can be detected.
2. Demonstrate that cellobionate can be produced from lignocellulosic materials. Show that conversion of cellulose to cellobionate and cellooligosaccharide aldonate is more than 50 percent.
3. Confirm that ethanol will be the major fermentation product using gluconate as the carbon source. Demonstrate that the yield of ethanol from gluconate is more than 80 percent of the theoretical yield.

2.2.4 Outcomes

1. At the proposal stage of this project the genome sequence of Trichoderma reesei was unknown, but the literature suggested that two bgl gene copies existed. Subsequently the genome sequence was published, revealing seven copies of the bgl gene. The

researchers selected an alternate microorganism, Neurospora crassa, due to the availability of single bgl knockout strains available at the Fungal Genetic Stock Center. Researchers used genetic crossing methods to construct strains with up to six copies of bgl knocked out.

2. The researchers measured cellobionate concentration in the fermentation broth of the six bgl knockout strain at approximately 0.2 g/L prior to addition of exogenous CDH and just over 1.0 g/L after the addition. Researchers detected no cellobionate in the wild type strain with zero bgl knockouts. They measured the yield of cellobionate from cellulose at about 5 percent.

The researchers fermented gluconate to yield approximately 90 percent of the theoretical yield of acetic acid and ethanol and trace amounts of lactic acid. More than 40 g/L of ethanol could be produced from a glucose and gluconate mixture in five days without pH control.

2.2.5 Conclusions

1. Although the researchers were successful in knocking out bg l1 and bg l2, the original objective was to remove all copies of bgl. They were unable to knock down all copies of the bgl gene and therefore did not satisfy the objective. Strain F123467 had one remaining bgl copy detectable.

2. The researchers were successful in demonstrating that cellobionate can be produced from lignocellulosic materials. However the yield of cellobionate at 5 percent was less than the target yield of 50 percent.

3. The researchers were successful in meeting the objective to produce ethanol at more than 80 percent of the theoretical yield. They did not provide sufficient detail relating to the experimental procedure to comment on the efficacy or expeditiousness of the process. While the researchers did suggest that the processing time for fermentation was lengthy, it is not clear whether this would be detrimental to the viability of the proposed technology.

2.2.6 Recommendations

The researchers were unable to meet enough of the project objectives to prove feasibility of the proposed technology. The final report provided a good preliminary foundation for the development of the technology. This technology will require significant effort and further experimentation to improve ethanol yield, address concerns relating to the time rate of production, and prove that the technology is a viable alternative to conventional ethanol production. The researchers plan to continue development of the proposed technology by further mutating N. crassa to increase the cellobionate concentration. As part of continued development of this technology, the Program Administrator recommends that the following tasks be completed:

1. Provide more detailed and quantified results of past and future experimentation.

2. Provide calculations on the kinetics of the reactions involved.

3. Analyze the fermentation reactions for all possible fermentation end products and conduct carbon balance and electron balance analyses.

4. Provide detailed information regarding production rate.
5. Compare unit costs of production between conventional and proposed methods.

After taking into consideration (a) research findings in the grant project, (b) overall development status, and (c) relevance of the technology to California and the PIER program, the Program Administrator has determined that the proposed technology should be considered for subsequent funding within the PIER program.

Receiving subsequent funding ultimately depends upon (a) availability of funds, (b) submission of a proposal in response to an invitation or solicitation, and (c) successful evaluation of the proposal.

2.2.7 Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the public from this research is increased affordability of fuel in California. Because the technology is in the early stage of development, the researchers were unable to quantify precisely the potential savings to the State of California. The California Biomass Collaborative estimated that California produces approximately 22.6 million dry tons of cellulosic materials annually, which could be used in the production of ethanol. This would provide for an annual production of about 2.9 billion gallons of ethanol. The researchers estimated that the technology could save approximately $0.02 per gallon in the production of ethanol. This would result in potential savings of $58 billion per year over current production costs.

2.2.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

The researchers have not yet performed a market analysis. This technology could serve the bio fuels industry.

Engineering/Technical

The key technical challenge is to produce oligosaccharide aldonic acids at a high concentration. Further research will require three to five years and approximately $2 million to complete development.

Legal/Contractual

The researchers have filed for a provisional patent, which was converted to a PCT on April 30, 2010.

Environmental, Safety, Risk Assessments/ Quality Plans

Environmental, Safety, Risk Assessments, and Quality Plans have not yet been developed. The researchers do not anticipate negative effects with regard to public safety or the environment.

Production Readiness/Commercialization

The researchers have not developed a commercialization plan and will require support to pursue commercialization.

2.3 Micro-Optic Slab Concentrators for Low Cost Solar Panels

Awardee: University of California San Diego

Principal Investigator: Joseph Ford

2.3.1 Abstract

Concentrator photovoltaic (CPV) systems promise higher efficiency and lower cost electricity than fixed photovoltaic (PV) panels. The potential benefits will occur when large areas of PV cells are replaced by lower cost concentrator hardware which couples the same amount of sunlight into very small but highly efficient multiple junction PV cells. A tradeoff for this higher efficiency is that CPV requires a mechanical tracking system. This project was an investigation of a new planar non-imaging solar concentrator that used micro-optic lenslets and a glass waveguide to trap sunlight and guide it to small high efficiency PV cells. The planar geometry allowed use of self-alignment and roll processing of microlenses onto window glass substrates. This combination offered potential cost reduction over current systems. The physical geometry allowed less costly tracking mechanics because of the thin nature and light weight of the concentrators. The researchers used optical modeling to study the concentrator design. They also conducted an experimental demonstration and characterization of the concentrator structure.

Optical models of an optimized system design predicted greater than 80 percent optical efficiency with 300X concentrations. The researchers used off-the-shelf molded acrylic lenslets and BK7 glass plates for the experimental demonstration. A key result was the demonstration of self-aligned fabrication of micro-facets under each lenslet. In a bench top experiment this hardware showed concentration of 37X with 52 percent optical efficiency. To demonstrate feasibility of electrical power generation, the concentrator was integrated with a commercial multi-junction PV cell. The commercial cell used had about 40 percent conversion efficiency at 500 suns and about 35 percent efficiency at 40X. The demonstration was successful. Finally, the researchers prepared a preliminary cost analysis comparing the new tracking planar micro-optic system to a conventional Fresnel lens array system. In this analysis the new system produced an estimated overall cost savings of just over 20 percent for the optics and mechanics when compared with the Fresnel based system.

Keywords: Concentrator technology, PV concentrator, solar concentrator, solar electricity, mirror facets

2.3.2 Introduction

The primary goal of this research was to lower the overall cost of PV solar to electric energy conversion for the California ratepayer. The performance of the industry dominant single junction cell architecture is limited by the junction band gap energy. A single band gap cannot match the entire solar spectrum. At present, research on single junction silicon based cells has advanced to 24.7 percent efficiency under standard global AM1.5 spectrum.[8] Further improvements will be difficult. Series connected monolithic multi-junction cells composed of thin layers of stacked junctions with the higher band gap junction on the top facing the sun circumvent the problem of matching one band gap to the solar spectrum. The top junction efficiently absorbs the higher energy part of the solar spectrum, allowing the low energy photons to pass through to a lower band gap junction that efficiently absorbs them. This multi-junction approach has produced higher efficiency of 32 percent under AM1.5 spectrum. Multi-junction cells coupled with solar concentrators have even higher efficiencies of up to 43.5 percent.[9,10] The series of expensive steps in fabricating the junctions makes them prohibitively expensive for most terrestrial applications. However, when a small high efficiency multi-junction PV cell is combined with a low cost solar concentrator, the capital cost and the cost per unit electrical output can be reduced drastically.

If a low cost concentrator based system could be developed, the potential payoff would be very large. The technical solar potential for PV in California exceeds 17 million MW of capacity.[11] Realizing even a small fraction of this potential would bring great benefits to California ratepayers. These include lower GHG emissions, greater future price stability, and reduced need for new expensive central generating plants. California Solar Energy Industries Association (CALSEIA) has released a study on Feed in Tariff (FIT) pricing showing that the increased value of renewable generation is between 5 and 12 cents per kWh over the wholesale price of electricity from natural gas.[12] This additional value is based on the environmental, transmission, and reliability values of adding renewable generation to California's electricity supply.

The advancement of science proposed in this project was a novel type of non-imaging solar concentrator coupled to a commercial high efficiency triple junction PV cell to lower the cost of PV modules. The commercial triple junction cell had an efficiency of 37 percent at 500X concentration, two to three times that of commercial silicon PV cells. Although the cell was expensive, the combination of 500X concentration ratios and three times greater efficiency reduced the cost per electrical output significantly. To realize overall lower system cost, the concentrator itself must be inexpensive. Here the researchers proposed an entirely new class of

8 http://www3.interscience.wiley.com/cgi-bin/fulltext/114281801/PDFSTART

9 http://en.wikipedia.org/wiki/File:PVeff(rev110408U).jpg

10 http://en.wikipedia.org/wiki/Solar_cell_efficiency

11 http://www.energy.ca.gov/2005publications/CEC-500-2005-072/CEC-500-2005-072-D.PDF

12 http://calseia.org/?option=com_directory&page=viewListing&lid=324&Itemid=70

concentrator, shown schematically in Figures 4 and 5. The approach used molded micro-lenses, Figure 4, and self-aligned reflecting facets at the focus of each lens, Figure 5, to inject light into a multimode waveguide that guided the light to thin PV cells at the edges of the thin slab. Using slab waveguides to guide solar power to PV cells is not new, but this new approach used transparent low index materials coating the wave guide to guide the light by total internal reflection. The tiny mirror facets at the focus of each micro-lens injected the light into the slab while maintaining 80 percent overall transmission efficiency to the PV edge cell. This approach is compatible with inexpensive roll processing of plastic materials mounted on a piece of inexpensive float glass. Photolithographic processing can be used to form injection features self-aligned with the lenslets. This research was to be the first experimental demonstration and proof of principle of micro-optic slab concentrators.

Figure 4: Drawing of Device Showing an Array of Lenslets on a Slab Waveguide

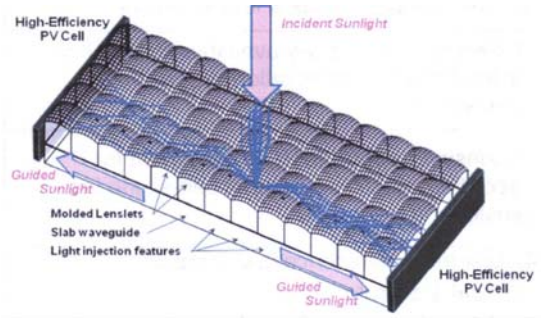
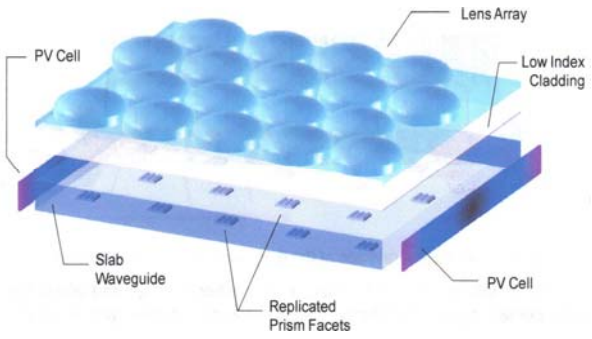


Figure 5: Schematic of Device Showing Tiny Mirror Facets at the Focus of Each Microlens



The prism facets with 120^0 apex angle deflect the light down the slab where it is guided by total internal refection to the PV cells. The total area of the facets is approximately 0.01percent of the overall slab area.

2.3.3 Objectives

The goal of this project was to determine the feasibility of a new class of solar concentrators, a micro-optic patterned slab, which could become the first inexpensive mass producible 500X

concentrator needed for highly efficient multi-junction photovoltaic cells. The researchers established the following project objectives:

1. Design a prototype optical system. Confirm design efficiency exceeding 90 percent trapping of sunlight for oriented panel with at least 80 percent efficient guiding of trapped light into edge facets for 75 percent overall efficiency.
2. Identify commercially available photovoltaic cells for testing integration with slab concentrator. Focus on available triple junction high efficiency PV technology.
3. Construct an optical table arrangement for recording injection apertures self-aligned to lenslet array. Demonstrate uniform exposure within +/- 10 percent over full 15x15 cm aperture.
4. Assemble slab concentrator panels: coat substrate, attach lenslets to float glass substrate, expose and develop injection apertures, and attach reflective injection surface. Fabricate at least one panel with surface area at least 15 x15 cm for efficiency and alignment tolerance testing.
5. Characterize concentrator optics. Measure efficiency vs. wavelength. Determine alignment tolerances. Demonstrate at least 50 percent actual surface to edge coupling efficiency. Match measured loss mechanisms to optical design. Revise design to reflect prototype.
6. Characterize photovoltaic performance by attaching PV cell to concentrator and characterize using Newport solar test source. Demonstrate efficient (> 95 percent) coupling of guided light into commercial photovoltaic cell. Characterize total power efficiency of concentrated vs. direct insolation.
7. Perform manufacturing cost analysis: analyze tolerance/cost tradeoff and identify volume suppliers of materials. Demonstrate overall cost/kW of concentrator combined with high efficiency PV cell of less than $1/W.

2.3.4 Outcomes

1. The researchers designed a prototype optical system. The design yielded an 81.9 percent overall efficiency at 300X geometrical concentration. The researchers' design calculations incorporating a secondary concentrator showed the potential of 91percent overall efficiency.
2. The researchers found that the concentrator system was compatible with commercially available triple junction PV devices. They obtained commercial samples from Boeing/Spectrolab and Cyrium.
3. The researchers constructed an ultraviolet exposure system using a modified arc lamp and custom optics and used it to fabricate two generations of concentrator prototypes. They found that the efficiency of the first 5 x 7.5 cm prototype was lower than modeled, so they spent their efforts to revise prototype optics for higher efficiency instead of scaling the area of the first prototype to 15 x 15 cm as was proposed.

4. They fabricated prototype slab concentrator panels from commercially available lenslet arrays and 75 mm x 50 mm x 1 mm thick glass microscope slides. They developed self-aligned fabrication procedures using the lens focus to permanently form the coupler region on the back surface of the slab waveguide.

5. The researchers assembled a custom solar simulator by adding custom optics to control the divergence of an arc lamp system and measured an overall optical efficiency of 52 percent of the second concentrator prototype.

6. The researchers integrated the solar concentrator with a commercial Cyrium triple junction PV cell and measured full coupling of the concentrated light into the PV device, achieving the specified optical electric conversion efficiency for that concentration. They demonstrated compatibility of the micro-optic concentrator with commercial high efficiency PV cells.

7. The researchers conducted a preliminary manufacturing cost analysis that indicated the baseline micro-optic solar concentrator would provide a 20 percent reduction of the cost for optics and tracking as compared to existing conventional Fresnel lens array concentrators. They estimated the manufacturing cost for the micro-optic concentrator system would be $1.06/W.

2.3.5 Conclusions

1. The researchers met this objective. They established design efficiency of 81.7 percent, exceeding the 75 percent overall efficiency goal.

2. The researchers identified commercially available triple junction high efficiency photovoltaic cells for testing integration.

3. The researchers constructed an optical table arrangement that recorded injection apertures self-aligned to lenslet array. However they found that the efficiency of the first 5 x 7.5 cm prototype was lower than modeled, so they spent their efforts to revise prototype optics for higher efficiency instead of scaling the area of the first prototype to 15 x15 cm. Thus they met this objective only in part.

4. The researchers fabricated smaller slab concentrator panels than stated in the objective.

5. The researchers measured an optical efficiency of 52 percent for the second concentrator prototype, exceeding the design goal of 50 percent. The lens array and waveguide exhibited almost no spectral variation. They met this objective.

6. The researchers established efficient coupling of wave guided light into a commercial photovoltaic cell.

7. The researchers estimated manufacturing cost for the micro-optic concentrator system would be $1.06/W, almost meeting the target of $1/W.

The program largely demonstrated this approach to solar concentrators. In addition, the researchers suggested new methods for secondary concentration that could provide concentrators with higher efficiency and potentially lower overall cost than the baseline micro-optic concentrator.

2.3.6 Recommendations

The Program Administrator recommends that the researchers investigate fixed, non-tracking performance more explicitly, at least from a system trade basis. Since the concentrator is non-imaging, it should function better with off-axis illumination than imaging concentrators, as implied by the researchers. In addition, increasing the area of the reflectors under the lenslets slightly and perhaps altering their shape may provide better off-axis performance albeit at the expense of increased scattering and loss of total internal reflection. The optimum tradeoff could be identified with a systematic trade study. At this point it seems that the prototype slab was much thinner than the PV cell's width. This raises the question of whether the researchers would be able to find a commercial cell that is a good fit to a final slab design at reasonable cost.

2.3.7 Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the ratepayer from this research is reduced environmental impacts of the California electricity supply or transmission or distribution system. If a low cost concentrator system with high efficiency output could be developed, the potential payoff could be very large. The technical solar potential for PV in California exceeds 17 million MW of capacity.[13] Realizing even a small fraction of this potential would bring great benefits to Californian ratepayers. These include lower GHG emissions, greater future price stability, and reduced need for new expensive central generating plants. California Solar Energy Industries Association (CALSEIA) has released a study on Feed in Tariff (FIT) pricing showing that the increased value of renewable generation is between 5 and 12 cents per kWh over the wholesale price of electricity from natural gas.[14] This additional value is based on the environmental, transmission, and reliability values of adding renewable generation to California's electricity supply. A secondary benefit of a low cost concentrator system could ultimately be increased affordability of electricity in California.

2.3.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

13 http://www.energy.ca.gov/2005publications/CEC-500-2005-072/CEC-500-2005-072-D.PDF

14 http://calseia.org/?option=com_directory&page=viewListing&lid=324&Itemid=70

Marketing/Connection to the Market

The researchers published two papers on their work in conference proceedings and have another journal article in preparation. The researchers conducted preliminary market analysis.

Engineering/Technical

The researchers plan to continue development to achieve higher (80 to 90 percent) efficiency. They also plan to work with a commercialization partner to develop a product that is easy to manufacture. The researchers received an additional $75,000 grant from the National Science Foundation to investigate reactive solar concentrators.

Legal/Contractual

The University of California has filed a patent application. Two companies have negotiated licenses for related intellectual property. They plan to commercialize the technology.

Environmental, Safety, Risk Assessments/ Quality Plans

A commercialization partner will have to address these issues.

Production Readiness/Commercialization

The researchers are making good academic progress that is relevant to commercialization. Production readiness is unlikely to proceed until a commercialization partner is on the team.

2.4 Biomimetic Anti-Reflective Coatings for Highly Efficient Solar Cells

Awardee: University of Florida

Principal Investigator: Peng Jiang

2.4.1 Abstract

The photovoltaic (PV) solar cell market is currently dominated by crystalline silicon, although other PV materials are rapidly coming on line. All these cell materials require an anti-reflective coating (ARC) to reduce the reflection losses at the front surface. Due to the high refractive index of silicon, more than 30 percent of incident light is reflected and is not absorbed, which proportionally reduces its conversion efficiency. The problem of front surface reflectivity is also an issue with the glass or polymer cover plates that protect the cells. Existing ARCs, however, exhibit high manufacturing costs and less than ideal broadband performance over the solar spectrum.

This project aimed to develop an inexpensive yet scalable templating nanomanufacturing technology that enables the large-scale production of broadband ARCs for high efficiency solar cells. The approach taken was inspired by low reflectivity surfaces found in nature such as the corneas of nocturnal moths. The researchers developed broadband moth eye sub-wavelength structured surface relief ARCs on silicon and on glass to suppress the reflectance from solar cells. The research team demonstrated silicon moth eye ARCs with less than 1.0 percent reflection, which represented more than 97 percent suppression of reflection from flat silicon wafers on single crystalline including (100) and (111) and multi-crystalline wafers. Typical moth eye ARCs on transparent glass substrates exhibited less than 0.5 percent optical reflection,

which represented more than 90 percent suppression of reflection from a flat glass substrate. The researchers achieved improved power conversion efficiency on a low efficiency (9.5 percent) single crystal silicon solar cell with integrated moth eye ARCs over a silicon control cell. The technique has not yet been demonstrated on a high efficiency silicon solar cell.

Keywords: Photovoltaic, anti-reflective coating, biomimetic, self assembly

2.4.2 Introduction

Direct photovoltaic (PV) conversion of sunlight to electricity is a very attractive low pollution, renewable energy source. However its widespread application has been slowed by low conversion efficiency and high cost. For this reason there is great interest in technology that increases PV efficiency without significant increase in cost. One feature that limits a PV cell's efficiency is its loss of ability to absorb sunlight due to the reflection of light at its front surface prior to absorption. Light reflection occurs because of the sharp discontinuity in the index of refraction from air outside the cell to the index of refraction in the cell material. The index in air is very close to that of vacuum, namely one, while in the important case of crystalline silicon, for example, the refractive index is variable but is about 3.4 in the visible spectrum.[15] Untreated, this discontinuity in index from 1 to 3.4 results in a reflection of about 35 percent and thus a proportional efficiency loss. All PV materials suffer from front surface reflectivity. Light passing through glass cover plate also undergoes a reflection loss of about 8 percent. To minimize these reflection losses, practical cells have an anti-reflective coating (ARC) applied to them with intermediate index value. With proper choice of coating index and thickness, it is possible to reduce the reflection loss to zero, but only for light of one wavelength. As the light wavelength deviates from the ideal design value, its effectiveness diminishes. Typically the ideal wavelength chosen is in the middle of the solar spectrum. It is possible to extend the low reflective properties to a broader band of wavelengths using multiple layers of coatings. However, these coatings are produced by expensive high vacuum, high temperature processes that make this method more costly. If a low cost broadband method of reducing front surface reflection were available, there would be a large payoff in cell efficiency and thus reduced cost per watt output.

Reduction in cell cost would offer potential benefits to Californian ratepayers from increased solar penetration into the energy marketplace. These benefits include lower GHG emissions, greater price stability in the future, and reduced need for new expensive central generating plants and long distance transmission line expansion. Highlighting these benefits, "The California Solar Energy Industries Association (CALSEIA) released a study on Feed in Tariff (FIT) pricing showing that the value of renewable generation is between 5 and 12 cents per kWh *over* the wholesale price of electricity from natural gas, a fossil fuel."[16] This additional value is based on the environmental, transmission, and reliability values of adding renewable generation to California's electricity supply. It has been noted that the less solar power costs the more favorably it compares to conventional power and the more attractive it becomes to both utilities and energy users. Utility-scale solar power can now be delivered in California at prices well below $100/MWh ($0.10/kWh), less than most other peak generators, even those running

15 http://www.pveducation.org/pvcdrom/appendicies/optical-properties-of-silicon

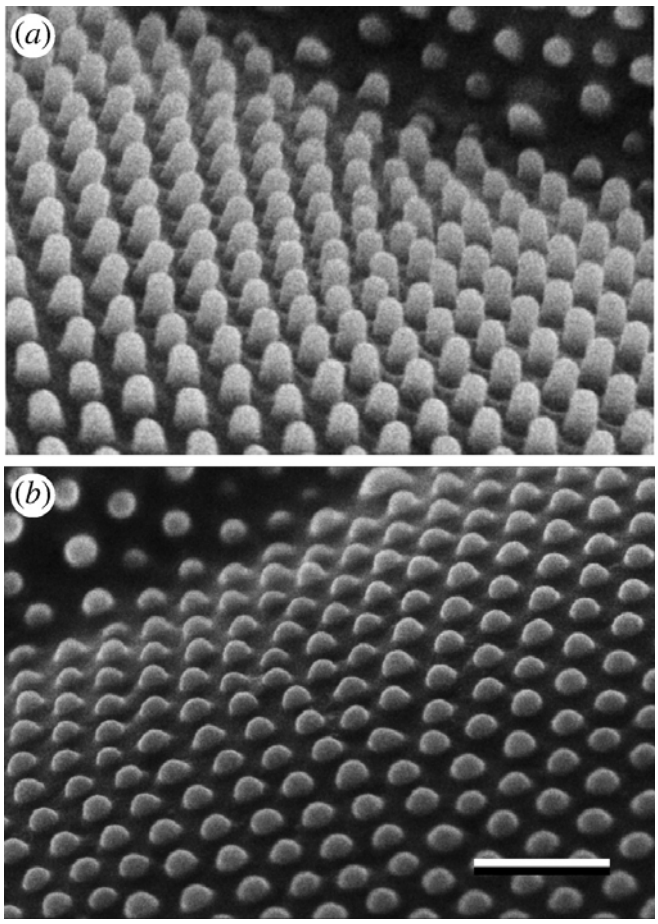
16 http://calseia.org/feed-in-tariff-for-california/

on low cost natural gas.[17] What has limited realization of these benefits until recently has been the small fraction of the energy market of solar derived electricity. Any new developments that reduce cell cost per unit output will speed the installation new PV capacity and thus permit the California ratepayer to obtain these benefits.

The advancement of science or technology proposed here to achieve a broadband anti-reflective surface is a "biomimetic" approach taken from nature. This is inspired by the natural grainy microstructures on the corneas of some nocturnal insects (e.g., moths), as shown in Figure 6 below. The outer surface of the corneal lenses consists of an array of conical nipples, typically of sub-300 nm height and spacing. As the period of the nipple array is small compared to the wavelength of visible light, the optical properties of such a surface is governed by effective medium theory and a graded transition of refractive index is thus established. This leads to minimized reflection over a broad range of wavelengths and angles of incidence for the moth. Guided by this, the researchers proposed to develop a nanofabrication technology applicable to single crystal silicon based solar cells and to their glass protective cover plates. For silicon, a spin-coated mono-layer of colloidal crystals would be used as an etching mask during a

17 http://en.wikipedia.org/wiki/Photovoltaics

Figure 6: Corneal Nipple Arrays in the Nymphalid Polygonia-C-Aureum (a) and the Lycaenid-Pseudozizeeria Maha (b), Showing Differences in Nipple Height and Shape



Source: Proceedings of The Royal Society B Biological Sciences.

22 March 2006 vol. 273 no.1587, pp.666-667

chlorine-reactive ion etching (RIE) process. This would produce an array of sub-wavelength silicon pillars directly on the substrate. The pillar array would provide a graded index of refraction similar to the moth eye and would give excellent broadband anti-reflective performance. The ARC for the glass cover plate would use the dry etched silicon pillar arrays with high aspect ratio as templates to cast polymer masters and then replicate the patterns onto glass substrates. Both transparent polymer (non-fluorinated and fluorinated) and glass the ARC would be replicated by photo polymerization of monomers and sol-gel reaction using commercial spin-on glass precursors. Both the silicon and glass surfaces with ARC would then be characterized by reflectivity measurements. Finally, an efficiency of higher than 20 percent for both multi crystalline and single crystal silicon solar cells with templated moth eye ARC would be demonstrated.

2.4.3 Objectives

The goal of this project was to determine the feasibility of using bio-inspired, nanostructured anti-reflective coatings produced by an inexpensive and scalable nanofabrication technology to

increase conversion efficiency and reduce manufacturing cost for crystalline silicon solar cells. The researchers established the following project objectives:

1. Optimize a moth eye ARC on silicon. Demonstrate normal incidence specular reflection of less than 1.0 percent from a silicon ARC for wavelength from 400 to 1100 nm. Demonstrate total hemispherical reflectance of less than 1.5 percent from the silicon ARC for wavelength from 400 to 1100 nm.

2. Develop a transparent ARC with self-cleaning functionality on glass. Demonstrate apparent water contact angle of higher than 150° on templated polymer and glass moth eye ARC. Demonstrate total hemispherical reflectance of less than 0.75 percent from the polymer and glass ARC for wavelength from 400 to 1100 nm.

3. Extend the templating nanofabrication to multi crystalline silicon. Demonstrate total hemispherical reflectance of less than 1.5 percent from a multi crystalline silicon ARC for wavelength from 400 to 1100 nm. Demonstrate total reflectance change of less than 1.0 percent when heated at 250° C for 100 hours.

4. Characterize efficiency of silicon solar cells with an integrated ARC on both silicon and glass encapsulation layers. Demonstrate efficiency of higher than 20 percent for both multi crystalline and single crystal silicon solar cells with a templated moth eye ARC.

2.4.4 Outcomes

1. The researchers employed dry and wet etch techniques to generate controlled nanopillar arrays on single crystal silicon. They showed normal incidence specular reflection data on an ARC of about 1.0 percent for wavelength from 400 to 1100 nm. The researchers reported total hemispherical reflectance of less than 1.5 percent from a silicon ARC for wavelength from 400 to 1100 nm, but they did not present measured data.

2. The researchers used the silicon pillar arrays to create polymer molds to form glass and polymer nipple and dimple arrays on glass slides. They showed water contact angle of higher than 150° on these templated polymer and glass arrays. The researchers reported normal incidence specular reflectivity of less than 0.5 percent. They did not give total hemispherical reflectance data.

3. The researchers developed a wet transfer method to transfer ordered colloidal arrays to multi crystalline silicon which was then ion dry etched to form nanopillar arrays on the silicon surface. They did not report total hemispherical reflectance data. They gave some specular reflectance data, but did not completely describe it. The researchers reported environmental aging tests to 80° C (but not 250° C) for up to 60 days with no changes in specular reflectivity.

4. The researchers compared the I-V characteristics of a template moths eye ARC on a silicon PV cell having a control cell with a standard quarter wave ARC. The measured efficiency of the moth eye cell was only 9.5 percent, but it was higher than the otherwise identical control cell.

2.4.5 Conclusions

1. The goal of an ARC for silicon was substantially met, although the researchers did not present measured total hemispherical reflectance data.
2. The researchers successfully developed a transparent ARC with self-cleaning functionality on glass. The researchers reported normal incidence specular reflectivity of less than 0.5 percent but not total hemispherical reflectance data. Thus they largely, but not completely, met this goal.
3. The extension of the templating nanofabrication technique to multi crystalline silicon was successful. However it was not clear if the researchers met the goal of demonstrating total hemispherical reflectance of less than 1.5 percent from multi crystalline silicon.
4. The researchers did not meet the goal of demonstrating efficiency of higher than 20 percent for both multi crystalline and single crystal silicon solar cells with a templated moth eye ARC.

The researchers partially demonstrated the feasibility of using bio-inspired, nanostructured anti-reflective coatings to reduce reflection losses of crystalline silicon solar cells. Future work must determine if this technology would be inexpensive enough to reduce manufacturing costs and whether it would increase the important property of surfaces mediated free carrier recombination that could spoil cell efficiency.

2.4.6 Recommendations

The Program Administrator recommends that the researchers carry out a true side-by-side test with representative high efficiency single and poly-crystalline silicon solar cells. If a positive increment in cell efficiency is found, it would be useful to estimate the incremental cost of the standard ARC production step that the moth eye replacement would have to meet for breakeven. It is also very important to verify by measurement that the nano-pillar surface texture on the cell does not increase the surface mediated recombination velocity to such an extent that cell efficiency is actually lowered.

2.4.7 Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the ratepayer from this research would be reduced environmental impacts of the California electricity supply or transmission or distribution system. A reduction in cell cost would offer potential benefits to California ratepayers from increased solar penetration into the energy marketplace. These include lower greenhouse gas emissions, greater

price stability in the future, and reduced need for new expensive central generating plants and long distance transmission line expansion. Highlighting these benefits, the California Solar Energy Industries Association (CALSEIA) released a study on Feed in Tariff (FIT) pricing declaring, "The value of renewable generation is between 5 and 12 cents per kWh over the wholesale price of electricity from natural gas, a fossil fuel."[18] This additional value is based on the environmental, transmission, and reliability values of adding renewable generation to California's electricity supply. It has been noted that the less solar power costs the more favorably it compares to conventional power and the more attractive it becomes to utilities and energy users. Utility scale solar power can now be delivered in California at prices well below $100/MWh ($0.10/kWh) less than most other peak generators, even those running on low cost natural gas.[19] What has limited realization of these benefits until recently has been the small fraction of the energy market of solar derived electricity. Any new developments that reduce cell cost per unit output will speed the installation new PV capacity and thus permit the California ratepayer to obtain these benefits.

2.4.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

The researchers are working with Sunstate Thin Films and the REC Group to take this technology to market.

Engineering/Technical

The researchers plan to work with several solar cell manufacturers to test the efficiency of the cells and to investigate the market readiness of the technology. They estimate two to three years to complete the development and demonstration. The researchers have received follow-on funding from DOE, NSF, and Emcore totaling $750,000.

Legal/Contractual

The researchers plan to apply for patents in the near future.

Environmental, Safety, Risk Assessments/ Quality Plans

Because of the status of the technology, it is premature to develop plans in these areas.

Production Readiness/Commercialization

The researchers had not developed a commercialization plan when they completed this project. They did identify relatively high cost of manufacturing early in rollout phase as a risk to commercialization.

18 http://calseia.org/feed-in-tariff-for-california/

19 http://en.wikipedia.org/wiki/Photovoltaics

2.5 Proportional Time Delay Relay For Air Conditioner Latent Capacity Recovery

Awardee: Proctor Engineering Group, Ltd.

Principal Investigator: John Proctor

2.5.1 Abstract

Residential central air conditioners reduce interior moisture through condensation during the cooling cycle. Condensed water is largely removed through a drain, although some is re-evaporated as the unit's fan runs for a pre-determined period at the end of each cycle. The length of this period is set on a nationwide basis, and in the case of dry climates, it is often not long enough to allow evaporation of most condensed moisture, losing the opportunity to further cool the coil and increase efficiency. Since moisture reduction is not necessary in dry climates, this presents an opportunity to increase fan run times in such locations and gain efficiency.

Researchers in this project successfully demonstrated an extended fan delay (enhanced time delay or ETD) proportional to the length of compressor run time in ten single-family residences in California's warmer and drier climate zones. They analyzed data collected over four to six months for operation with and without the ETD device, which is a simple relay in the fan control circuit. Results from this demonstration, supported by extensive laboratory testing, confirmed energy savings averaging 16 percent. Installation time for the ETD was less than 15 minutes, and total installed cost was estimated to be roughly $81.

Keywords: Air conditioner efficiency, latent capacity recovery, dry climate air conditioner, ETD

2.5.2 Introduction

Residential central air conditioning accounts for a significant portion of California's residential peak load and total energy consumption. Neither the existing stock of such air conditioning units nor the new units offered in California have been optimized for operation in dryer climates where little if any moisture removal is required. As a consequence, most moisture that has condensed on the evaporator coil is drained away, missing the opportunity to provide additional cooling through its evaporation at the end of each cooling cycle.

If a cost effective and simple to install device to tailor fan run time for optimal efficiency could be added to residential central air conditioners in California's dryer climate zones, overall peak and energy demands could be reduced, saving customers money and reducing emissions.

The researchers proposed to develop and demonstrate such a device, termed enhanced time delay (ETD) that would extend the period of evaporator fan run time at the end of each cycle. Present run times are set by the manufacturer on a nationwide basis, whereas the ETD duration would be proportional to the length of the compressor run time. Expected energy savings were at least 7 percent from this approach and were to be demonstrated in field trials at ten residences.

2.5.3 Objectives

The goal of this project was to determine the feasibility of using a time delay relay (enhanced time delay or ETD) retrofitted to the indoor fan motor in existing air conditioners to recover otherwise wasted cooling capacity in hot, dry climates. The researchers proposed to demonstrate the benefits of using an extended run time for this fan to capture added cooling by evaporating condensed moisture on the coil in a variety of air conditioners and their connected duct systems in California. They established the following project objectives:

1. Demonstrate a control method that results in electrical energy savings of more than 7 percent in the laboratory. Evaluate two methods for determining the duration of recapture: proportional, where the length of the condenser's run time determines the period, and temperature dependent, where the temperature differential between the return register and a supply duct determines the period.
2. Confirm the enhanced time delay design is applicable to air handling equipment commonly used in central air conditioning systems and installed ETD cost is under $100.
3. Confirm properly functioning ETD and data-logging equipment is ready for installation at ten sites.
4. Confirm agreement from the homeowners to participate in the project.
5. Confirm the feasibility of ETD installation on air conditioning systems of various makes, models, and vintages found at the selected test sites.
6. Confirm a minimum of three weeks of data collection at each site with and without ETD in operation.
7. Demonstrate actual energy savings from the ETD in the field meet or exceed 7 percent.

2.5.4 Outcomes

1. Laboratory tests at Proctor Engineering's California laboratory and Intertek's Texas facility[20] yielded sensible EER improvements of at least 25 percent using the proportional method. The temperature dependent method did not yield measurable savings.
2. The ETD relay design is consistent with industry standard 24 volt operation and did not require any specialized installation techniques. Field installation time averaged 15 minutes, with an estimated ETD device cost of roughly $64, for a total customer cost of approximately $81 for the proportional method. The total estimated cost for the temperature dependent method was approximately $146.
3. The researchers used commercially available data loggers and sensors to determine fan and compressor state, power consumption, inside and outside dry bulb temperature, and indoor and outside relative humidity.

20 Intertek offers a wide range of HVAC testing capability. See http://www.intertek.com/news/2009/11-09-hvac-facility/

4. Owners of ten single-family homes agreed to participate in the project, although four dropped out before the proportional method could be tested at their sites.

5. The researchers installed ETD devices on air conditioning units of various makes, models, and vintages in Bakersfield, Fresno, Clovis, Stockton, Tracy, Lemoore, and Hughson, California. Unit sizes ranged from two to five tons of cooling capacity.

6. The researchers logged an average of six weeks of data per site, collected in three-week intervals.

7. Time weighted energy savings for the proportional method ranged from 9 percent to 25 percent, averaging 16 percent. The temperature dependent method did not produce savings.

2.5.5 Conclusions

The researchers proved the feasibility of using an enhanced time delay relay to extend the run time of a residential air conditioner's internal fan and recover otherwise wasted cooling capacity.

1. Only the proportional method demonstrated savings under laboratory conditions, easily meeting the targeted improvement. Optimum time delay for ducted systems installed outside the conditioned space with roughly six minute compressor cycles and airflow near 350 CFM per ton was roughly 300 seconds for a permanent split capacitor motor unit, yielding a potential increase in sensible EER from 2.45 to 3.89 assuming 20 percent duct losses. Testing similar airflow and duct losses with a more efficient brushless permanent magnet motor unit and a 600 second delay yielded a potential increase in sensible EER from 3.07 to 5.23.

2. The assumptions used to estimate total installed cost for an ETD were reasonable and suggest a cost well below the target for the proportional method, but well above target for the temperature dependent method.

3. The equipment used to measure and record test data was appropriate and appeared to function without issue throughout the project.

4. Selection of the ten test sites provided a wide diversity of location, size, type, and vintage of air conditioning applications. Although only six sites were available for testing the proportional method due to attrition, the consistency of these results suggested they were sufficient to support the conclusions in the report.

5. See Conclusion 4 above.

6. With the exception of the four sites not available for proportional method testing, the researchers collected all required data for periods exceeding the original goals. Inspection of sample data showed consistency among readings, suggesting that equipment functioned reliably throughout the test period.

7. The project confirmed the feasibility of using a proportional time delay relay to extend run time for the internal fan and deliver energy savings above 7 percent. Although researchers did not find savings for a temperature dependent method of extending run

time, they identified several opportunities for further research that may lead to savings in future designs.

2.5.6 Recommendations

The researchers demonstrated clear savings in energy consumption for residential air conditioners in the dry, hot locations included in testing. This work also illuminated the importance of achieving optimal balance between extended fan run time and subsequent duct losses. The next steps that arise from this project should include:

1. Conduct further testing of the fan delay approach in a larger number of test locations to increase the robustness of conclusions.
2. Include research focused on finding the optimum balance between airflow, fan delay, and duct losses.
3. Investigate further the temperature dependent approach to determine whether it has potential to deliver cost effective energy savings.
4. Explore a commercial relationship with relay manufacturers to offer products for sale in California.
5. Begin a dialogue with regulators, utilities, and manufacturers to explore ways to encourage retrofitting in existing residential units and inclusion in new central air conditioners offered in the California market.

After taking into consideration (a) research findings in the grant project, (b) overall development status, and (c) relevance of the technology to California and the PIER program, the Program Administrator has determined that the proposed technology should be considered for subsequent funding within the PIER program.

Receiving subsequent funding ultimately depends upon (a) availability of funds, (b) submission of a proposal in response to an invitation or solicitation, and (c) successful evaluation of the proposal.

2.5.7 Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the ratepayer from this research is increased affordability of electricity in California. Achieving an average 16 percent reduction in the estimated average annual

household central air conditioning consumption of 1290 kWh,[21] at an estimated rate of 30c/kWh, could save customers $62/year. Depending on penetration rate and generation mix during air conditioner operation, adding an ETD device to central air conditioners could also provide emissions reductions through avoided power generation.

2.5.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

The researchers have not performed a market assessment. They have stated that there has not been much emphasis on retrofitting existing equipment to save energy. Thus the opportunity exists to offer retrofitted ETD devices to owners of existing central air conditioners and possibly to persuade manufacturers to include them in new products intended for the California market.

Engineering/Technical

The researchers claim that no additional engineering work is necessary because the ETD is now a commercially available product.

Legal/Contractual

The researchers have filed a patent application.

Environmental, Safety, Risk Assessments/ Quality Plans

Although the addition of an ETD relay operating at 24 volts is a simple process, it will be important to demonstrate compliance with relevant codes and standards. The researchers also note that the ETD's reliability must be equivalent to that of the central air conditioner, typically 10 to 20 years.

Production Readiness/Commercialization

The researchers indicate that a commercial-ready device exists and a major player in the relevant marketplace has expressed interest in helping to commercialize it. Remaining steps include obtaining necessary patents and licenses and finalizing manufacturing and commercialization agreements.

2.6 Semiconductor Quantum Dot Based Hetero Structures for High Efficiency Photovoltaics

Awardee: University of California at San Diego

Principal Investigator: Edward Yu

21 See page 21 of http://www.energy.ca.gov/2006publications/CEC-400-2006-009/CEC-400-2006-009.PDF, and also Energy Information Administration, Office of Energy Markets and End Use, Table CE3-7c of the 1997 Residential Energy Consumption Survey, California

2.6.1 Abstract

This project attempted to prove the feasibility of using gallium arsenide (GaAs) and indium gallium arsenide (InGaAs) quantum dot based p-i-n hetero structures to improve the power conversion efficiency of photovoltaic (PV) devices, especially concentrated photovoltaic (CPV) applications. The use of low band gap quantum dots within the semiconductor region of a PV device enables absorption of photons with wavelengths longer than those absorbed in the surrounding material. This approach has the potential to reach PV power conversion efficiencies of 45 to 60 percent as compared to 18 to 20 percent for conventional (single homo junction based p-n) concentrated photovoltaic (CPV) devices.

Researchers developed various p-i-n quantum dot (GaAs, InGaAs, InAs) hetero structures using molecular beam epitaxy and then fabricated them into functional photovoltaic devices. The researchers observed optical absorption and photocurrent generation for these devices to have wavelengths well beyond conventional (GaAs p-i-n homo junction) devices and (GaAs/InGaAs quantum well) solar cell structures, thus confirming the performance improvement of quantum dot structures. Researchers also treated the surface of the quantum dot solar cell structures with metal and dielectric nanoparticles to exploit nanostructure optical scattering effects and increase photon propagation lengths. These techniques increased short circuit current density and power conversion efficiency by approximately 16 percent. Researchers also developed processes and designs to fabricate ultra thin solar devices based on the use of quantum dot cell structures.

The research performed thus far is promising. This project demonstrated the potential to improve the performance, cost effectiveness, and adoption of concentrating CPV utility scale and customer applications. The market potential for this product could be as high as $400 million per year in California. If the concept is successful, ratepayers would benefit due to lower cost of renewable energy produced by utility scale and onsite CPV systems. The technology, however, is still considered to be in the early stages of development. Further work is needed to optimize design parameters, build functional prototypes, and validate the performance of this concept for various solar applications. The most crucial research is the layer transfer and demonstration of thin film PV cells based on quantum dot semiconductors. An economic analysis, including estimated manufacturing costs, will help validate its commercial viability.

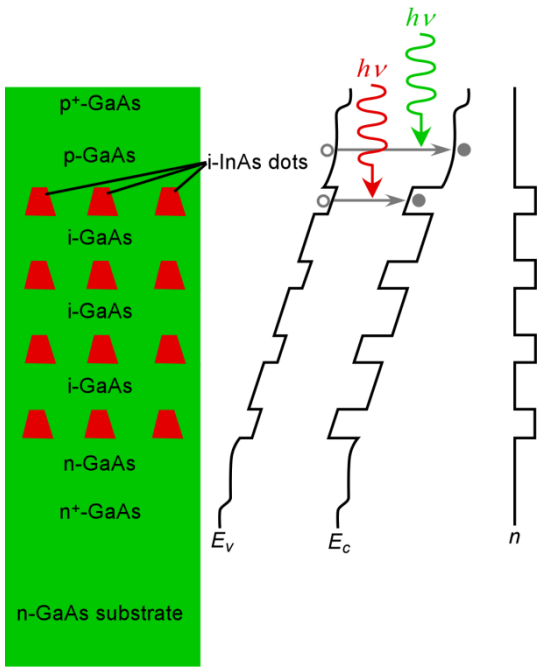
Keywords: Solar cells, photovoltaics, GaAs, InAs, quantum dots, hetero structures

2.6.2 Introduction

On November 17, 2008, Governor Arnold Schwarzenegger signed Executive Order #S-14-08 that raised California's renewable energy goals to 33 percent by 2020. Legislation signed by Governor Edmund G. Brown, Jr. in April 2011 codified this 33 percent renewable energy goal for the state. Solar energy is a key element of California's renewable energy program goals. California has permitted more than 4,000 megawatts (MW) of utility scale solar power, a portion of which is based on photovoltaic (PV) technology. In addition, the Go Solar California campaign provides incentives designed to encourage Californians to install 3,000 megawatts of solar energy systems on homes and businesses by the end of 2016. The bulk of on-site solar power is expected to utilize PV and/or concentrated PV (CPV) technology. The cost effectiveness and adoption curve for solar PV is impacted by system cost, durability, balance of plant, and the conversion efficiency of solar to electricity.

The focus of this research project was to significantly improve the conversion efficiency of single junction CPV devices. This would benefit ratepayers and consumers in California. Researchers investigated the feasibility and potential of using gallium arsenide (GaAs)/indium gallium arsenide (InGaAs) quantum dot based p-i-n hetero structures to improve power conversion efficiency. See Figure 7.

Figure 7: Schematic Diagram of InAs/GaAs Quantum Dot Based p-i-n Diode Hetero Structure with Corresponding Energy Band Edge a Refractive Index Profiles



In theory the use of quantum dot based p-i-n hetero structures for single junction CPV cells could enhance power conversion efficiency from 18—20 percent to 45—60 percent, similar to the efficiency of multi-junction cells. Multi-junction cells are stacked vertically and connected electrically in series. Thus they must satisfy a current matching operating constraint. The photocurrent generated within each individual cell layer must be the same, otherwise the actual current in the device will be that of the cell generating the least amount of photocurrent. Multi-junction tandem cells are highly sensitive to the spectral distribution of incoming sunlight. For outer space applications this is a minor issue. However for terrestrial applications, inevitable variations in spectral distribution of incoming sunlight could severely degrade performance. In this project researchers sought to explore a design for single junction cells that would match the conversion power efficiency levels of multi-junction cells yet remain robust when operating under conditions in which substantial variations in spectral distribution of incident sunlight can occur.

Conventional p-n junction photovoltaic devices, used by essentially all terrestrial solar PV technologies, are constrained by the fundamental physics of their operation to power conversion efficiencies no greater than the so called Shockley-Quiesser limit[22] – approximately

22 W. Shockley and H. J. Queisser, "Detailed Balance Limit of Efficiency of P-N Junction Solar Cells," *J. Appl. Phys.* 32, Pp. 510-9 (1961).

31 percent for devices under typical single sun illumination conditions.[23] So-called quantum well solar cells, such as intermediate band cells, have been predicted to enable power conversion efficiencies of 45 percent to over 60 percent. [24,25]

Incorporation of quantum wells within the intrinsic region of a p-i-n junction PV device can enable absorption of long wavelength photons and, consequently, increased photocurrent generation relative to a homo-junction device with minimal reduction in open circuit voltage.

Key challenges for highly efficient quantum well solar cells are:

- Efficient extraction of photo generated carriers from quantum well regions, requiring the use of thin multiple quantum well layers to maintain a vertical electric field sufficiently high to assist in carrier escape.
- Achieving complete absorption of long wavelength photons in the quantum well region. This typically requires design and growth of a thick multiple quantum well layer within the constraints of lattice mismatch and strain relaxation.

The dual requirement for high efficiency in carrier photo generation and in collection of photo-generated carriers imposes conflicting requirements on the thickness of the multiple quantum well layers in a quantum well solar cell. Only a modest improvement of about 10 percent in power conversion efficiency has been reported for quantum well solar cells, even with the use of a Bragg stack reflector beneath the p-i-n diode to reflect photons back to the quantum well region.

Researchers in this project demonstrated a novel approach that increased optical path length over a broad range of wavelengths. This was accomplished by scattering incident photons by metal or dielectric nanoparticles fabricated on the PV device surface. See Figure 8.

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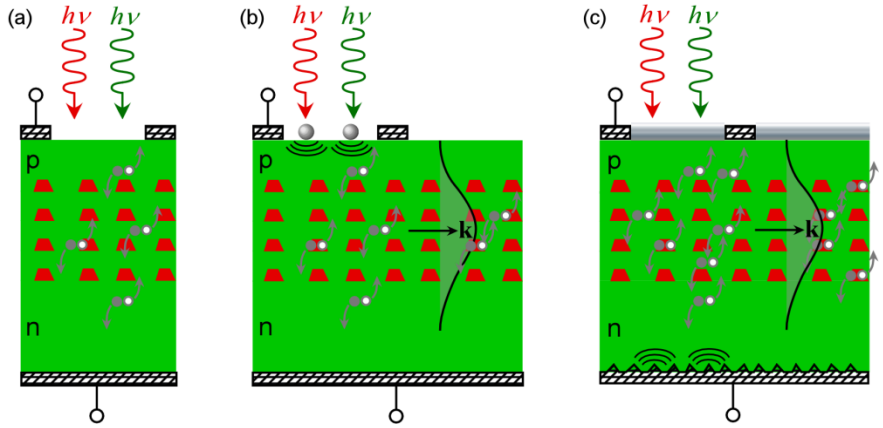
23 C. H. Henry, "Limiting Efficiencies of Ideal Single and Multiple Energy Gap Terrestrial Solar Cells," *J. Appl. Phys.* 51, pp.4494-500 (1980).

24 G. Wei, K.-T. Shiu, N. C. Giebink, and S. R. Forrest, "Thermodynamic Limits of Quantum Photovoltaic Efficiency," *Appl. Phys. Lett.* 91, 223507-1-3 (2007).

25 S. P. Bremner, R. Corkish, and C. B. Honsberg, "Detailed Balance Efficiency Limits with Quasi-Fermi Level Variations," *IEEE Trans. Electron Devices* 46, pp.1932-9 (1999).

Figure 8: Schematic Illustrations of Carrier Photo Generation and Photon Propagation

(a) InAs/GaAs Quantum Dot Solar Cell, (b) InAs/GaAs Quantum Dot Solar Cell with Nanoparticles on Surface to Scatter Photons into Lateral Propagation Paths (shown), and (c) InAs/GaAs Quantum Dot Solar Cell with Nanoparticles and Separated from Original Substrate for Improved Photon Coupling to Lateral Propagation Paths



Nanoparticles can be fabricated on device surfaces by very simple colloidal deposition or thin film deposition/annealing processes that are inexpensive and scalable to large areas. The use of quantum dots (as opposed to quantum wells) enables longer wavelength absorption that can exploit a greater portion of the solar spectrum for current and power generation.

Researchers were able to demonstrate:

- Photocurrent generation via absorption of long wavelength photons in InAs quantum dots incorporated within a GaAs based device structure
- Engineered scattering of incident photons to maximize photon absorption and electrical current generation from quantum dot structures
- Transfer of active semiconductor photovoltaic device layers onto alternate, e.g., transparent or flexible support substrates

The research performed thus far is promising. This project demonstrated the potential to improve the performance, cost effectiveness, and adoption of concentrating CPV utility scale and customer applications. The market potential is excellent. Using an average installed cost of $5 per watt for larger PV systems (greater than 500 kW), the market potential for targeted utility scale CPV in California is about $200 million per year. If the concept is fully developed and meets its performance targets (that is, the conversion power efficiency of single junction CPV is approximately 40 percent), the projected market potential for utility scale and customer based CPV in California could more than double to $400 million per year. Ratepayers would benefit due to lower cost of renewable energy produced by utility scale and onsite CPV systems. The technology, however, is still considered to be in the early stages of development. Further work is needed to optimize design parameters, build functional prototypes, and validate the performance of this concept for various solar applications. The most crucial research is the layer transfer and demonstration of thin film PV cells based on quantum dot semiconductors. An economic analysis, including estimated manufacturing costs, will help validate its commercial viability in the marketplace.

2.6.3 Objectives

The goal of this project was to investigate the feasibility of using GaAs/InGaAs quantum dot based p-i-n hetero structures to fabricate photovoltaic devices which exceed the power conversion efficiency of conventional single junction photovoltaic (PV) cells. The researchers established the following project objectives:

1. Demonstrate non-zero photocurrent generation from quantum dot based photon absorption under illumination at wavelengths up to 1000 nanometers.
2. Demonstrate that metal or dielectric nanoparticles can be successfully deposited onto functional device surfaces at densities of 1×10^{9} cm^{-2} or greater.
3. Demonstrate a greater than 10 percent increase in short circuit current and power conversion efficiency in solar PV devices due to nanoparticle deposition.
4. Demonstrate a photovoltaic device using quantum dots and nanoparticle deposition with total semiconductor thickness less than two micrometers.

2.6.4 Outcomes

1. The researchers achieved non-zero photocurrent generation from quantum dot based photon absorption under illumination at wavelengths up to 1000 nanometers. They measured photon absorption up to 1150 nanometers.
2. The researchers demonstrated that metal or dielectric nanoparticles can be successfully deposited onto functional device surfaces at densities of 1×10^{9} cm^{-2} or greater.
3. The researchers achieved greater than 10 percent increase in short circuit current and power conversion efficiency in solar PV devices due to nanoparticle deposition.
4. Researchers were able to design photovoltaic devices with total thickness less than two micrometers and initiated fabrication development for demonstration of such a device. However they spent more time than anticipated designing and fabricating advanced nanostructured scattering elements. Although they made substantial progress, due to time constraints they did not fabricate a fully functional device.

2.6.5 Conclusions

1. It appears that quantum dot structures can actually extend the photocurrent response of quantum well solar cells to wavelengths well beyond the quantum well absorption edge.
2. Optical scattering from nanoparticles was shown to enhance substantially the performance of quantum dot solar cells by coupling incident light into waveguide modes of the quantum dot structure
3. The use of quantum dot solar cells, combined with nanoparticle scattering effects, increases short circuit current density and power conversion efficiency. Researchers were able to improve power conversion efficiency by approximately 16 percent using early prototype materials, exceeding the target of 10 percent. Larger improvements should be possible by designing and optimizing fabrication of ultrathin devices (approximately one to two micrometers) in which scattering of incident light into

optically confined modes within the thin film device can be accomplished more efficiently.

4. It appears that fully functional prototype devices could be successfully fabricated given additional time and funding.

2.6.6 Recommendations

The proposed concept appears to be technically feasible but needs additional work before any conclusions can be reached concerning its practical feasibility and market potential. Further development is needed on semiconductor hetero-structures such as quantum wells and quantum dots that can deliver high power conversion efficiency under a broad range of illumination conditions. The Program Administrator recommends the following specific research tasks:

- Refine development of the substrate removal process for high yield fabrication of ultrathin devices
- Design and fabricate ultrathin devices with optimized metallic nanostructures and antireflection coatings
- Perform experimental characterization of the resulting fabricated devices
- Fabricate and test the performance, reliability, and durability of various cell prototypes
- Conduct a risk analysis to help better understand the technical, manufacturing, and commercialization challenges

A detailed cost analysis of the manufacturing process is also needed to estimate production costs for panels at varying production volumes. It should then be possible to estimate the installed cost of using this concept for various solar PV applications to determine its market potential and commercial viability. In addition, an economic analysis is required to ensure viability of the concept compared to other solar technologies.

Researchers should also consider partnering with a major manufacturer of CPV panels after the technology has been further developed and tested for durability and reliability.

After taking into consideration (a) research findings in the grant project, (b) overall development status, and (c) relevance of the technology to California and the PIER program, the Program Administrator has determined that the proposed technology should be considered for subsequent funding within the PIER program.

Receiving subsequent funding ultimately depends upon (a) availability of funds, (b) submission of a proposal in response to an invitation or solicitation, and (c) successful evaluation of the proposal.

2.6.7 Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system

- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the ratepayer from this research is increased affordability of electricity in California. This project demonstrated the potential to improve the performance, cost effectiveness, and adoption of CPV utility scale and customer applications. At the end of 2008 the cumulative installed solar PV generating capacity in California was 441 MW, most of which was based on single junction cell technology. It is expected that more than 20,000 MW of renewable generating capacity will be added in California by 2020, a portion of which will be based on CPV technology. California has already permitted more than 4,000 MW of utility scale solar power systems. Assuming a CPV market share of at least 10 percent for utility scale solar, CPV could achieve an installed capacity in California of at least 400 MW over the next ten years, an average of 40 MW per year. Using an average installed cost of $5 per watt for larger PV systems (greater than 500 kW), the market potential for targeted utility scale CPV in California is about $200 million per year.

The concept under consideration is still in its very early stage of development. As such it is difficult to project market penetration at this time. However if the concept is fully developed and meets its performance targets (that is, the conversion power efficiency of single junction CPV is approximately 40 percent), the projected market value for utility scale and on site CPV in California could more than double to at least $400 million per year. Ratepayers would benefit due to lower cost of renewable energy produced by utility scale CPV systems.

2.6.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

The primary markets for this technology concept are utility scale and customer based concentrated solar PV (CPV) applications. The research team has done a good job obtaining interest and support from Spire Semiconductor and Boeing.

Engineering/Technical

The research team recognizes additional development work is needed to validate the viability and optimize performance of the concept. The most crucial research tasks are the layer transfer and the demonstration of thin film PV cells based on quantum dot semiconductor. The researchers plan to optimize device designs and to test the performance of highly optimized devices. They also plan to demonstrate high yield manufacturing processes.

Legal/Contractual

The researchers have not applied for patents. The research team conducted a patent search in coordination with the UCSD Technology Transfer Office.

Environmental, Safety, Risk Assessments/ Quality Plans

The researchers recognize the need for these plans but have not yet quantified sufficient data to complete the plans. A development or manufacturing partner can help with this phase of work.

Production Readiness/Commercialization

The concept is not yet sufficiently developed for commercialization. Additional funding is needed to complete development work, optimize design, and build and test prototypes.

2.7 Heat Activated Cooler With Two Stage, Multi-Fluid Ejector and Novel Mixing Chamber

Awardee: ThermAvant Technologies, LLC

Principal Investigator: Joe Boswell

2.7.1 Abstract

The goal of this project was to determine the feasibility of a highly efficient jet cooler with a coefficient of performance (COP) up to 1.36 using low-grade heat (± 120° C) as its power source. The proposed system incorporated a number of features: immiscible fluid pairs for higher heat transfer capabilities and gravity separation, two stage ejector system for fluid entrainment of a supersonic primary fluid with a subsonic refrigerant while minimizing kinetic energy and shock wave losses, multi-nozzle mixing chambers to increase the entrainment ratio and maximize shear stress efficiency of the fluid pair, and highly efficient thin film evaporators to maximize heat transfer rates.

The researchers were successful in identifying environmentally friendly fluid pairs with favorable thermodynamic properties. However the system performance failed to approach the target COP and did not prove viability. Although they tested several multi-nozzle configurations, they failed to meet design criteria due to high friction losses. The researchers were successful in demonstrating ultra-low thermal resistance heat transfer with the innovative thin film evaporator.

Keywords: Ejector, steam jet refrigeration, thin film evaporation, heat actuated cooling, thermally driven cooling, supersonic refrigeration

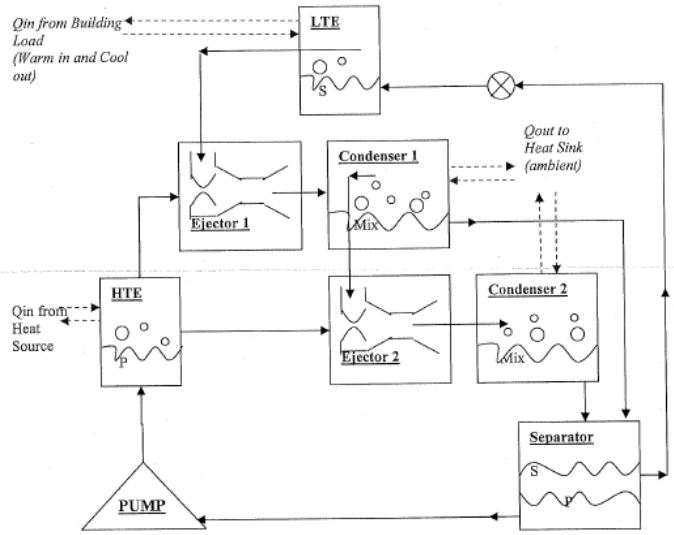
2.7.2 Introduction

Residential and commercial space cooling and water chilling account for nearly 30 percent of California's total peak energy demand. The researchers proposed to reduce significantly this demand by introducing a low heat, thermally powered ejector vapor compression refrigeration system. Input energy for the system could be provided more cost effectively than electrical systems through the use of natural gas or could be generated off grid through the use of solar heating or capture of waste heat from commercial CHP plants.

The proposed system included a multi-fluid, two-stage ejector cooling cycle as shown in Figure 9. The researchers selected fluid pairs, including a proprietary high-density propellant that was used to evaporate and entrain water as the refrigerant for maximum heat transfer and ease of post-condensation separation. They expended significant effort on optimizing mixing chamber and diffuser configuration and material selection. The goal was to maximize efficiency and

minimize kinetic energy and shock wave losses introduced during supersonic mixing of the primary fluid with the subsonic refrigerant. They incorporated a thin film evaporator to maximize the system's thermodynamic efficiency. To compete with current electrically powered air conditioners and chillers, the proposed system would need to demonstrate a coefficient of performance (COP) greater than 1.0. Early modeling work completed by the researchers predicted COPs ranging from 1.36 to 2.2 for condenser temperatures ranging from 30° C to 40° C, with an input temperature of 120° C and output temperature of 5° C. However empirical COPs failed to approach predicted values, with a maximum COP measured at 0.27 after 63 test permutations. Although the primary objective was not achieved, the researchers did meet success through the superior efficiency of the thin film evaporator component. Without achieving the minimum 1.0 COP for the system as a whole, the system did not prove viable. Thus the researchers did not include manufacturing costs or quantify benefits to California for the heat-activated cooler.

Figure 9: Schematic of Proposed Multi-Fluid, Two Stage Ejector Cooling Cycle



2.7.3 Objectives

The goal of this project was to determine the feasibility of a highly efficient jet cooler with a coefficient of performance (COP) up to 1.36 using low-grade heat (± 120° C) as its power source. The researchers established the following project objectives:

1. Finalize optimal fluid selection using internal theoretical models.
2. Complete the design and fabrication or purchase of new ejector system components.
3. Assemble reliable accurate ejector refrigeration test rig. Input power from electrical resistance heater and potentiometer for 0 to 4 kW input power at 0° C to 150° C temperatures. Make assembly vacuum tight and leak proof. Verify ± 5 percent accuracy of pressure transducers and temperature gauges using separate manual and digital measurements.
4. Demonstrate COP =1.36 at $T_{high\text{-}temp}$ 120° C/248° F; $T_{low\text{-}temp}$ 5° C/41° F, and $T_{condenser}$ 40° C/104° F. Demonstrate COP =2.2 at $T_{high\text{-}temp}$ 120° C/248° F; $T_{low\text{-}temp}$ 5° C/41° F, and $T_{condenser}$ 30° C/86° F.

5. Demonstrate thin film evaporators with < 3° C superheat (e.g., $T_{heat\ source} - T_{vapor} < 3.1°$ C).

6. Perform manufacturing cost analysis for minimum 1,000 units produced. Meet residential price target for a 4 ton unit < $500/ton and commercial price target for a 50 ton unit < $900/ton.

2.7.4 Outcomes

1. The researchers used computer analysis to identify optimal fluid pairs for the system.

2. The researchers designed and fabricated or purchased fifteen Laval nozzles, five mixers including one turbine compressor, three diffusers, two low temperature evaporators, two condensers, four insertable supersonic airfoils, and two high temperature evaporators. Nozzles with a throat diameter < 0.1 inch, including all multi-nozzles, failed to meet suction pressure and lift ratio requirements due to high friction losses. Mixer/diffuser tests indicated that a variable diameter stainless steel diffuser with a 0.88 inch diameter throat performed best. The turbine compressor design proved too inefficient due to bearing resistance.

3. The testing apparatus included a 10 point temperature and a 5 point pressure data acquisition system. Thermocouples were capable of operating from -270° C to 1372° C with an error of ± 0.25° C. Pressure measurements were taken up to 1000 mm Hg with an error of ± 0.12 percent.

4. The researchers conducted 63 tests with a variety of configurations including single nozzle, single fluid; single nozzle, multi fluid; multi nozzle, single fluid; and multi nozzle, multi fluid. They conducted tests with input temperatures ranging from 100° C to 150° C, condensing temperatures ranging from 10° C to 40° C, evaporating temperatures ranging from 5° C to 10° C, and operating temperatures ranging from 100° C to 180° C. The maximum COP measured was 0.27 with $T_{high\text{-}temp}$ 165° C/329° F, $T_{low\text{-}temp}$ 30° C/86° F, and $T_{condenser}$ 47° C/117° F.

5. The researchers constructed a 12 inch by 12 inch by 2.5 inch thin film evaporator and tested it using water as the working fluid. They used thermocouples at the inlet and outlets of the heat exchanger. The thin film evaporator achieved an average temperature difference of 3.1° C between the heat source and the vapor temperature leaving the thin film chamber.

6. The researchers deferred completion of this objective until a viable prototype could be developed.

2.7.5 Conclusions

1. The researchers were successful in identifying a fluid pair capable of attaining a high COP while demonstrating a low global warming potential and zero ozone layer impact.

2. The researchers met the objective to design and construct the ejector system components. However inefficiencies of individual system components, primarily the Laval nozzle, led to a low COP for the system as a whole (see Objective 4).

3. The researchers met the objective to assemble a reliable and accurate test rig.

4. The researchers did not meet the objective to demonstrate COP approaching predicted values. Because the measured COPs were less than 1.0, the system was not a viable alternative to electrically powered coolers.
5. The researchers nearly met the objective to demonstrate thin film evaporators with < 3° C superheat. However this component outperformed traditional heat exchangers that have a typical temperature difference of 10° C.
6. The researchers did not complete this objective.

The researchers were unable to demonstrate viability for the proposed heat activated cooler. Because measured COPs were less than 1.0, the system would not provide a cost benefit to California nor be competitive with existing electrically powered cooler units.

2.7.6 Recommendations

The researchers plan to continue development of the proposed technology with a focus on nozzle and mixing chamber development to improve efficiency. As part of continued development of this technology, the Program Administrator recommends that the following tasks be completed:

1. Investigate market need and uses for the thin film evaporator.
2. Quantify the benefit to California for the thin film evaporator.
3. Continue development of the heat activated cooler components to achieve predicted COP.

2.7.7 Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the ratepayer from this research is increased affordability of electricity in California. Because empirical results did not validate predicted performance, the proposed technology did not prove viable. Current demonstrations do not indicate cost savings for California.

2.7.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

The researchers have performed a detailed market analysis. This technology could serve all consumer markets.

Engineering/Technical

The researchers face significant challenges in improving efficiency of the nozzle and mixing chamber design to demonstrate a COP approaching predicted values. The researchers anticipate that development will take approximately one year and $500,000 in funding.

Legal/Contractual

The researchers have filed U.S. Patent Application 12/745,168 and Europe Patent PCT/US2008/084968. Both patents are pending approval.

Environmental, Safety, Risk Assessments/ Quality Plans

Environmental, Safety, Risk Assessments, and Quality Plans have not yet been developed. The researchers do not anticipate adverse health effects from the fluids used within the system.

Production Readiness/Commercialization

The researchers have developed a commercialization plan and will need support to pursue commercialization.

2.8 Transient Operation and Control of Fuel Cell Temperature Variations

Awardee:	National Fuel Cell Research Center
	University of California, Irvine
Principal Investigator:	Jacob Brouwer

2.8.1 Abstract

This project developed a temperature control system for a simulated simple cycle solid oxide fuel cell (SOFC) system. The project found that with proper system design and controls it may be feasible for high temperature fuel cell systems to load follow with low spatial temperature variations within the fuel cell electrode-electrolyte solid assembly. This is important to maintain fuel cell integrity and lifetime. Load following capabilities are increasingly important as intermittent technologies increase their share of generation. Having load following capabilities will allow fuel cells, an extremely efficient generation technology, to back up higher quantities of intermittent technologies such as wind and solar.

Minimizing temperature gradients throughout the SOFC electrode-electrolyte solid assembly should result in decreased thermal stresses and decreased cell degradation and premature failure. Simulation results indicated the fuel cell spatial temperature variation could be maintained to within 10 degrees of nominal when experiencing significant 50 percent load swings.

Keywords: SOFC, integrated system, dynamic simulation, transient performance, fuel cell system control, dynamic response

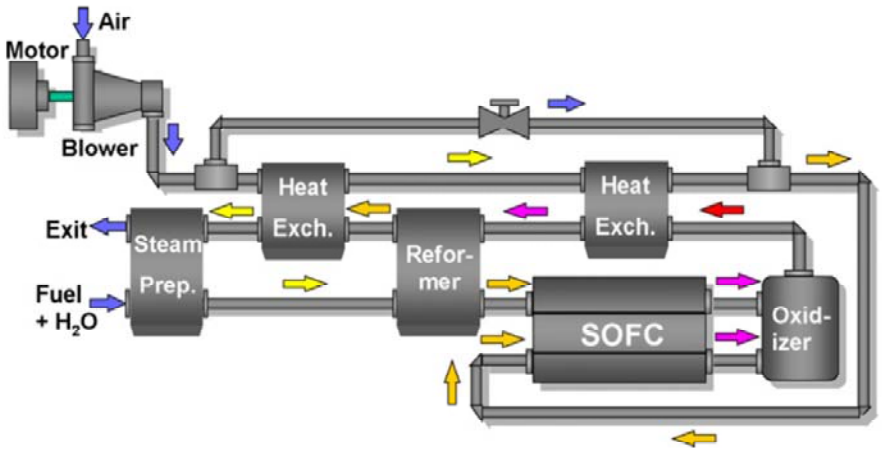
2.8.2 Introduction

California's Renewable Portfolio Standard requires utilities to supply an increasing portion of their energy mix from renewable energy sources. California is blessed with significant renewable resources and remains a global leader in the application of these technologies. However most of the renewable resources and their development impose integration costs on the grid and connected generators in the form of balancing requirements that require generators to ramp up and down rapidly. This phenomenon degrades generator efficiency, raising the conflicting goals of achieving high overall efficiency while increasing renewable generation levels.

Fuel cells are generation sources that have extremely high inherent efficiency but suffer from the inability to ramp up and down rapidly in response to load swings or changes in renewable generation. A major reason for this lack of ramping ability is the build-up of thermal stress within the fuel cell. High thermal stress caused by significant temperature differences within the c

This project developed a control system to maintain the fuel cell system operating conditions and minimize temperature variations. Minimal temperature variations in the SOFC electrode-electrolyte solid assembly result in decreased thermal stresses. High temperature fuel cell systems designed and controlled for rapid load following capability with minimal spatial temperature variations can greatly improve SOFC system operating flexibility and thereby allow it to respond rapidly to load changes on the grid. Figure 10 illustrates the fuel cell system the researchers studied.

Figure 10: Schematic of the Fully Integrated SOFC System



2.8.3 Objectives

The goal of this project was to demonstrate the feasibility of transient operation of high temperature fuel cell systems and to develop technology for controlling high temperature fuel cell systems within acceptable operating temperature constraints. To meet these goals the project established several objectives:

1. Develop a model that is simple enough for control system development but sophisticated enough to characterize the governing fuel cell physics and critical system interactions.

2. Mitigate fuel cell thermal stresses to increase system lifetime by devising and evaluating control strategies that maintain fuel cell electrode-electrolyte assembly temperature profiles as closely as possible.

3. Maintain fuel cell electrode-electrolyte assembly temperature profile to within a few degrees when subjected to diurnal temperature and fuel composition disturbances.

4. Demonstrate that the controls will work in a fuel cell system that accounts for all major balance of plant components and critical interactions.

5. Maintain the fuel cell electrode-electrolyte assembly temperature to within five degrees Celsius during a 50 percent to 100 percent power load increase.

2.8.4 Outcomes

1. The researchers developed a quasi three-dimensional model of a solid oxide fuel cell that could resolve temperature distributions. They developed a three-dimensional and spatially resolved SOFC model that was implemented into a fully integrated SOFC system model. The researchers linearized the non-linear SOFC model.

2. The researchers developed single input, single output (SISO) control methods and applied them to the system, including simple air flow manipulation and air flow and inlet temperature manipulation, which when modeled were unable to maintain the temperature profile to within $\pm$ 5° C for the load swings investigated. The researchers then developed advanced multi input, multi output control strategies especially focused upon the H-infinity approach.[26]

3. The researchers' simulation showed that the advanced control allowed the fuel cell electrode-electrolyte assembly temperature profile to be maintained to within $\pm$ 5° C, but not less, during diurnal and fuel composition disturbances.

4. The researchers calculated that with the advanced centralized feedback control the system could accommodate input temperature and output load excursions. The fuel cell stack closed loop response to an instantaneous 150° change in anode inlet temperature, an increase in cell voltage from 0.75 V to 0.8 V, and a 50 percent increase in cell resistance resulted in a stable temperature differential across the cell of about 8° ($\pm$ 4° C) that remained unchanged after approximately 10 minutes.

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26 H∞ (H-infinity) methods are used in control theory to synthesize controllers achieving robust performance or stabilization. To use H∞ methods a control designer expresses the control problem as a mathematical optimization problem and then finds the controller that solves this. H∞ techniques have the advantage over classical control techniques in that they are readily applicable to problems involving multivariable systems with cross coupling between channels. Disadvantages of H∞ techniques include the level of mathematical understanding needed to apply them successfully and the need for a reasonably good model of the system to be controlled.

5. The researchers found that the advanced control results indicated that a nominal temperature profile could be maintained to within ± 5° C during a load change from 50 percent to 100 percent of capacity.

2.8.5 Conclusions

1. The researchers developed a model that appeared capable of simulating temperature profiles within high temperature fuels cells like solid oxide fuel cells. The model has not been validated with physical tests.

2. Computer simulation results indicated that high temperature fuel cell control systems could enable minimal spatial temperature variation. The researchers achieved this by manipulating the cathode inlet temperature and the cathode airflow rate. They met this project objective.

3. Simulations demonstrated temperature control to less than ± 5° C may not be possible under diurnal temperature and fuel composition changes, but + 5° C is possible. The researchers met this project objective.

4. The inability to control to less than five degrees was likely due to limiting physical phenomena such as fluid flow residence time and heat transfer physics. Hence the best controller utilizing air flow and inlet air temperature manipulation alone may not achieve better than a 10 degree spread (i.e., ± 5° C).

5. The researchers claimed that their results were not sensitive to fuel cell size, which seemed to conflict with the inability to control to less than five degrees being a function of fluid flow residence and heat transfer, both of which would be size sensitive. The control scheme developed by the researchers appeared to reduce spatial temperature variations to within ± 5° C under a simulated load change from 50 percent to 100 percent. The researchers met this project objective.

The researchers achieved the overall goal project to demonstrate the feasibility of transient operation of high temperature fuel cell systems and to develop technology for controlling high temperature fuel cell systems within acceptable operating temperature constraints, although the boundaries of acceptable operation remain unspecified. Control to + 5° may or may not be necessary to protect the physical integrity of the fuel cell and system.

2.8.6 Recommendations

The researchers should continue investigation of advanced control strategies for use in high temperature fuel cell systems such as solid oxide and molten carbonate fuel cells (MCFC). The Program Administrator recommends the following actions:

- Investigate control approaches that minimally increase complexity beyond airflow and cathode inlet temperature.

- Investigate active cooling of cathode inlet flow in addition to simple heat exchanger bypass manipulation.

- Determine applicability to molten carbonate fuel cell technology.

- Document the modeling results with instrumented fuel cell stacks, using a variety of sizes.
- Determine the effects of transient operation within the temperature constraints identified on overall system efficiency.
- Document the tradeoffs between precise control of temperature gradients and the risk of premature fuel cell failure. Less precise control may provide adequate protection at lesser costs.
- Coordinate with the California Independent System Operator (CalISO) to refine the performance parameters used to determine load-balancing requirements.
- Conduct tradeoffs of temperature control precision and increased complexity against lower cost, simplicity, and ease of maintenance. The fuel cell system itself may be engineered to be more tolerant of temperature variation to allow simplification of the control scheme.

While the researchers showed the control system maintained temperature within + 5° C in moving from 50 percent to 100 percent load, they need to:

- Determine the time period(s) limiting such an excursion. It is one thing to make such a transition over five hours and another thing to do so over five minutes, which is typical of intermittent technology swings imposing load variations on today's grids.
- Determine the capability of the control system to accommodate real world load following (e.g., rapid cycling up and cycling down) in short time frames (circa 10 minutes full cycle) and verify the modeled results with instrumented cell stacks.
- Determine the temperature stability and homogeneity across the cell from a large and rapid reduction in load.
- Document the real world tolerance of high temperature fuel cells to temperature gradients and the impact of those gradients on cell life and premature failure to estimate life cycle tradeoffs in fuel cell performance and economics.

After taking into consideration (a) research findings in the grant project, (b) overall development status, and (c) relevance of the technology to California and the PIER program, the Program Administrator has determined that the proposed technology should be considered for subsequent funding within the PIER program.

Receiving subsequent funding ultimately depends upon (a) availability of funds, (b) submission of a proposal in response to an invitation or solicitation, and (c) successful evaluation of the proposal.

2.8.7 Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system

- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the ratepayer from this research is from reduced environmental impacts of the California electricity supply or transmission or distribution system. These environmental benefits derive from increased efficiency and reduced emissions of generation while coping with cycling/ramping caused by increasing levels of intermittent renewable technologies. Studies have shown high levels of intermittent generation have actually caused net system increases in emissions in some locales, due to degradation of efficiency in the back-up plants needed to guarantee firm power. Achievement of renewable portfolio goals is threatened unless efficiency in balancing generation can be maintained.

The technology developed in this project could enable up to 2000 GW of high temperature fuel cell capacity to operate on bio-fuels such as landfill, digester, and biomass gases. Renewable fuel operation could support greenhouse gas emissions reductions mandated by Assembly Bill (AB) 32, the California Global Warming Solutions Act. Without application of the control systems technology developed in this project, bio-fuel fuel composition disturbances could result in fuel cell temperature fluctuations

Assuming a 20 percent penetration of the load balancing mix, the developed control technology could offset 100 million tons of CO_2 through efficiency increases by supporting the increased installation of intermittent renewable power generation and increased biomass fueled generation.

2.8.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

The researchers are well connected to both manufacturers and users of fuel cell technology. Both Fuel Cell Energy and Rolls Royce Fuel Cell Systems have expressed interest in the control system work under this project. At the conclusion of this project, the researchers had not identified a commercial partner.

Engineering/Technical

The researchers plan to identify an appropriate and willing commercial fuel cell systems developer to work with them to implement the developed controls. They also expect the commercial partner to participate in writing the development plan. The researchers expect remaining tasks prior to commercialization to take approximately three years.

Legal/Contractual

The researchers had not completed a patent search nor had they filed for patent protection at the conclusion of the project. In addition, they had not published any of their findings in a scholarly journal.

Environmental, Safety, Risk Assessments/ Quality Plans

The researchers and their commercial partner will incorporate these plans into the development plan.

Production Readiness/Commercialization

The technology and system are not yet ready for production or commercialization.

2.9 Nitric Oxide Reduction Using Oxy-Combustion in Stationary Power Engines

Awardee: University of California at San Diego

Center for Energy Research

Principal Investigator: Robert Cattolica

2.9.1 Abstract

The goal of this research project was to prove feasibility of meeting CARB 2007 engine exhaust NO_x levels in a natural gas fueled internal combustion engine using oxygen enriched (nitrogen depleted) intake air as a replacement for ambient intake air. To test the viability of this concept, researchers conducted experiments in the Engine Laboratory at the University of California, Berkeley, using a Cooperative Fuel Research (CFR) single cylinder engine and methane for fuel.

The research team substituted the use of ambient intake air with varying mixtures of oxygen and nitrogen to reduce overall nitrogen levels and determine the impact of each composition to NO_x emissions in the exhaust stream. The researchers employed exhaust gas recirculation (EGR) to help obtain the desired intake air composition, maintain a constant maximum in cylinder combustion temperature, and keep the power level constant at approximately 1.48 kW. The research team selected the use of a readily available oxygen generator, vacuum swing adsorption (VSA) technology for this project.

The results demonstrated that NO_x emissions decreased in a somewhat linear fashion as the nitrogen content of the intake air was reduced. Researchers were able to lower the nitrogen level of the intake air to 2.0 percent using the selected VSA system. This resulted in a significant reduction of NO_x emissions in the exhaust stream. Researchers then extrapolated the test results and calculated NO_x emission reductions achievable using a VSA system with a very efficient engine (35 percent efficiency). In this best-case scenario, the research team calculated a NO_x emission reduction of 94 percent (to 0.31 g/kWh), including parasitic losses to operate the VSA unit.

Researchers estimated that the overall cost of NO_x reductions for this best-case scenario was about $5.05 per kilogram or $23.45 per megawatt-hour (MWh). This cost is within the range of other commercially available NO_x reduction technologies. However the technique was not able to meet the stringent California Air Resources Board (CARB) 2007 standard of 0.0323 g/kWh or 0.071 pounds per megawatt-hour (pounds/MWh) for distributed generation applications. Thus this technology is not ready for commercial deployment.

Researchers recommend further study to determine whether VSA can be integrated with another emission controls device/technique to meet CARB 2007 standards and produce a cost effective product alternative for stationary internal combustion engines.

Keywords: Oxidizer, oxy-combustion, exhaust gas recirculation, nitrogen oxide, emissions, vacuum swing adsorption

2.9.2 Introduction

California energy policy supports expansion of Combined Heat and Power (CHP) as an environmentally beneficial technology. The policy foundations supporting expanded adoption of CHP are contained in climate change legislation, AB 32, and subsequently in the Climate Change Scoping Plan published by the California Air Resources Board (CARB). The AB 32 scoping plan states, "California has supported CHP for many years, but market and other barriers continue to keep CHP from reaching its full market potential. Increasing the deployment of efficient CHP will require a multi-pronged approach that includes addressing significant barriers and instituting incentives or mandates where appropriate."[27] The Scoping Plan set a target for new CHP installations totaling 4,000 MW statewide by 2020.[28]

CHP systems typically produce electricity for on site use and recover/utilize waste heat to provide hot water, process heat, and/or chilled water via absorption cooling equipment. Total system energy efficiency of well designed CHP systems typically fall in the range of 70—85 percent. Base technologies used for CHP systems include internal combustion reciprocating engines, microturbines, mid to large turbines, and fuel cells.

CHP systems in California are subject to extremely tight emission standards. For instance, the current nitric oxide (NO_X) emission standard for distributed generation systems in California is 0.0323 grams/kilowatt-hour (g/kWhr) or 0.071 pounds per megawatt-hour (lb/MWhr).[29] CHP systems based on reciprocating engines have had an especially tough challenge meeting and maintaining this strict standard over the life of the system. Consequently many CHP systems based on the use of reciprocating engines have been shut down over the past few years because they could not easily be retrofitted to meet the new strict air quality regulations.

Engine manufacturers and university researchers are working on various ways to solve this problem. One concept is to remove nitrogen (N_2) from the intake air. Over the past 10 years researchers have been exploring the use of 100 percent oxygen (O_2) as intake air, otherwise known as oxy-fuel combustion, to eliminate the formation of NO_X emissions during combustion. There have been several studies over the past 10 years, mostly funded by the U.S. Department of Energy (DOE), regarding the use of oxy-fueled combustion for fossil fuel combustion systems to achieve zero emissions. DOE has also funded several technology

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27 California Air Resources Board (CARB), Climate Change Scoping Plan (pursuant to AB-32), December, 2008, (http://www.arb.ca.gov/cc/scopingplan/document/adopted_scoping_plan.pdf) p.44

28 CARB Climate Change Scoping Plan (pursuant to AB-32), December, 2008, pages 43-44

29 CARB 2007 Fossil Fuel Emission Standards, California Code of Regulations, Sections 94200-94214, article 3, subchapter 8, chapter 1, division 3 of title 17, http://www.arb.ca.gov/energy/dg/2006regulation.pdf

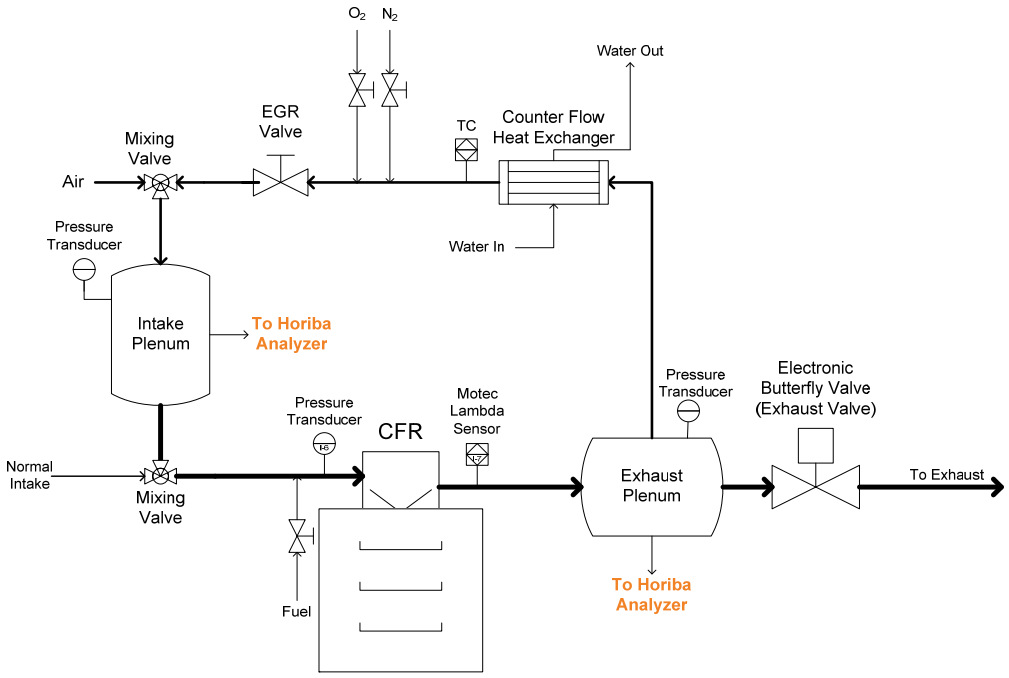
demonstration projects using coal derived hydrogen and synthetic gas techniques in an effort to eliminate emissions. These techniques are promising from a technical perspective. However they are typically capital cost intensive and have higher parasitic power losses. Thus they are usually not practical and cannot be considered for smaller scale CHP applications, especially those less than 1.0 MW.

Another method gaining interest in the research community is the use of oxygen enrichment that significantly reduces (but does not eliminate) the amount of nitrogen in the intake air. Enriched oxygen air products are much less costly compared to oxy-fueled systems and thus have the potential of being a more practical and cost effective technique of significantly reducing NO_X emissions. The goal of this research project was to determine the level of NO_X emission reductions that can be achieved by the use of enriched oxygen air in a natural gas fueled internal combustion engine.

Researchers discovered that enriched oxygen products based on vacuum swing adsorption (VSA) technology are now available in the marketplace. The primary question was whether this approach could meet CARB 2007 emission standards and be deployed in a cost effective manner. The researchers conducted experiments using a Cooperative Fuel Research (CFR) engine that was modified to operate with an oxidizer. The research was collaborative with research teams at the University of California laboratories at San Diego and Berkeley.

During tests the researchers realized that the use of enriched oxygen required a replacement gas for the nitrogen that had been removed upstream to provide sufficient dilution to prevent an increase in combustion temperature and the associated increase in NO_X production from the remaining nitrogen. The obvious choice for nitrogen replacement was the use of exhaust gas recirculation (EGR) that contains primarily H_2O and CO_2. See Figure 11. Using EGR is generally a simple way to reduce combustion temperatures by operating at slightly reduced power. The research team hypothesized that operating the engine at slightly reduced power would lower NO_X emissions with only a small negative impact on efficiency or other emissions.

Figure 11: Schematic of the EGR Experiment with Two Surge Plenums to Buffer Pressure Fluctuations



Water was retained in the EGR recycle loop by maintaining gas lines heated to 100° C. The researchers tested the oxidizer using air with 15.0, 5.0, and 2.5 percent nitrogen. They maintained stoichiometric air-fuel ratio conditions (Lambda = 1) using a MOTEC control system for fuel injection. They used electronic mass flow meters and controllers to measure the flow of fuel, oxygen, and nitrogen, and a Horiba exhaust gas analyzer to measure NO_x, O_2, CO_2, CO, and total unburned hydrocarbon (THC) in the exhaust.

The results show that the NO_x emissions on a gram per kilowatt-hour (g/kWh) basis decreased almost linearly with the decrease in nitrogen content in the intake air. Compared to combustion with ambient air (78 percent N_2), this approach reduced NO_x emissions by about 95 percent from 10.3 g/kWh to 0.54 g/kWh. In the test, the researchers used an oxidizer that produced only 2.6 percent nitrogen in the intake air. Reducing nitrogen content in the intake air by a factor of 30 reduced NO_x emissions by a factor of 19, not counting energy consumed by the VSA unit.

Researchers extrapolated the test results and calculated NO_x emission reductions that could be achieved using a VSA system for a very efficient engine (35 percent efficiency). In this best-case scenario the research team calculated NO_x emission levels of 0.31 g/kWh. Note that the reduction was only 94 percent and not 96 percent because powering the VSA unit slightly decreased engine efficiency and increased emissions. The results of this work translate into an overall NO_x reduction cost of $5.05 per kilogram or $23.45 per megawatt-hour (MWh). This cost is within the range of other commercially available NO_x reduction technologies. However the VSA system is, by itself, not sufficient to meet the existing CARB standard of 0.0323 g/kWh. As such, any consideration of VSA requires complementary mitigation techniques to meet CARB standards.

It is possible that the oxygen-enriched concept, by itself, can never be practical or cost effective. However additional refinement and integration with other emission reduction techniques has promise and should be further explored. The UC Berkeley CFR engine is one of the few experimental engines available that enables researchers to optimize system performance at minimal incremental cost. For instance, it would be interesting to understand better the impact of increased levels of EGR versus engine efficiency, lower combustion temperatures, and NO_x emissions. Researchers also surmised that the use of condensing water in a cooled EGR mode could be beneficial and should be explored in the next phase of research. Allowing more recycling of the exhaust gas back through the engine would lower the net exhaust leaving the system. It is not clear how this would affect the raw concentrations leaving the engines, but they would likely increase less than the exhaust flow was reduced. Finally, additional work is needed to integrate the oxygen-enriched concept with another emission controls device/technique to meet CARB 2007 standards and produce a cost effective alternative for stationary reciprocating engines.

2.9.3 Objectives

The goal of this project was to prove the feasibility of using enriched oxygen air in a natural gas fueled internal combustion engine to meet the CARB 2007 air emissions standards for NO_X. The researchers established the following project objectives:

1. Determine the correct temperature and amount of EGR required for nitric oxide reduction consistent with engine hardware design. The correct flow rate of EGR is necessary to operate the engine at a constant power level with similar in cylinder temperatures. NO_x emissions are strongly influenced by combustion temperatures and nitrogen content.
2. Implement design requirements of the exhaust recirculation system into the CFR engine to achieve the desired flow rate in the EGR loop.
3. Implement design requirements of the heat exchange system into the CFR engine to achieve cooling of the EGR flow to the desired temperature in the intake and to prevent materials from overheating.
4. Demonstrate operational control of EGR, temperature control, and measurement of NO_x, CO, and CO_2 with gas monitoring equipment. Operational control is important to show that the data collected in the final experiments are reliable.
5. Determine NO_x emission reduction as a function of operational parameters and operating conditions necessary to exceed regulation of NO_x to less than 0.071 lbs/MWhr. Quantifying the NO_x emission reduction is necessary to determine the performance of the oxygen enriched oxidizer method of NO_x reduction compared to other methods.
6. Determine the cost of reducing NO_x emissions using an oxygen-enriched oxidizer on MWhr basis to compare with other emission control methods.

2.9.4 Outcomes

1. Researchers were able to achieve relatively stable combustion temperatures under various operating conditions.

2. The research team designed and built an EGR loop, connecting the exhaust plenum to the intake plenum. They achieved stable operation of the exhaust recirculation system using EGR and exhaust valves to maintain desired EGR flow rates.

3. Researchers designed and implemented a heat exchange system for the EGR on the CFR engine.

4. The researchers demonstrated operational control of EGR, temperature control, and measurement of NO_x, CO, and CO_2 with gas monitoring system.

5. The results showed that the NO_X emissions on a gram per kilowatt-hour (g/kWh) basis decreased almost linearly with the decrease in nitrogen content in the intake air. Compared to combustion with ambient air (78 percent N_2), this approach reduced NO_x emissions by about 95 percent (from 10.3 g/kWh to 0.54 g/kWh). In the test, the researchers used an oxidizer that produced only 2.6 percent nitrogen in the intake air. Reducing nitrogen content in the intake air by a factor of 30 reduced NO_X emissions by a factor of 19, not counting energy consumed by the VSA unit.

6. The researchers estimated the cost of reducing NO_x emissions using an oxygen-enriched oxidizer based on VSA technology at $5.05 per kilogram or $23.45 per megawatt-hour (MWh).

2.9.5 Conclusions

1. Relatively constant engine combustion temperatures can be maintained across a variety of intake air compositions and EGR blends.
2. The availability of the UC Berkeley Cooperative Fuel Research (CFR) engine enabled researchers to design an EGR loop and control system suitable for this research project.
3. The heat exchanger/intercooler design performed as expected. It reduced the gas temperature from about 160° C to 96° C. The cooling water was preheated to 96° C with a counter-current heat exchanger and an electric heater to prevent water condensation in the intercooler. Operating the EGR at 96° C eliminated water condensation in the loop.
4. Researchers were able to control and monitor EGR flow rates, combustion temperature, and criteria pollutants. Thus the engine test bed could easily be used for additional experimentation.
5. Researchers extrapolated the test results and calculated NO_X emission reductions that could be achieved using a VSA system for a very efficient engine (35 percent efficiency). In this best case scenario, the research team calculated NO_X emission levels of 0.31 g/kWh. Note that the reduction was only 94 percent and not 96 percent because powering the VSA unit slightly decreased engine efficiency and increased emissions. Oxygen enrichment using VSA technology could only reduce NO_x emissions by 95 percent, whereas more than 99 percent is needed to meet CARB 2007 regulations.
6. The estimated cost was within the range of other commercially available NO_X reduction technologies. However the system must be integrated with a complementary emission reduction system to meet CARB 2007 standards. Therefore it is not possible at this time to determine whether the use of oxygen enrichment is viable from a technical perspective or feasible from a cost effective point of view.

The researchers demonstrated that reduced nitrogen in the inlet air could reduce NO_x emissions in a fairly predictable, almost linear manner. However the concept was not able to meet the stringent CARB requirements and does not yet appear to have any advantage in terms of cost compared to other products in the marketplace. For instance, researchers estimated the cost of oxygen enrichment to be approximately $5.05 per kilogram NO_x reduced (equivalent to $23.45/MWh). For comparison purposes, the installed cost of commercially available NO_x reduction control systems which currently meet CARB 2007 regulations range between $0.30 and $12.00 per kilogram depending on the size of the CHP system and whether the engine is rich burn (stoichiometric) or lean burn. Thus the cost of the proposed system falls within the range of available commercial products. However additional work is needed to improve system performance and further reduce capital cost for this system to be considered as a viable emissions reduction strategy in the marketplace.

While this project did not prove feasibility, the approach pursued is unique, and there is a need for additional innovation in the area of emission reduction techniques. Researchers are encouraged to pursue additional refinement of this concept in partnership with other key stakeholders.

2.9.6 Recommendations

Additional research is needed to determine whether emissions can be reduced below CARB 2007 required levels. Prior to undertaking any new work in this area, the researchers should conduct a patent search to ensure that their work does not conflict with prior art.

It is not clear that the concept as proposed will ever reach the marketplace without a fundamental breakthrough in technology performance and system cost. The researchers were not able to meet CARB 2007 NO_x emissions standards for CHP systems. Additional work is needed to improve performance (e.g., optimize the use of EGR flow rates, incorporate the use of after treatment techniques, etc.) and reduce capital and operating costs.

Now that the CFR engine has been equipped with EGR, additional parametric studies to optimize the oxygen enrichment system could be performed. For instance it could be helpful to better understand the relationship between NO_x emission reductions and lower combustion temperatures by marginally increasing the level of EGR. Additional research is also needed to explore the knock limits at high EGR ratios. This would yield important conclusions about improvements in efficiency, which is a necessary aspect for engines utilizing EGR. The CFR engine could also be used to determine the potential benefits of using condensing water in a cooled EGR mode.

Further research is also needed to determine whether this oxygen enrichment concept can be used in conjunction with other emission reduction strategies, such as the use of catalysts in the exhaust stream, to meet CARB standards. The researchers also need to determine if the capital cost can be reduced so this concept can be a practical, reliable, and cost effective emissions control strategy in the marketplace. The research team is strongly encouraged to partner with an engine manufacturer or supplier of advanced emission controls for stationary engines to ensure that the various technologies under consideration can be properly integrated and commercialized as a reliable, viable, cost effective package.

2.9.7 Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the ratepayer from this research is reduced environmental impacts of the California electricity supply or transmission or distribution system.

California policy strongly supports expansion of combined heat and power (CHP) as an environmentally beneficial technology. The policy foundations supporting expanded adoption of CHP are contained in climate change legislation, AB 32, and subsequently in the Climate Change Scoping Plan published by the California Air Resources Board (CARB) and in subsequent regulation by the California Public Utilities Commission (CPUC).

CHP systems in California are subject to extremely tight emission standards. The current nitric oxide (NO_x) emission standard for distributed generation systems in California is 0.0323 grams/kilowatt-hour (g/kWhr) or 0.071 pounds/megawatt-hour (lb/MWhr).[30] CHP systems based on internal combustion (reciprocating) engines have had the toughest time meeting and maintaining this strict standard that was adopted in 2007. Consequently, many CHP systems based on the use of internal combustion engines have been shut down over the past five years because they could not easily be retrofitted to meet the new strict air quality regulations.

California ratepayers would benefit from additional deployment of reliable distributed generation (DG) systems installed on customer premises. CHP systems typically have overall fuel utilization rates of 70 percent to 85 percent, depending on the application. Small systems can utilize gasoline, diesel, or natural gas fuels if they can meet CARB 2007 emissions goals. They also offer high reliability due to on site generation. CHP systems can reduce the need to expand electricity substations and can provide islanding service during emergencies. Finally, CHP systems reduce the use of electricity transmission and distribution lines. These benefits should provide reduced energy costs to California ratepayers.

2.9.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

30 CARB 2007 Fossil Fuel Emission Standards, California Code of Regulations, Sections 94200-94214, article 3, subchapter 8, chapter 1, division 3 of title 17, http://www.arb.ca.gov/energy/dg/2006regulation.pdf

Marketing/Connection to the Market

The researchers do not plan to take this technology to market.

Engineering/Technical

The researchers demonstrated that the costs of NO_x reduction using the proposed technology are not lower than competing after-treatment solutions. In addition, they did not meet CARB 2007 NO_x goals. They do not plan to continue this work.

Legal/Contractual

Researchers did not conduct a patent search and filed no new patents.

Environmental, Safety, Risk Assessments/ Quality Plans

If additional research is pursued, the integrity of the system will need to be thoroughly tested to ensure that it meets standard industry safety and permitting requirements.

Production Readiness/Commercialization

The concept is not yet sufficiently developed for commercialization. Additional work is needed to improve performance and reduce cost.

2.10 Nanowire Thermoelectrics for Industrial Waste Heat Recovery

Awardee: Nanotron, Inc.

Principal Investigator: Nathan Hiller

2.10.1 Abstract

The objective of this project was to develop low cost, high efficiency thermoelectric materials for converting industrial waste heat into electrical power. Converting industrial waste heat into electricity would increase the supply of electricity resulting in significant savings to California ratepayers. Economic recovery of thermal energy that is now wasted would also make manufacturing companies more likely to expand their operations in California and possibly add jobs. The project goals were to make and measure the thermoelectric properties of nanowires. The researchers planned to make the nanowires by drawing a large assembly of thermoelectric wire in a plastic carrier. The drawing process was similar to that used to draw fiber optic strands.

The project produced micro-size wires. However the researchers could not locate nano-size wires sufficiently long that they could measure the thermoelectric properties. More effort is needed to produce usable wires at sufficiently small diameters that exhibit enhanced thermoelectric properties.

Keywords: Seebeck coefficient, electricity, power plants, efficiency, high temperature, thermoelectric

2.10.2 Introduction

California's industrial sector discharges large quantities of energy into the atmosphere or liquid cooling systems as thermal losses. While some thermal energy rejection cannot be avoided, most industrial processes do not operate near their theoretical maximum efficiency. Industries using

large quantities of energy employ several techniques to recover that unused energy. Most employ some form of waste heat recovery boilers. Combined heat and power systems are regularly used in medium to large industrial applications. Cost effective waste heat recovery is needed for smaller applications and for those that discharge energy at relatively low temperatures. Thermoelectric conversion is well suited to smaller applications because of its inherent simplicity. There are no moving parts. Because of the numerous applications and the specific requirements of each application, it is difficult to accurately assess the amount of heat energy that could be economically recovered using thermoelectric conversion devices. While any heat recovery technology is effective only if there is a use for the recovered energy, most applications can use additional electricity. Thermoelectric conversion is a promising technology to produce electricity from low-grade heat energy.

Thermoelectricity is a reliable technology for converting heat into electrical energy. Thermoelectric (TE) materials are semiconductor solids that produce an electric current when joined together and subjected to a temperature difference across the junction. This property makes it possible to produce electric current by applying waste heat on one side of a TE material while exposing the other side to lower or ambient temperature surroundings. Useful TE power generation is achieved by combining a TE module consisting of an array of hundreds of TE material junctions, a hot-side heat exchanger, a cold-side heat exchanger, and a power electronic module to provide the desired voltage and current output.

TE materials available prior to about 1995 produced thermal to electric conversion efficiencies up to 5 percent and were used only in small niche applications. However recent significant advances in the scientific understanding of nanostructure effects on TE properties create the opportunity for advanced TE materials with potential conversion efficiencies of over 10 percent or possibly higher. The advent of these advanced TE materials offers new opportunities to recover waste heat more efficiently and economically with highly reliable and relatively passive systems that produce no noise and vibration. The efficiency of thermoelectric material is dependent on its figure of merit, Z, defined as $\sigma S^2/\lambda$ where σ is the electrical conductivity, λ is the thermal conductivity, and S is the Seebeck coefficient (μV/K). The greater a material's Z, the greater its thermoelectric efficiency. Although increasing σ and decreasing λ will increase Z, increasing S is far more effective because that term is squared in the Z formula.

Theoretical studies predict huge increases in ***S*** for nanostructure materials.[31,32] In general, the greater the confinement of charge carriers, the greater the value of ***S.*** Experimental studies also confirm the theoretical predictions of huge increases in ***S*** for nanostructures. Some researchers are compacting nanoparticles into bulk materials to create thermoelectric materials with a high Z and the capability to operate at relatively high temperatures.[33]

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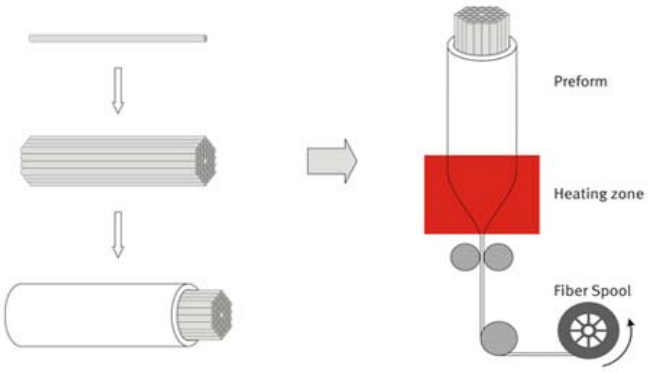
31 X. Sun, Z. Zhang, and M.S. Dresselhaus, 1999, "Theoretical Modeling of Thermoelectricity in Bi Nanowires," *Applied Physics Letters*, Vol.74, pp. 4005-4007.

32 M. Shelley and A. A. Mostofi, 2011, "Prediction of High zT in Thermoelectric Silicon Nanowires with Axial Germanium Heterostructures," *EPL*, 94: 67001 doi:10.1209/0295-5075/94/67001.

33 Hamish Johnston, "Nanoparticles Boost Thermoelectric Efficiency," physicsworld.com. January 26, 2011.

In this project the researchers proposed to make thermoelectric nanowires using techniques that are similar to those used to draw fiber optic strands. They used a conventional drill to produce deep, narrow holes in a plastic carrier. They proposed to insert a thick thermoelectric wire into each hole and then draw that assembly (fiber) down to a much smaller diameter (Figure 12). The researchers also proposed to measure the Seebeck coefficient of the resulting nanowires. Their goal was to produce a thermoelectric wire with a high Seebeck coefficient at a low price.

Figure 12: The Fiber Drawing Process



The plastic rod/wire assembly is heated at one end in a furnace to the point at which it softens, and then it is drawn into fiber.

2.10.3 Objectives

The goal of this project was to prove feasibility of a low cost, high volume manufacturing process for nanowire based thermoelectric materials using optical fiber manufacturing technology.

The researchers' objectives were to:

1. Assemble the first stage preform (thermoelectric wire inserted into a plastic rod). Confirm through visual inspection that the resultant assembly is compact and free of loose components.

   Draw the first stage preform into a fiber. Demonstrate by measurement that the fiber has a diameter of 60 μm ± 5 μm, and the single wire is at the center of the plastic rod/fiber.

2. Assemble the second stage preform. Confirm through visual inspection that the resultant wire assembly is compact and free of loose components. This assembly contains three holes in the plastic rod, each filled with thermoelectric wire.

3. Draw the second stage preform into a fiber. Demonstrate by measurement that the fiber from that draw has a diameter of 60 μm ± 5 μm.

4. Measure the nanowire wire diameters and crystal orientation using SEM and X-ray diffraction. Demonstrate that the wires from the fiber assembly have a diameter of 7 nm ± 2 nm.

5. Construct the Seebeck tester and use it to measure the Seebeck coefficient of the second fiber. Demonstrate that the measured Seebeck coefficient for the fiber is > 1,000 μV/K.

2.10.4 Outcomes

1. The researchers constructed the plastic rod/wire assembly. Visual inspection found it to be compact and free of loose components.
2. The researchers measured the diameter of the fiber made from the first perform at 60 μm ± 2.7 μm.
3. The researchers constructed the second plastic rod/wire assembly. Visual inspection found it to be compact and free of loose components.
4. The researchers measured the diameter of the fiber made from the second preform at ~100 μm.
5. The researchers were not able to measure the diameters of the nanowires because they were not able to locate the wires using a scanning electron microscope.
6. The researchers were not able to complete this objective since they could not find any nanowires in the fiber to test.

2.10.5 Conclusions

1. The researchers met this objective.
2. The researchers met this objective
3. The researchers were able to make a compact assembly with no loose components.
4. The researchers did not achieve this objective. They did not explain why they could not achieve the smaller fiber diameter, nor did they indicate if they tried to accomplish this objective more than once.
5. The researchers did not complete this objective since they could not locate nanowires to measure.
6. The researchers could not address this objective because they had no wires.

The researchers did not prove feasibility of producing thermoelectric wires with a diameter of 7 nm ± 2 nm. Neither did the researchers define or calculate what "low cost" meant.

2.10.6 Recommendations

The researchers claim to have a development path to continue their work after the completion of this project. The Program Administrator recommends that the researchers include the following in their plan:

1. Investigate alternate materials for the carrier rod.
2. Investigate alternate methods for creating the hole(s) in the rod. Laser drilling and the EDM method are two possibilities.
3. Investigate methods of vapor deposition of the carrier material onto the thermoelectric wire.
4. Develop and describe methods of retrieving the wire from the carrier material after the drawing process.

5. Develop cost goals and allocate portions of the cost goal to each process.

2.10.7 Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

If this project were successful it could lead to increased affordability of electricity in California. Unfortunately project feasibility was not proven. Because of the large potential benefits of recovery of low-level energy, this type of research should be addressed in the future. The benefits accrue to industrial companies that reject large quantities of low-level heat energy. Recovering that heat and converting it to useful electricity could lower the cost of manufacturing in California. The exact benefits are difficult to quantify since the researchers in this project did not establish a cost goal for thermoelectric produced electricity or the capital required to produce the electricity.

2.10.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

The researchers did not indicate any connection with potential partners or distributors for the proposed product. They claim to have surveyed potential customers for interest, but gave no further details.

Engineering/Technical

The researchers claim to have an engineering requirements specification and to be able to complete product development and demonstration in one to two additional years.

Legal/Contractual

The researchers claim to have filed an application for one patent. No application number was provided.

Environmental, Safety, Risk Assessments/ Quality Plans

Due to the technology development status, the researchers have not yet developed environmental, safety, risk assessments, and quality plans.

Production Readiness/Commercialization

The researchers have not developed a commercialization plan and will need support to pursue commercialization.

2.11 Improving High Solids Biomass Conversion Efficiency Using Spray Dried Enzymes

Awardee: University of California, Davis

Principal Investigator: Tina Jeoh

2.11.1 Abstract

Biofuel produced from non-food natural resources is emerging as an important new renewable fuel that can be used for a number of everyday applications including transportation, food processing, and the generation of electricity. California is well positioned to take advantage of this opportunity due to its abundance of agricultural residues. However establishment of a cost effective bio-refinery has not been fully achieved, largely due to uncertainties and inefficiencies with the overall process. The goal of this project was to improve efficiency by developing and testing a more effective means to deliver enzymes to the saccharification reaction (converts biofuel feedstock into sugar) in a bio-refinery, particularly under high solids loadings. Specifically, the researchers targeted delivery of specific synergistic activities in high solids saccharification reactions. This work demonstrated that the concept of targeted enzyme delivery has potential. However, in this project the encapsulation strategy could not effectively release the enzymes as initially hoped. Further research and testing is required to validate the concept. In the process of developing this project the researchers invented a technology to directly cross-link alginates during spray drying for encapsulating the biological moieties. Moieties are specific groups of atoms within a molecule that are responsible for characteristic chemical reactions of that molecule. This invention may prove to have marketable benefits in the California biotechnology sector.

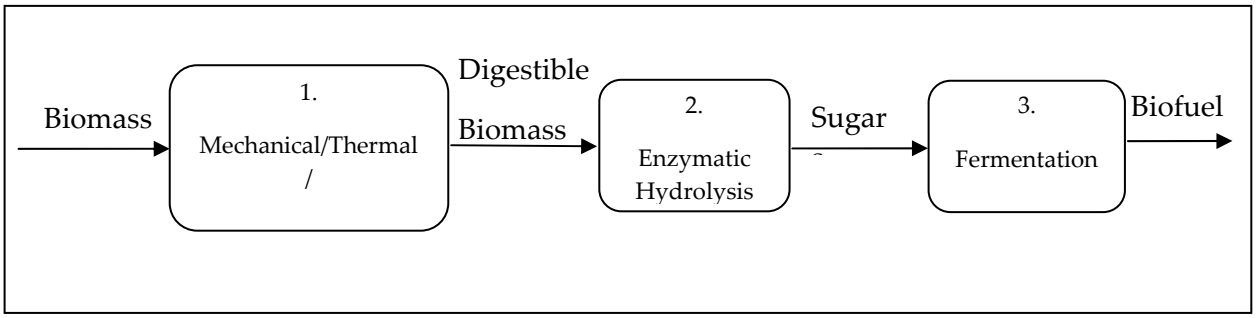
Keywords: Encapsulation, spray drying, alginates, high solids saccharification, mass transfer limitations, cellulose

2.11.2 Introduction

Biofuels are emerging as an important new renewable resource that can be used for a number of everyday applications including transportation, food processing, and the generation of electricity. Biomass, organic matter that can be converted into fuel, can help meet state goals for increasing the amounts of electricity and fuels from renewable resources under the Renewable Portfolio Standard (RPS) and the Low Carbon Fuel Standard (LCFS). California is well positioned to take advantage of this opportunity due to its abundance of agricultural residues. For instance, lignocellulosic biomass (plant based material composed of cellulose, hemicellulose, and lignin) is an ideal non-food feedstock for liquid fuels and biochemical products. A bio-refinery platform that utilizes agricultural residues as feedstock has the potential of simultaneously producing liquid biofuels and a higher value animal feed in the form of a concentrated protein stream. Lignin produced from the bio-refinery can also be used as a blending fuel to generate electricity in a conventional power plant.

Extensive construction of bio-refineries has not been possible in the United States largely due to their high cost and the uncertainty and inefficiency of the conversion process. One phase of the conversion process, called saccharification, converts sugar derivatives or complex carbohydrates such as cellulose biomass into simple soluble fermentable sugars. Within the saccharification process there is uncertainty about how to optimize the efficiency of selecting, matching, and distributing specific enzymes to biomass feedstock under varying compositions and conditions, particularly under high solids loadings. The biochemical process that releases sugars from the cell walls of lignocellulosic biomass ultimately relies on the concerted action of many different enzymes produced by saprophytic microorganisms. See Figure 13, Step 2.

Figure 13: Biochemical Process for the Conversion of Lignocellulosic Biomass to Biofuels



Current industry practice consists of mixing enzymes in a liquid broth (predetermined aliquot) and adding the mixture in some fashion to the biomass at an insoluble solids loading of less than 10 percent. This strategy is very inefficient because various enzymes have differing affinities to substrates. There is no certainty that the most appropriate enzymes for specific substrates are located where they need to be to produce a well-orchestrated and efficient reaction. It is essentially a hit or miss exercise and conversion efficiency is compromised as a result. Furthermore this process consumes high quantities of water. For example, 526 gallons of water are required to saccharify one metric ton of pretreated biomass (e.g., pretreated wheat straw or sugar beet pulp) with a biomass moisture content of 85 percent (15 percent solids) in a reaction at 5 percent final solids loading. A cellulosic ethanol plant that processes 100,000 metric tons of pretreated biomass at 85 percent moisture per day requires up to 52.6 million gallons of additional water use per day exclusively for the saccharification reaction. The prospect of reducing water requirements for saccharification at solids loading of 15 percent or greater would be attractive to the industry.

Researchers proposed a new method of targeting and distributing enzymes to higher mass biomass feedstock in an effort to improve the saccharification process and conversion efficiency, both necessary to achieve a cost effective commercial scale production plant. They first encapsulated enzymes containing synergistic ratios using a spray drying technique and then distributed them to the biomass feedstock. Such a delivery and distribution method of synergistic ratios of the enzymes on a large scale throughout the biomass could enhance saccharification rates and ultimately conversion efficiency.

The potential benefits of a new enzymatic saccharification process for biomass at high solids loadings are:

1. Reduced reactor size that lowers capital cost.
2. Increased product concentration that reduces the capital cost of separation and distillation equipment.
3. Reduced process water use and wastewater generation, thus lowering operating costs.
4. Lower energy consumption of the plant.

The researchers noted that a key challenge associated with the efficient execution of this process lies in overcoming mass transfer limitations in the system. It is important to ensure homogeneous incorporation of enzymes that dissolve plant cell walls within the biomass to achieve optimal ratios to the substrate.

Figure 14 illustrates a comparison of the conventional manner of delivering enzymes to the saccharification process with the proposed strategy of encapsulating micro-aliquots of aqueous enzymes resulting in a more homogeneous distribution of enzyme activities.

Figure 14: Diagrams Contrasting the Current State-of-Art for Delivering Enzymes to the Saccharification Reaction with the Strategy Employed in this Project

Marketable enzyme mixtures that degrade plant cell walls typically consist of stabilized fermentation broths from a high secretion cellulolytic fungal strain. Saccharification efficiency is maximized when the optimal formulation of these enzymes is co-located at the reaction sites while minimizing the accumulation of products. Researchers in this project attempted to use the spray drying encapsulation matrix to produce stable and reproducibly encapsulated enzymes that could then be placed into contact with pretreated biomass feedstock and released gradually. The team determined that an ideal encapsulation matrix would allow controlled release, not contribute or leach undesirable components during release, and be conducive to spray drying. Additionally, the encapsulation of choice would have to be obtainable from a sustainable source, be non-toxic, and be relatively inexpensive. The team determined that the use of alginates as the encapsulation matrix could satisfy all these requirements. Alginates are derived from green algae (a sustainable and potentially inexpensive source), are commonly used as a thickener in food applications, and are non-toxic. Alginates can be cross-linked by calcium, making an alginic acid matrix that is capable of controlled release characteristics.

Test results were mixed. The delivery of the developed spray enzymes to high solids saccharification was not successful because the strategy did not allow effective release of the enzymes as initially hoped. However distributed delivery of synergistic enzyme mixtures to biomass, as opposed to mixing one single aliquot containing all the enzymes, showed potential to be commercially viable. Further research and testing are required to fully evaluate this idea using lower enzyme-to-biomass ratios and/or larger reactions.

2.11.3 Objectives

The overall goal of this project was to determine the feasibility of improving the efficiency of high solids biomass saccharification for the generation of renewable electricity. The researchers established the following project objectives:

1. Demonstrate that the encapsulating matrix is capable of controlled release of at least 95 percent of the encapsulated enzyme activity over a period of 24 hours in an acetate buffer at a pH level of 5.0.
2. Demonstrate that the activity of spray-dried enzymes on pretreated switchgrass is within 5 percent of the activity of the original liquid culture on a protein-loading basis.
3. Target greater than 50 percent xylan remaining in the pretreated substrate.
4. Demonstrate greater than 20 percent improvement in saccharification efficiency attributable to the use of spray-dried enzymes.

2.11.4 Outcomes

1. The encapsulated protein matrix was only able to release up to 65 percent of the encapsulated enzyme activity.
2. Researchers were not able to demonstrate that spray drying of enzymes on pretreated switchgrass could be achieved within 5 percent of the activity of the original liquid culture primarily because the encapsulation strategy could not effectively release the enzymes as initially hoped.

3. Test results demonstrated greater than 50 percent xylan remaining for mildly alkali pretreated switchgrass.

4. The research team was not able to demonstrate a greater than 20 percent improvement in saccharification efficiency attributable to the use of spray-dried enzymes. Under unbuffered conditions, the use of spray-dried enzymes far outperformed liquid enzymes at all solids loadings. However further analysis revealed that this result was caused by the buffering capacity of the spray-dried matrix. When controlled for pH, the researchers found that the particles limited diffusion of the enzymes out of the encapsulation matrix, thus yielding lower saccharification efficiency compared to the liquid enzyme broth.

5. In the process of developing this project, the research team invented a technology and method to directly cross-link alginates during spray drying for encapsulating biological moieties. Alginates have been used for decades for the encapsulation of biological molecules, cells, and chemicals. However the products are instable and subject to dissolution in the target environment. Also, the usual method of cross linking alginates is a two step process that first requires cross linking of alginates in a solution followed by a drying process. The two-step method typically yields larger particles and cannot be easily scaled up. Furthermore, cross-linked alginate encapsulation was incompatible with spray drying. The research team invented a one step, industrially scalable process that yields micro-scale, stable alginate beads as a result of cross linking that resists dissolution even in dilute suspensions. The researchers have filed a provisional patent and discussions are currently underway with two enzyme companies, one based in California. This technology, not available prior to this project, could have commercial benefits for the pharmaceutical, food, and biotech industries in California.

2.11.5 Conclusions

1. The researchers found alginate encapsulation was not a successful strategy for targeted delivery of cellulolytic enzymes to high solids in the saccharification process.

2. The strategy of distributing small aliquots of enzymes throughout the biomass by delivering alginate encapsulated spray-dried enzymes was not successful.

3. Cellulase and xylanase activities of the encapsulated enzymes were not compromised during the spray drying process. Results from initial saccharification tests on switchgrass at varying solids loadings were highly promising, suggesting that spray-dried enzymes were indeed superior in performance to using liquid enzyme broth. These initial results suggested that the spray-dried enzymes performed twice as well as the liquid enzymes at low solids loadings.

4. Distributed (versus targeted) delivery of cellulolytic enzymes is a potentially viable strategy. However further work is needed.

5. Development of the one step process is an important achievement of this project.

The researchers found targeted delivery of spray-dried cellulolytic enzymes to high solids saccharification was not a viable concept because the encapsulation strategy could not effectively release the enzymes as initially hoped. Researchers discovered, however, that

distributed delivery of synergistic enzyme mixtures to biomass (as opposed to mixing one single aliquot containing all the enzymes) showed potential and could be commercially viable. Further research and testing using lower enzyme-to-biomass ratios and/or larger reactions is required to fully evaluate the initial concept.

2.11.6 Recommendations

The proposed concept of targeted enzyme delivery appears to have promise but needs additional research and testing before any conclusions can be reached concerning its technical feasibility and market potential. Specific research regarding targeted distribution of synergistic enzymes should be pursued further. Viable solutions are needed to improve saccharification reactions, particularly at high solids loadings. Distributed delivery of synergistic enzyme mixtures to biomass (as opposed to mixing one single aliquot containing all the enzymes) could be potentially viable with further research and testing.

Currently, the world's largest cellulosic biofuels facility (Inbicon in Kalundborg, Denmark) includes high solids saccharification as part of the overall process. The enzyme delivery in this particular process is achieved by simply dripping bulk enzyme broth without consideration for targeted distribution of the synergistic activities. Although this method has its advantages, targeted enzyme delivery can undoubtedly improve the efficiency of the process and increase yield rates.

2.11.7 Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the ratepayer from this research is reduced environmental impacts of the California electricity supply or transmission or distribution system.

Biomass constitutes a major renewable energy resource for California, with more than 30 million tons per year of in-state production estimated to be available on a sustainable basis for electricity generation, biofuels production, and other industrial processing. Biofuel production from these resources could exceed two billion gallons of gasoline annually, while providing opportunities for agricultural and rural economic development. Biomass can help meet state goals for increasing the amounts of electricity and fuels from renewable resources under the Renewable Portfolio Standard (RPS) and the Low Carbon Fuel Standard (LCFS).

If successful, this concept could contribute to developing large scale, cost effective bio-refineries that convert agricultural residues to various bio-products such as liquid biofuels, renewable electricity, and higher value animal feed. The technology developed in this project to directly cross link alginates by spray drying has potential commercial benefits for the pharmaceutical,

food, and biotech industries in California. It is premature to quantify the benefits of this proposed technology at this juncture. The research team intends to market the intellectual property that was developed as part of this work and pursue partnerships with California companies for commercialization purposes.

2.11.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

The research team is pursuing discussions with two enzyme companies, one based in California, regarding the commercial potential for a new technology that was developed as part of this project.

Engineering/Technical

The researchers do not have a clear path to continue development of this technology.

Legal/Contractual

The researchers have filed a provisional patent on a one step, industrially scalable process that yields micro-scale, stable alginate beads. The researchers conducted an informal literature search and produced no evidence of potential infringement on existing patents or intellectual property.

Environmental, Safety, Risk Assessments/ Quality Plans

No safety or environmental risks have been identified with this concept. Existing industry standards and practices should be adequate and mitigate any risk associated with targeted delivery of enzymes.

Production Readiness/Commercialization

The concept is not yet sufficiently developed for commercialization. Additional research and testing is needed to determine technical feasibility and commercial viability.

2.12 Developing Ultra High Efficiency Thermal To Electric Energy Conversion Technique....

Awardee: University of California, San Diego

Principal Investigator: Yu Qiao

2.12.1 Abstract

This project was an investigation into a new method to convert waste heat into electricity. Although waste heat is generally at low temperature, typically below 200° C, it is still a potential energy source of significant magnitude. However, previous attempts to harvest it have been hampered by very low conversion efficiencies, making its recovery uneconomic except in special circumstances.

In this project the researchers investigated a new conversion method that has the potential for much greater efficiency and lower cost. This method uses the phenomenon of surface charge induced on cell electrodes that are immersed in an ionic electrolyte. The amount of induced surface charge is strongly temperature dependent so that two cells at different temperatures develop a substantial potential difference between them. When the two cells are placed in electrical contact through an external circuit, an electric current will flow between them, thereby converting heat to electricity. A key innovation in this study was the use of special nanoporous electrode materials of very large surface specific area, of the order 1000 m^2/g, which greatly magnified the amount of induced charge. Researchers performed a systematic investigation with nanoporous electrodes and electrolytes of different compositions. They fabricated and tested both single cells and networks of multiple cells. The observed circuit cell voltages and currents were encouraging, although conversion efficiency measurements have not yet been successful. A comprehensive market research study for the technique also gave encouraging results.

Keywords: Waste heat, energy harvesting, thermal to electric energy conversion, electrolyte cell, nanoporous electrodes

2.12.2 Introduction

Any energy conversion process that involves heat has inherent inefficiencies. These inefficiencies result in the production and loss of waste heat energy. Waste heat is a valuable potential resource.[34] Significant amounts of waste heat are produced by renewable energy sources such as concentrated solar photovoltaic cells and solar thermal generators. Non-renewable powered sources such as fossil fueled generators also produce very large amounts of waste heat, as do geothermal sources and automotive vehicles. Generally waste heat is released at low temperatures, often below 200° C, which has made it extremely difficult to harvest for practical electricity generation. Previous attempts to recover electrical energy from waste heat have included indirect conversion by organic fluid Rankine engines and by direct conversion with thermoelectric materials. However these efforts have been hampered by low efficiency of conversion.

The amount of waste heat produced and dissipated to the ambient is large. The U.S. consumes about 100 quads of energy a year.[35] A quad is a quadrillion (10^{15}) Btus that is equivalent to about $2.93X10^{13}$ kWh of energy.[36] Of the 100 quads of energy consumed per year, 55 percent to 60 percent gets lost as waste heat. Based on a per capita estimate, California's share of this waste heat is estimated to be in the range of 5—10 quads. Ten quads of energy are equivalent to $2.93X10^{12}$ kWh of energy. If this could be converted to electricity with 10 percent efficiency, it would represent 293,000 GWh of electricity, nearly equal to California's annual electricity production in 2010, in state plus imports, of 290,187 GWh.[37] At an electricity price of $0.10/kWh the annual economic benefit to California ratepayers would be $29 B. Clearly actual benefits

34 http://en.wikipedia.org/wiki/Waste_heat

35 http://www.greentechmedia.com/articles/read/tapping-americas-secret-power-source-5259/

36 http://www.aps.org/policy/reports/popa-reports/energy/units.cfm

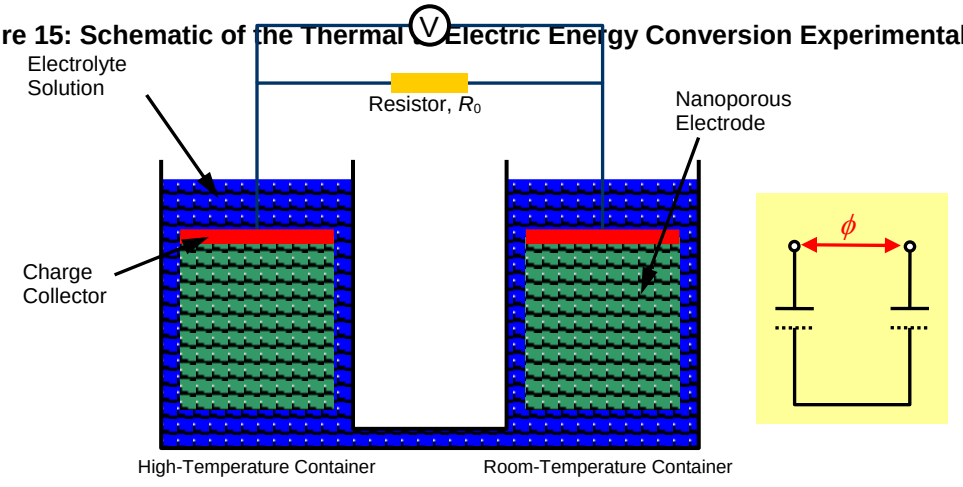
37 http://energyalmanac.ca.gov/electricity/total_system_power.html

would be less than this estimate that assumes 100 percent recovery. However, this calculation establishes that waste heat has a large potential economic value to California.

The advancement of science or technology that was proposed in this project was to harvest the waste heat with a novel heat to electricity direct conversion method entitled nanoporous thermal electric energy conversion system (NTEEC). The NTEEC system is shown schematically in Figure 15. It is based on the phenomenon that when an ionic electrolyte is in contact with a conducting electrode, a surface charge density is induced on the electrode, resulting in a net charge on the electrode surface. The amount of induced charge depends on materials properties of the electrode and, importantly, the temperature of the electrode. The difference of surface charge density on electrodes in cells at different temperatures determines the potential difference between the electrodes. The so-called zeta potential of the cells, dϕ/dT, controls system efficiency. To optimize the zeta potential, the researchers proposed to study new electrode materials of ultra high specific surface area material including nanoporous carbon and nanowires of metallic gold. Electrolyte solutions of greatest interest for study were highly polarizable aqueous solutions of alkali halides for temperatures below 100° C and ionic solutions for higher temperatures. While continuous operation would appear to be possible in principle, the researchers proposed a transient cyclical alternating mode of operation with two two-cell systems. In operation, one side of a two-cell system would be heated and the other side kept at ambient temperature to develop a potential difference with no electrical connect and current flow. Once charged with heat, the heat source would be removed and electrical contact established, causing an electron current to flow through the load resistor and an ionic current through the connecting channel. As the high temperature cell cooled, it would deliver electricity to the load. While one two-cell system was delivering electricity and cooling, the other system was reheated. In this way a net positive dc voltage could be maintained across the load.

Figure 15: Schematic of the Thermal to Electric Energy Conversion (NTECS) Experimental Setup. The potential difference between the two sides is illustrated on the right.

Figure 15: Schematic of the Thermal to Electric Energy Conversion Experimental Setup



2.12.3 Objectives

The goal of this project was to determine the feasibility of the new concept of thermal to electric energy conversion using nanoporous electrodes, demonstrating that the system can work reliably and in a cost efficient manner and that it can be adjusted to satisfy the diverse functional requirements of various applications. The researchers established the following project objectives:

1. Finalize system design. Complete documentation of materials processing and structural design.
2. Fabricate 15 single unit prototypes of various system parameters. The best prototype will demonstrate 1 W capacity and an energy conversion efficiency > 90 percent of Carnot cycle limit. Compare and analyze the performance of these prototypes.
3. Fabricate a multiple unit network. The network will consists of 100—1000 units, demonstrating ~1 kW capacity and an energy conversion efficiency > 80 percent of Carnot limit.
4. Conduct prototype testing. Measure energy conversion efficiency. Measure power density. Demonstrate efficiency > 80—90 percent of Carnot limit. Demonstrate power density > 1 W per unit (or 1 kW per network).
5. Develop a design protocol. Identify the suitable ranges of design variables for different power and working requirements.
6. Identify suitable initial market niche. Based on the findings of this project as well as additional market research, identify suitable initial markets in preparation for the next step of commercialization.

2.12.4 Outcomes

1. The researchers designed an experimental testing system. They provided documentation of materials processing and structural design.
2. The researchers fabricated more than 15 single unit prototypes of various system parameters. The best prototype demonstrated 0.12 J capacity in transient one shot measurements. Cell power output was not measured. The researchers tried to measure the energy conversion efficiency calorimetrically, but the measurements were not satisfactory. The researchers compared the performance of the prototypes.
3. The researchers fabricated networks of up to 10 cells. They found network capacity closely followed the sum of the individual cell capacities, namely 1 J for a network of ten 0.1 J units. They did not measure power and efficiency.
4. The researchers attempted to measure prototype energy conversion efficiency, but the measurements were not successful. They did not measure power.
5. The researchers discussed designs and ranges of design variables for different power and working requirements.

6. The researchers investigated application of NTEEC results to the niche markets of concentrated solar thermal systems, concentrated solar PV systems, coal power plants, geothermal energy fields, and internal combustion engine electric motor powered hybrid cars.

2.12.5 Conclusions

1. The researchers achieved this goal.
2. The researchers achieved the goal to fabricate 15 single unit prototypes with various system parameters. They did not achieve the goal to demonstrate 1 W/unit. The goal of energy conversion efficiency > 90 percent of Carnot was not demonstrated because efficiency measurements were not successful.
3. The researchers did not achieve the goal of fabricating large networks of 100—1000 units.
4. The researchers did not meet the goal of conducting prototype testing of energy conversion efficiency and power density since efficiency was not measured. They did not demonstrate efficiency > 80—90 percent of Carnot and power density > 1 W per unit (or 1 kW per network).
5. Researchers achieved this goal.
6. Researchers achieved this goal.

Although the researchers did not demonstrate many of the specific performance goals, they did observe some good qualitative results. These results are not enough to prove that feasibility was established, but they are encouraging.

2.12.6 Recommendations

The Program Administrator recommends that the apparatus to measure energy conversion efficiency (and power) be improved. The calorimetric method seems a clumsy way to approach this. Apparently this approach was dictated by the original cell layouts of pre-proposal research that did not allow steady state operation due to output voltage sagging under load, possibly due to poor ion equilibration. The researchers' new cell design with a thin electrolyte conducting path with low thermal conductivity should allow the heated cell to be thermally well insulated. This should provide quasi-adiabatic operation with respect to the ambient. An internal resistive heater in the adiabatic chamber would allow convenient and more precise measurement of heat added. Heater power without an external electrical load connected would establish the level of heat lost to the ambient to be corrected for. Heater power with a load connected would allow a determination of extra heat supplied and comparison with measured power delivered to the load would determine efficiency. Outcomes of this would be demonstration of steady state operation. The independent measurement of voltage and current would yield maximum power point for a device.

The Program Administrator recommends that the rate of ion equilibration in and around the electrodes be examined. Very useful information might be obtained by stirring the electrolyte during electrical load. Increased electrical power output with stirring would point to poor ion equilibration. This could guide the development of electrodes of improved physical design. If

steady state operation could be achieved, it would greatly simplify operation. If steady state operation is not possible for some fundamental reason, it is important to characterize the issue for optimizing non-steady state operation.

2.12.7 Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the ratepayer from this research is increased affordability of electricity. The potential savings to the California ratepayer is large because the amount of waste heat produced and dissipated to the environment is large. The U.S. consumes about 100 quads of energy a year. A quad is a quadrillion (10^{15}) Btus that is equivalent to about $2.93X10^{13}$ kWh of energy. Of the 100 quads of energy consumed per year, 55 percent to 60 percent gets lost as waste heat. Based on a per capita estimate, California's share of this waste heat is estimated to be in the range of 5—10 quads. Ten quads of energy are equivalent to $2.93X10^{12}$ kWh of energy. If this could be converted to electricity with 10 percent efficiency, it would represent 293,000 GW-hr of electricity, nearly equal to California's annual electricity production in 2010, in state plus imports, of 290,187 GWh. For an electricity price of $0.10/kWh, this would be an annual economic benefit to California ratepayers of $29B. Clearly actual benefits would be less than this estimate that assumes 100 percent recovery. This calculation establishes, however, that waste heat has a large potential economic value to California.

2.12.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

The researchers and UCSD have formed a company, ThermoCreek, Inc., to connect the technology to the marketplace. Once the system is fully developed, the researchers plan to follow the results of the marketing research. They speculate that the initial market will be the geothermal energy, and the final goal will be the wasted heat in power plants. They will consider other markets, such as vehicle engines and energy harvesting for bio-devices.

Engineering/Technical

The researchers plan to continue the technical work using a SBIR grant.

Legal/Contractual

UCSD and a spin off company, ThermoCreek, Inc., have received a $150,000 SBIR grant to continue the research.

Environmental, Safety, Risk Assessments/ Quality Plans

It is premature to pursue environmental and quality plans at the stage of the project.

Production Readiness/Commercialization

At this stage of development, commercialization is premature.

2.13 Innovative Biogas Hydrogen Sulfide Removal Technology

Awardee: Iowa State University

Principal Investigator: Shihwu Sung

2.13.1 Abstract

The goal of this project was to determine the feasibility of an innovative biogas hydrogen sulfide removal technology that improves biogas utilization for electricity generation in California. The proposed technology combines sulfide laden biogas with approximately 10 percent air within a sulfide oxidizing unit (SOU) to promote chemical precipitation of elemental sulfur. The researchers fabricated and tested pilot and full scale SOUs that successfully demonstrated the reduction of hydrogen sulfide (H_2S) to levels compatible with natural gas pipeline blending, fuel cell, and internal combustion engine applications. A full scale study at the Amana cattle farm in Iowa showed H_2S influent concentrations reduced to 10 ppm from1,300 ppm under a sulfide loading rate of 3.75 g-S/m^3-SOU-hour. Another full scale study at the SPM swine farm in Thailand resulted in reductions of influent H_2S to less than 200 ppm from 2,000 ppm under a sulfide loading rate of 25 g-S/m^3-SOU-hour. The researchers found that the medium's pH, alkalinity, temperature, and loading rate significantly affected the performance of the SOU sulfide removal system. The researchers were only able to recover approximately 25 to 45 percent of the elemental sulfur predicted using mass balance calculations.

Keywords: Anaerobic digester, sulfide removal, oxidation of sulfide, micro aeration

2.13.2 Introduction

Biogas produced from anaerobic digestion containing 50 percent to 70 percent methane can be used as a renewable energy source. However the presence of sulfur compounds in manure hinders the utilization of biogas. Anaerobic digestion of influents containing sulfur compounds results in hydrogen sulfide (H_2S) which is odorous, highly toxic, and corrosive. H_2S must be below 100 ppm for use in an internal combustion engine, below 10 ppm for fuel cells, and below 4 ppm for blending into natural gas pipelines.[38] Human health is affected at 10 ppm and death

38 S. M. Zicari, *Removal of Hydrogen Sulfide from Biogas using Cow-Manure Compost*. MS Thesis, Cornell University (2003).

is imminent at 600 ppm.[39] Consequently sulfide emissions are regulated through the 2007 California Air Resources Board (CARB). Removal of post combustion sulfide emissions is cost prohibitive in many cases, resulting in underutilization of biogas as a potential energy source. Although there are 5.2 million cattle raised in California, presently less than 1.0 percent of biogas from livestock manure is recovered as electricity.

The researchers proposed to convert H_2S into elemental sulfur through the use of a sulfide oxidizing unit (SOU) shown in Figure 16. They combined sulfide-laden biogas resulting from anaerobic digestion of agricultural waste with 10 percent air within the SOU where the sulfide oxidized to form elemental sulfur. They carefully controlled the oxidation reduction potential (ORP) to maximize the oxidation and sulfur production. The researchers performed tests by varying ORP, pH, alkalinity, temperature, and influent flow rate to optimize sulfide removal. They used mass balance calculations to estimate the maximum sulfide removal. Both pilot and field studies showed only 25 percent to 45 percent sulfur recovery, assuming that elemental sulfur was the only product in the reaction. The researchers anticipated the sulfur to precipitate and separate via gravity at the bottom of the SOU. However, it is likely that sulfur was lost through the effluent, attached to the surface of the SOU and diffuser or suspended in floating scum. Centrifugation of the gravity settled sludge indicated that sulfur cake contained 35 percent to 50 percent sulfur, along with other organic impurities. Ideally the sulfur sludge cake could be blended with nutrients and used as an organic fertilizer.

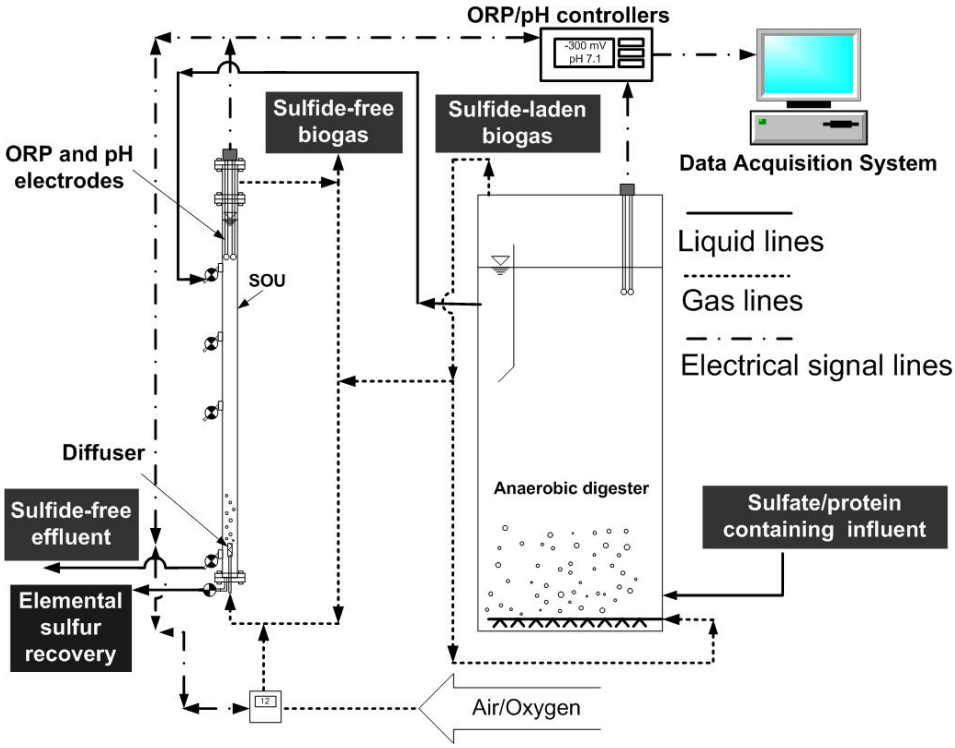
The proposed technology may be used alongside both agricultural and industrial anaerobic digesters. The researchers estimated that 60 percent of the waste treatment facilities in California have anaerobic digesters with sulfide-laden biogas which would benefit from this technology.

Incorporation of the SOUs into the existing processes would reduce sulfur emissions by 200 tons to 400 tons per year and render the biogas into a viable energy source capable of providing electricity for approximately 758 thousand people.[40]

39 R. L. Droste, *Theory and Practice of Water and Wastewater Treatment*. John Wiley & Son, Inc. (1997).

40 R. E. Brown and J. G. Koomey,"Electricity Use in California: Past Trends and Present Usage Patterns." *Energy Policy* 31(9), (2003), pp.849-864.

Figure 16: Schematic of the Integrated Sulfide Removal System



2.13.3 Objectives

The goal of this project was to determine the feasibility of an innovative biogas hydrogen sulfide removal technology that improves biogas utilization for electricity generation in California. The researchers established the following project objectives:

1. Build the SOU for existing anaerobic digesters of a 5,000 head cattle farm at capital cost less than $200/kW.
2. Demonstrate sulfide emissions of less than 100 ppm and sulfide removal rate more than 40 g/m^3/hr. Note that this objective is the one originally proposed. The final report modified the objective by reducing the removal rate for 100 ppm sulfides to 30 g/m^3/hr.
3. Demonstrate sulfide emissions of less than 4 ppm and sulfide removal rate more than 30 g/m3/hr. Note that this objective is also the one originally proposed. The final report included alternate objectives as follows:
    a. Sulfide emissions of less than 10 ppm and sulfide removal more than 35 g/m^3/hr.
    b. Sulfide emissions of less than 1 ppm and sulfide removal more than 40 g/m^3/hr.
4. Demonstrate that the sulfur solid is dewatered to more than 20 percent solids by mild pressure. Demonstrate potential beneficial use as soil conditioner.
5. Confirm the proposed operating cost of less than $0.1/lb H_2S removal.
6. Disseminate the innovative technology to Sacramento regulators and policy makers including the California Energy Commission staff and the California Air Resources Board.

2.13.4 Outcomes

1. Design and construction of the SOU for the Amana cattle farm were modeled after the pilot scale SOU with a goal of H_2S removal to less than 10 ppm in the biogas. The SOU volume of 100 m^3 was required to accommodate a biogas production rate of 6,882 m^3/day and sulfide removal rate of 10 g/m^3-SOU/hour, resulting in a cylinder 3.2 m in diameter and 30 m long. Active liquid heights ranged from 1.5 to 2.3 m. The SOU included a programmable logic controller to monitor and regulate influent flow, pH, ORP, and airflow. The capital expenditure for the Amana cattle farm SOU was $245/kW and operational costs totaled $1.81/lb of sulfur removed.

2. Field studies were performed at the Ames Water Pollution Control Facilities (AWPCF) facility using three media under various operating conditions: plant effluent, mixed liquor, and digester supernatant. The SOU demonstrated the greatest H_2S removal efficiencies with the digester supernatant. Several trials were able to achieve a sulfide concentration below 100 ppm with loading of greater than 40 g/m^3/hr with operating conditions as follows:

Table 2:

Fluid height (m)	pH	ORP	Sulfide Loading (g/m3/hr)	Sulfide at Outlet (ppm)
2.3	7.0	-215	42.5	83
2.3	7.5	-179	42.5	2
2.3	7.5	-183	45.5	3
1.5	7.5	-190	41.7	3
1.5	7.5	-239	59.6	17
1.5	7.5	-241	65.8	32

Three trials described in Outcome 2 above were able to achieve a sulfide concentration below 4 ppm with loading of greater than 30 g/m^3/hr with operating conditions as follows:

Table 3:

Fluid height (m)	pH	ORP	Sulfide Loading (g/m3/hr)	Sulfide at Outlet (ppm)
2.3	7.5	-179	42.5	2
2.3	7.5	-183	45.5	3
1.5	7.5	-190	41.7	3

3. These same three trials met the revised objective to achieve sulfide concentration below 10 ppm with loading of greater than 35 g/m3/hr. None of the trials met the revised objective to achieve sulfide concentration below 1 ppm with loading of greater than 40 g/m3/hr.

4. The researchers performed sulfur extraction using a centrifuge on gravity settled sludge samples collected from pilot and full scale SOUs. The centrifuge arm radius, operating duration, and rpm were 6 inches, 20 minutes, and 2000 rpm. Researchers measured the solids content of the sulfur sludge cake between 35 percent and 50 percent. Impurities in the sludge cake included microbial cell mass, organic solids, and debris. This extract may be blended with other nutrients to produce an organic fertilizer. Note that the sulfur cake included only 25 percent to 45 percent of the elemental sulfur anticipated based on mass balance calculations.

5. The researchers calculated operational costs for the three field SOU studies. They ranged from $1.26 to $4.49/lb sulfur removed.

6. During the course of the investigation the researchers met with several marketing partners to disseminate the technology. Additionally, the proposed technology has been presented in one peer reviewed publication and has been submitted for inclusion in additional publications.

2.13.5 Conclusions

1. The researchers successfully built the SOU for the Amana cattle farm, but exceeded anticipated capital expenditures. The SOU constructed for the SPM swine farm was closer to the goal, with capital expenditures totaling $231/kW. The capital outlay for either SOU was well below the alternative technology LO-CAT® (Merichem Company).

2. The researchers met the goal to reduce the sulfide outlet concentration below 100 ppm for loading rates greater than 40 g/m^3/hr.

3. The researchers met the goal to reduce the sulfide outlet concentration below 4 ppm for loading rates greater than 35 g/m^3/hr as originally proposed.

4. The researchers met the objective to extract more than 20 percent of the elemental sulfur from the SOU sludge. Although no scientific testing or analyses were performed to demonstrate the potential beneficial use of the sulfur cake extracted as soil conditioner, this is intuitively evident.

5. The researchers' calculated operational cost was 10 times higher than the target operational cost objective. Although the original objective appeared to be targeted at matching the operational costs of the alternate technology, LO-CAT®, the proposed technology could be more cost effective due to lower capital costs.

6. The researchers met the goal to disseminate information through their final report, peer reviewed publications, and marketing efforts.

2.13.6 Recommendations

The researchers were successful in proving the viability and cost effectiveness of the proposed technology. Although they were able to gravity settle and extract less than half of the elemental sulfur precipitate, the beneficial use of this byproduct as fertilizer is secondary to the more significant benefit of improving the quality of biogas so that it may be less toxic and more readily used as an environmentally friendly fuel source. This technology appears to be cost effective, safe, and directly beneficial to most anaerobic digester installations as part of a new installation or retrofit. The researchers plan to continue development of the proposed technology through to commercialization. As part of continued development of this technology, the Program Administrator recommends that the following tasks be completed:

1. Investigate methods to more efficiently capture elemental sulfur precipitate.
2. Perform a more thorough parametric study to identify the range of operating conditions (flow rate, pH, alkalinity, temperature, etc.) under which the technology is beneficial.
3. Perform a life cycle cost analysis.
4. Perform a detailed market analysis and pursue commercialization.

After taking into consideration (a) research findings in the grant project, (b) overall development status, and (c) relevance of the technology to California and the PIER program, the Program Administrator has determined that the proposed technology should be considered for subsequent funding within the PIER program.

Receiving subsequent funding ultimately depends upon (a) availability of funds, (b) submission of a proposal in response to an invitation or solicitation, and (c) successful evaluation of the proposal.

2.13.7 Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the public from this research is increased affordability of fuel in California. Currently only 0.7 percent of biogas from livestock manure is recovered as electricity in California.[41] The vast majority of the biogas from agricultural digesters is unusable due to

41 J. Sloe, "Biogas, A Growing Niche for Distributed Generation," *E-Source*, DE-21, (May, 2003).

high sulfur content. The researchers estimated that removal of sulfur from the biogas would allow for recovery of biogas methane sufficient to provide electricity for 758,000 people. In addition to decontaminating a significant amount of otherwise unusable biogas, this technology could reduce sulfur emissions from water pollution control facilities by 200 tons to 400 tons per year in the state of California. Further, the removed sulfur could provide a valuable source of fertilizer.

2.13.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

The researchers have performed a market analysis and have prepared a preliminary business plan. This technology is applicable to all anaerobic digesters, but would be most beneficial for agricultural digesters that face significant sulfur contamination.

Engineering/Technical

The technology relies on simple chemical reactions. Although the researchers will work toward more efficient elemental sulfur capture, this benefit is secondary to the proven ability to reduce hydrogen sulfide levels in anaerobic digester biogas to meet operational requirements.

Legal/Contractual

The researchers have performed a patent search and filed for a patent through Iowa State University.

Environmental, Safety, Risk Assessments/ Quality Plans

Environmental, Safety, Risk Assessments, and Quality Plans have not yet been developed. The researchers do not anticipate negative effects with regard to public safety or to the environment since no chemicals are used for treatment and no hazardous materials are generated.

Production Readiness/Commercialization

The researchers have not developed a commercialization plan and will need support to pursue commercialization.

2.14 Printing Low Cost Solar Cells with Ultrasonic Ejection

Awardee: Alion, Inc

Principal Investigator: Mark Topinka

2.14.1 Abstract

The objective of this project was to develop low cost PV cells using printing techniques. Photovoltaic (PV) electric generation is an emissions free source of energy. High up front capital cost of PV generation is the main disadvantage to the California ratepayer for widespread adoption of PV generation. To address the high cost of PV solar installations, this Energy

Innovations Small Grant provided the resources for developing a new low cost thin film PV manufacturing method: ultrasonic printing.

Prices of solar cells have been decreasing rapidly during the past two years due to increased manufacturing capacity and improved technologies. Thin film solar panels are the cost leaders of the PV industry. For example, Sun Electric advertises solar panels at prices between $0.98 and $2.00 per watt with many at $1.28 per watt.[42] Using ultrasonic ejection to print thin film photovoltaic modules, the researchers attempted to develop an even lower cost manufacturing technique. Their proposed technology would directly pattern every layer of a thin film PV module without using expensive vacuum equipment. The researchers thought this new method would leapfrog both current vacuum deposition techniques as well as other non-vacuum deposition techniques being developed in industry. The researchers expected to produce thin film PV modules for well below $1/watt and to sell modules profitably for $1/watt.

During the execution of this grant, the researchers learned that acoustic printing has throughput limitations that make it unsuitable for PV module manufacturing. However the researchers proceeded with development of alternative deposition techniques that they claimed could ultimately lead to low cost solar power for the California ratepayer. They did not describe the new technology that they plan to pursue.

Keywords: Photovoltaic, printing, low cost manufacture

2.14.2 Introduction

Photovoltaic (PV) electric generation is an emissions free source of energy. The high up front capital cost of PV generation is the main disadvantage to the California ratepayer for widespread adoption of PV generation. To address the high cost of solar installations, this Energy Innovations Small Grant provided the resources for developing a new low cost thin film PV manufacturing method: ultrasonic printing. Thin film solar cells on the market today are the cost leaders of the PV industry. For example, First Solar, Inc. produces more than 1 GW/year of thin film PV modules at a manufacturing cost of less than $0.80 per watt. See Table 4.

42 www.sunelec.com

Table 4: Photovoltaic Manufacturing Cost Models

	Unit	Alion cost model	First Solar model
Key parameters			
Module efficiency		10%	11%
Uptime		0.9	0.9
Yield		0.95	0.95
Cost structure			
Material	$/Wp	0.35	0.41
Labor	$/Wp	0.06	0.08
Other	$/Wp	0.08	0.12
Unyielded Manufacturing Costs	$/Wp	0.49	0.61
Cost of lost yield	$/Wp	0.02	0.03
Yielded Manufact. Cost	$/Wp	0.51	0.64
Depreciation Cost	$/Wp	0.08	0.12
Total Unit Cost	$/Wp	**0.60**	**0.76**

Using ultrasonic ejection to print thin film photovoltaic modules, the researchers attempted to develop an even lower cost manufacturing technique. By providing the means to pattern directly every layer of a thin film PV module without using expensive vacuum equipment, their printing technology attempted to leapfrog both current vacuum deposition techniques as well as other non-vacuum deposition techniques being developed in industry. Acoustic printing works by focusing an ultrasonic pulse on the surface of a liquid. When the acoustic pressure of the focused pulse exceeds the surface tension of the liquid, a single liquid droplet is ejected. Compared to vacuum deposition, the current state of the art for fabricating thin film solar panels, acoustic printing offers lower capital, energy, and maintenance costs along with reduced capital costs.

The researchers expected to produce thin film PV modules for well below $1/watt and to sell modules profitably for $1/watt. During the execution of this grant, the researchers successfully built and tested an acoustic printer. They learned that acoustic printing has throughput limitations that make it unsuitable for PV module manufacturing. However the researchers

subsequently developed alternative deposition techniques that could ultimately lead to low cost solar power for the California ratepayer.

2.14.3 Objectives

The goal of this project was to demonstrate the feasibility of acoustic printing, a low cost deposition technique for manufacturing thin film photovoltaic panels. The researchers established the following project performance and cost objectives:

1. Demonstrate a single ejector capable of printing droplets of particle loaded slurry at a unit cost per print head of less than $200.
2. Demonstrate a translation stage capable of digitally moving the printhead relative to substrate at 100 mm/sec with 0.05 mm resolution.
3. Demonstrate continuous printing of 1.0 micron particles across 10 cm^2 without nozzle clogging.
4. Demonstrate printed film with maximum resistivity of 100 ohm/square.
5. Demonstrate a printed line with maximum width 100 microns and maximum linear resistance of 10 ohms per cm.
6. Develop and demonstrate the capability to print all necessary active layers of a 5 percent efficient CIS, CIGS a-Si, or CdTe thin film solar cell.
7. Confirm that printing solar cell materials is achievable for a cost of less than $60 per square meter and a capital cost of $0.30/watt.

2.14.4 Outcomes

1. The researchers successfully constructed printheads capable of printing particle loaded slurry with 16 ejectors. The material cost of the printhead in small volumes was less than $100 including the piezoelectric actuator and aluminum lenses. Estimated unit production cost in volume of printheads was less than $100.
2. The researchers installed a programmable XY stage capable of moving at 400 mm/sec with 0.001 mm resolution.
3. The researchers printed 10 cm^2 of 1 micron CdTe particles as well as conductive Ag particles. They printed graphite, CdTe, and silver films with no nozzle clogging. However printhead throughput was insufficient for large scale manufacturing.
4. The researchers demonstrated high conductivity printed Ag with resistivity less than 1 ohm/sq as measured by a four point probe.
5. The researchers demonstrated high conductivity printed Ag strips.
6. Although they determined acoustic printing to be unsuitable for photovoltaic module manufacturing, the researchers used alternative non-vacuum techniques developed with internal funding to demonstrate a 5.7 percent efficient solar cell.
7. The researchers built financial models based both on top down competitor analysis and bottom up manufacturing costs. The models converged on manufacturing costs less than $60 per square meter and capital costs higher than the initial estimate. Depending on the factory configuration, capital cost model estimates ranged from $0.35 to 0.70/watt.

2.14.5 Conclusions

The researchers successfully designed, built, and tested an acoustic printer. During the project the researchers determined that acoustic printing is not well suited to material deposition for solar panels. The researchers cited throughput limitations of the proposed technique as their reason for abandoning that technology. They continued internal development of other non-vacuum deposition techniques suitable for low cost PV manufacturing. The researchers stated that they did not prove feasibility of the original proposed technology.

2.14.6 Recommendations

It is not possible to provide recommendations for future engineering development. Because of the intense worldwide competition in solar panels, the Program Administrator recommends that the researchers reduce their target selling price from $1.00 per watt to $0.5 per watt.

2.14.7 Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the ratepayer from this research is reduced environmental impacts of the California electricity supply or transmission or distribution system. Replacing 20 percent of CO_2 emitted by California electricity generation in 2004 by widespread adoption of solar energy would eliminate 150 MT/yr of carbon emissions.[43]

Reduced cost of solar panels could translate into lower costs to California ratepayers for utilities to meet mandated RPS standards. Hundreds of millions of dollars of savings are possible if the 1 GW+ of permitted PV projects[44] in California were built with solar panels at a price of $1/W instead of the $1.5/W price of solar panels used as a basis for the analysis. Because of the severe worldwide competition to gain dominance in the solar panel business, prices continue to drop. In some cases specific solar panels are selling for considerably less than $1 per watt. Any new entrants into this market should target selling prices of $0.5 per watt.

2.14.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

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43 *Inventory of California Greenhouse Gas Emissions and Sinks: 1990 to 2004*, Staff Report, Publication # CEC-600-2006-01

44 *Status of RPS Projects*, Mar. 1, 2011, www.cpuc.ca.gov/PUC/energy/Renewables

Marketing/Connection to the Market

The researchers indicated that they had performed a market analysis and sized the potential market for new non-project technology at about $1 billion/year, growing at 30 percent per year.

Engineering/Technical

The researchers stated that they had abandoned the technology proposed for this project and instead adopted another unspecified technology that was funded with their internal funds.

Legal/Contractual

The researchers claim no patents for the project technology. Environmental, Safety, Risk

Assessments/ Quality Plans

The researchers made no statements regarding any of these plans for the proposed technology or for the adopted technology.

Production Readiness/Commercialization

The researchers plan to commercialize the technology developed outside of this grant without partnering with another organization.

2.15 High Efficiency Nanowire LEDs for Solid State Lighting

Awardee: UC San Diego

Principal Investigator: Deli Wang

2.15.1 Abstract

The goal of this project was to determine the feasibility of using new nanomaterials as electrodes and high efficiency phosphors for injection light emitting devices (i-LED). The researchers estimated that the new design would operate at 100 lm/W. The project encompassed the development, fabrication, and testing of light emitting diodes using a cathode and anode of novel design. The cold cathode employed field emission of electrons from a carbon nanotube (CNT) planar array. The emitted electrons were accelerated through a vacuum to bombard a novel planar anode structure of vertical ZnO nanowires. The ZnO nanowires emitted UV radiation by cathodoluminescence. The researchers showed that low cost commercial phosphors painted on the anode structure emitted visible RGB light by photoluminescence under the UV bombardment. After vacuum chamber testing of the bare components, the researchers fabricated prototype devices sealed in vacuum tubes and conducted preliminary tests including color-tuning analysis. The initial results from the prototype devices with green and blue phosphors indicated that light emission efficacy of green and blue light greater than100 lm/W is possible and lifetime could be greater than 15,000 hours. The researchers finalized the light bulb design and performed an initial manufacturing cost analysis and lifetime study. They estimated light bulb cost at less than $4.

Keywords: LED, CNT array, field emission, light emission, ZnO nanowire array, I-V measurements, color tuning

2.15.2 Introduction

Lighting comprises approximately one-fourth of California's electricity use.[45,46] Therefore the practical efficiency of light producing lamps is of great importance to the ratepayer. Practical efficiency is the amount of light energy output that can be seen by the human eye per electrical energy input to the lamp. Lumen (lm) is a unit of luminous flux that is a measure of the total amount of visible light or flux emitted by a source. Luminous flux differs from radiant power in that luminous flux measurements reflect the varying sensitivity of the human eye to different wavelengths of light, while radiant flux measurements indicate the total power of all light emitted, independent of the eye's ability to perceive it.[47] Thus the measure of practical lamp efficiency is termed lamp efficacy. It is measured in lumens per watt (lm/W). Today there are a variety of commercially available lamp types including incandescent, halogen, ceramic metal halide, fluorescent tube, compact fluorescent (CFL), high pressure sodium, and light emitting diode (LED).[48] For a variety of reasons involving color rendering and convenience, attention has been focused most on incandescents, CFL, and LED. The efficacy of these lamps varies from 10 lm/W to 15 lm/W for incandescents, 60 lm/W to 70 lm/W for CFLs, and approximately 100 lm/W for LEDs. The incandescent bulb has the advantage of very low cost but suffers from low efficacy and thus high power consumption. The CFL has good efficacy and moderate cost but requires toxic mercury for its operation, thus making its end of service disposal problematic. The LED has good efficacy, and thus good useful light output at low power, but suffers from high cost per lamp. If a low cost LED lamp could be developed, it would be a source of great benefit to the ratepayer.

The scale of this benefit is seen in the fact that California ratepayers consume 265,000 gigawatt hours of electricity per year.[49] Assuming an average electricity cost of $0.10/kWh, this electrical consumption represents a cost of $26.5 B per year to ratepayers. Since lighting is responsible for about one-fourth of this consumption, California lighting has an annual cost of about $6 B. California's AB 1109, known as the Huffman Bill, mandates the phase-out of traditional, low efficiency incandescent lamps by 2018. However supporting strategies and implementation activities are needed to achieve the higher goal of a 60 percent to 80 percent reduction in energy usage for lighting. Furthermore, the Huffman Bill requires California to reduce average statewide electrical energy consumption by not less than 50 percent from the 2007 levels for indoor residential lighting and not less than 25 percent from the 2007 levels for indoor commercial and outdoor lighting by 2018. It is thus apparent that a low cost more efficient LED

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45 http://www.cpuc.ca.gov/NR/rdonlyres/6234FFE8-452F-45BC-A579-A527D07D7456/0/Lighting.pdf

46 California Energy Commission, *California Energy Demand 2003-2013 Forecast: Staff Report in Support of the Electricity and Natural Gas Report under the Integrated Energy Policy Report Proceeding* (02-IEP-01), August 2003.

47 http://hyperphysics.phy-astr.gsu.edu/hbase/vision/lumpow.html

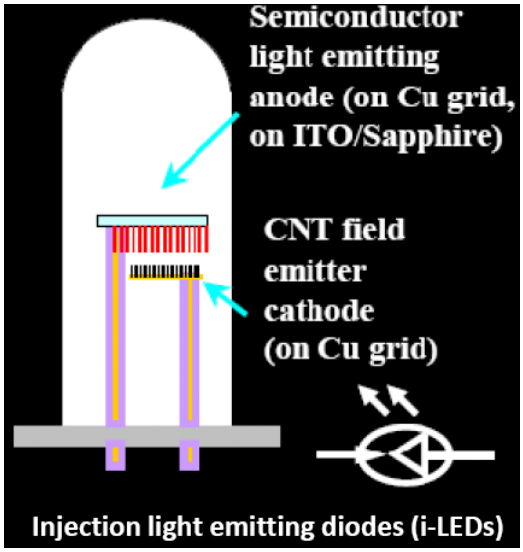
48 http://www.eleekinc.com/eleekchart.pdf

49 http://www.cpuc.ca.gov/cfaqs/howhighiscaliforniaselectricitydemandandwheredoesthepowercomefrom.htm

lamp offers California ratepayers a potential electricity savings of several billion dollars per year. But LED luminaries will be very expensive.

To achieve these savings, the advancement of science or technology proposed in this project was the development of a new LED device that could replace incandescent and compact fluorescent light bulbs. The light-emitting module would be sealed in a vacuum enclosure similar to a vacuum tube diode for a practical device. The proposed new LED consisted of a high efficiency field emission cathode constructed of carbon nanotubes (CNT) and a fluorescent semiconductor anode constructed of a mixture of cathodoluminescent nanowires. The electrons ejected from a field emission cathode gun were injected into a mixture of semiconducting nanowires (such as ZnO, GaN, InGaN, GaAs, CdSe) in the anode and recombined with holes and emitted white light as a result. See Figure 17. During the course of the project the researchers modified this approach. The new device promises enhanced energy efficiency and is estimated to consume only 1/10 of the power used by an incandescent light bulb and 1/2 of that by a CFL. In addition, the new light source operates at much lower temperatures than an incandescent light bulb and can utilize existing vacuum tube manufacturing facilities, which holds great potential for socket replacement of incandescent light bulbs. The new light source provides richer color rendering than a CFL by using different semiconductors as light emitting anodes and promises natural white light. In addition, it is dimmable and scalable, is mercury free, and does not need ballast.

Figure 17: Design Concept and Prototype Device of Nanowire Based Electron Injection LED (i-LED)



Anode with vertical nanowire arrays and cathodewith multi-wall carbon nanotubes would be sealed in a vacuum tube.

2.15.3 Objectives

The goal of this project was to determine the feasibility of using new nanomaterials as electrodes and high efficiency phosphors for injection light emitting devices (i-LED). The new light source could increase light emission efficiency, provide rich colors (RGBW), give more

natural white light, be dimmable, and be Hg free. The researchers established the following project objectives:

1. Fabricate electron emission cathodes using CNT arrays using both electrophoresis and stamping methods. Demonstrate electron emission efficiency < 2 V/micron in a vacuum.
2. Grow designed nanowires ZnO (UV-Blue), ZnCdO (Green), AlInAsP (Red), and fabricate fluorescent anodes. Test the photoluminescence using a spectrometer. Test the emission color spectra in RGB for different nanowires and white emission from a mixture of the nanowires (color temperature between 3,000 K and 5,000 K). Find the right composition of the RGB nanowires for white light emission.
3. Fabricate i-LED electrode modules and test them in a vacuum chamber. Measure the electroluminescence and spectrum for white light emission, with main peaks of emission to be in the range of 450 nm—700 nm and color temperature between 3,000 K and 5,000 K. Measure I-V characteristics.
4. Manufacture i-LED devices at E-beam, Inc. Enclose the i-LED modules in a vacuum tube. Perform initial test for I-V characteristics.
5. Test prototype i-LED light bulbs at UCSD. Demonstrate white i-LEDs. Measure light emission efficiency, brightness, color temperature, CRI, lifetime. Finalize i-LED module, light bulb design and fabrication process. Demonstrate 100 lm/W. Demonstrate brightness of 900 lumens. Demonstrate CRI > 90.
6. Perform manufacturing cost analysis. Confirm the projected $8 cost for a bulb with power efficiency of 100 lm/W and brightness of 900 lumens.
7. Perform life cycle cost analysis. Confirm that the projected lifetime is > 20,000 hours and life cycle cost is $45.76 or less.

2.15.4 Outcomes

1. The researchers fabricated electron emission cathodes of CNT arrays by the low cost method of forming a paste of CNTs in a solvent and binder that they applied to a substrate. They then evaporated the solvent and sintered the dried paste at 400^0 C. They removed CNT projected from the binder with adhesive tape. The CNT demonstrated electron emission at 750 V/micron in a vacuum.
2. The researchers grew nanowires of UV emitting ZnO for anode materials by hydrothermal growth, but not as a mixture of ZnCdO (Green), AlInAsP (Red), etc., as proposed. They demonstrated cathodoluminescence of the ZnO nanowires in the UV with a CNT field-emitting array. They fabricated these UV emitting anodes into planar CNT-ZnO diodes, and they painted the backside of the diode with commercial phosphors such as used in CFLs. In separate experiments they demonstrated that the UV emission caused different commercial phosphors to emit RGB radiation through photoluminescence. The researchers did not demonstrate white color from a nanowire anode mixture, and they did not perform associated color temperature measurements.

3. The researchers fabricated i-LED electrode modules with commercial phosphors that emitted only one color, not a mixture of different color photoluminescent phosphors. They did not measure a spectrum demonstrating white color. Neither did they measure associated color temperatures. The researchers successfully measured module I-V characteristics.

4. A collaborator's university laboratory fabricated a prototype i-LED device enclosed in its own vacuum tube enclosure. The researchers performed initial tests for I-V characteristics.

5. The researchers conducted tests of I-V characteristics and light emission on the prototype at UCSD. They demonstrated RGB light emission. They presented normalized spectra from the individual phosphors. They did not quantitatively measure light emission intensity. They estimated intensity of 30—50 lumens but did not describe how they made the estimate. They stated that this estimated intensity would indicate an efficacy of 10—150 lm/W. They did not test white color and associated color temperature. They stated that brightness of 900 lumens at 9 W is possible. They did not perform CRI (color rendering index) tests.

6. The researchers carried out a manufacturing cost analysis. The projected bulb cost of $4 was based on an assumption of power efficacy of 100 lm/W and brightness of 900 lumens.

7. The researchers performed stress tests over periods of several days. Over this period diode current light output and device current appeared to be constant. They estimated a device lifetime to be greater than 15,000 hours. Under these assumptions, this lifetime is consistent with a life cycle cost of $45.76 or less.

2.15.5 Conclusions

1. The researchers successfully produced CNT arrays. They observed electron emission at a planar field intensity of 750 V/micron, exceeding the objective of < 2 V/micron (in vacuum). Thus they met this goal.

2. The researchers grew nanowires of ZnO (UV-Blue) but not anode mixtures of ZnCdO (Green), AlInAsP (Red), etc. Thus they met only a fraction of this objective. The researchers stated that they, “Modified the approach of using RGB nanowires (from MOCVD growth), which is costly and hard to scale up in a manufacturable fashion, to low cost solution grown ZnO nanowires plus commercial available phosphors."

3. The researchers fabricated i-LED electrode modules and tested them in a vacuum chamber. They measured module I-V characteristics but not spectrum for white light emission by cathodoluminescence and color temperature between 3,000 K and 5,000 K. Thus they met this objective only in part.

4. A collaborator's university laboratory fabricated a prototype i-LED device enclosed in its own vacuum enclosure. The researchers met this objective.

5. The researchers tested prototype i-LED light bulbs at UCSD. However they did not demonstrate a white i-LED. Neither did they measure light emission efficiency,

brightness, color temperature, CRI, lifetime, etc. They did not demonstrate an efficacy of 100 lm/W. They estimated, but did not measure, a brightness of 900 lumens. Thus they met this objective only in part.

6. The researchers carried out manufacturing cost analysis that estimated a projected manufacturing cost of $4 per bulb based on an assumed efficacy of 100 lm/W and assumed brightness of 900 lumens. The result exceeded the goal of $8 per bulb, thus meeting this goal.

7. The researchers estimated a lifetime of 15,000 hours. The goal was 20,000 hours. They confirmed a life cycle cost of $45.76 or less. Thus they partly met this objective.

The main goals of this project were to determine feasibility of using new nanomaterials as novel cathode and anodes in high efficiency white light emitting LEDs. The researchers successfully demonstrated CNT field emitting cathodes. These cathodes were used to produce UV light by cathodoluminescence of ZnO. It was originally proposed to bombard an anode consisting of a mixture of cathodoluminescent nanomaterials emitting light over the visible spectrum and thus white light. While they did not demonstrate this second goal, the researchers successfully demonstrated a single nanomaterial anode emitting in the UV. They used this UV anode to excite commercial phosphors that could in principle be combined in a mixture to produce white light by indirect photoluminescence rather than direct cathodoluminescence. Thus the researchers achieved one of the two goals.

2.15.6 Recommendations

The Program Administrator recommends that quantitative measurements of emitted light intensity be made to assess the promise of this technique for a practical device. The Program Administrator also recommends that a quantitative performance comparison be made between the approach taken in this project, cathodoluminescence coupled with subsequent light emission by indirect photoluminescence, to the original proposal of a direct cathodoluminescent anode of mixed RGB materials. There may be performance or cost advantages to the direct method. This comparison should be followed by a cost/benefit ratio analysis.

2.15.7 Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the ratepayer from this research is increased affordability of electricity in California. The scale of this benefit is seen in the fact that California ratepayers consume 265,000 GWh of electricity per year. Assuming an average electricity cost of $0.10/kWh, this electrical consumption represents a cost of $26.5 B per year to California ratepayers. Since lighting is

responsible for about one-fourth of this consumption, California lighting has an annual cost of about $6 B. California's AB 1109, known as the Huffman Bill, mandates the phase-out of traditional, low efficiency incandescent lamps by 2018. However supporting strategies and implementation activities are needed to achieve the higher goal of 60 percent to 80 percent reduction in energy usage for lighting. It is readily apparent that a low cost more efficient LED lamp offers California ratepayers a potential electricity savings of several billion dollars per year.

A secondary benefit is reduced environmental impacts of the California electricity supply or transmission or distribution system due to the absence of mercury present in CFLs.

2.15.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

The researchers have licensed the technology to a San Diego based startup company. That company is interested in commercialization.

Engineering/Technical

The researchers estimated three years to complete engineering development. The San Diego Regional Renewable Energy Technology Acceleration Fellowship awarded the researchers some follow-on funding. They plan to solicit additional funding from the DOE, SBIR, and STTR.

Legal/Contractual

The researchers filed PCT, US patents, and US provisional applications, serial number 61/119,938 and 61/121,333 and PCT/US09/62356. A San Diego based startup company that plans to commercialize the technology has licensed the patent.

Environmental, Safety, Risk Assessments/ Quality Plans

The researchers plan to conduct additional testing in these areas as they complete engineering development.

Production eadiness/Commercialization

As stated above, a San Diego based startup company has licensed the technology. That company is working on a commercialization plan.

2.16 Renewable Energy Through Purification of Low BTU Landfill Gas

Awardee: Pacific Consolidated Industries LLC

Principal Investigator: James Yang

2.16.1 Abstract

The process of converting high Btu landfill gas to a clean fuel to fire electricity generators has been well documented and demonstrated in actual industry practice. Conditioning of raw

landfill gas is necessary to remove particulates and liquids. Many landfills, however, produce gas with relatively low energy content. It is very difficult to produce electricity using low Btu gas (less than 40 Btu per cubic foot). Landfill operators typically flare gas with low energy content to meet air quality regulations, thereby losing the energy potential of this resource.

The goal of this project was to enhance methane concentration in low Btu landfill gas by investigating the use of the low energy vacuum swing adsorption (VSA) process (a lesser known variant of pressure swing adsorption) to remove CO_2, thereby enhancing the energy content of the product gas. Researchers performed experiments using eight different adsorbents for the VSA process on a test stand in a laboratory environment. Quantitative experiments on lithium exchanged LSX and magnesium (Mg) molecular sieving zeolite demonstrated that the methane (CH_4) content of low Btu gas could be increased from 33 percent to greater than 40 percent, an improvement of more than 21 percent. In addition, experiments on both these materials demonstrated that the VSA process can also increase the methane content in a 55/45 CH_4/CO_2 mixture to greater than 98 percent.

Additionally, the researchers attempted to determine whether the use of carbon molecular sieves, along with two types of molecular sieving zeolites which favor the removal of nitrogen (N_2) in a N_2/CH_4 stream, were able to remove significant amounts of nitrogen from the landfill gas. The research team discovered that the use of carbon molecular sieves was not able to remove significant amounts of nitrogen from the landfill gas.

Researchers estimated that the manufacturing cost to build a large biogas conversion plant that produces 1288 kilowatts (kW) at 35 percent gas-to-energy efficiency was approximately $466/kW. The life cycle cost per kilowatt of electric power produced for a large scale 1288 kW plant was estimated to be $1284/kW.

Keywords: Landfill gas, waste-to-energy, pressure swing adsorption, vacuum swing adsorption, low Btu

2.16.2 Introduction

The production and use of biofuels is encouraged by California state policy. Specifically, Assembly Bill (AB) 32, Senate Bill (SB) 107, SB 2 (1X), Executive Order S-06-06, and the 2011 California Bioenergy Action Plan make it abundantly clear that the goal of the state includes aggressively promoting renewable energy and alternative transportation fuels to achieve environmental goals.

In April 2006, Governor Schwarzenegger signed Executive Order S-06-06 directing state agencies to promote in-state bioenergy production and use. This legislative policy set the following targets to increase in-state production and use of bioenergy:

- Regarding biofuels, the goal was to produce a minimum of 20 percent of biofuels consumed within California by 2010, 40 percent by 2020, and 75 percent by 2050.
- Regarding the use of biomass for electricity, the goal was to meet a 20 percent target within the established state goals for renewable generation for 2010 and 2020.[50]

50 Minimum of 20 percent of RPS should come from the use of biomass for electricity.

The process of converting high Btu landfill gas to electricity has been well documented and demonstrated in actual industry practice. Landfill gas with adequate energy content must be conditioned to remove certain particulates and liquids that would otherwise be harmful to electric generating equipment. Conditioned gas is then used as feedstock to operate electric generation devices such as internal combustion engines, microturbines, or fuel cells. Landfill gas has varying levels of energy content measured by its British thermal unit (Btu) value or methane (CH_4) content.

Typically, landfill operators flare low Btu gas to meet air quality regulations. Otherwise it has no useful market value. The energy potential of flared gas is lost to the atmosphere. For low Btu landfill gas to have some useful purpose, it must be conditioned. For instance, the energy content of low Btu gas needs to be elevated (e.g., methane level must be at least 40 percent) to produce electricity in an internal combustion engine. Additional conditioning of the landfill gas is necessary if the gas is to be injected into the natural gas pipeline system.

There are other gas separation technologies in the marketplace today (such as liquid absorption, solid adsorption, cryogenics, and membranes) that can be used to enhance the quality and value of low Btu landfill gas. However, the capital costs and/or operating costs of each of these technologies have served as barriers to successful commercialization in this particular market space.

The goal of this project was to enhance methane concentration in low Btu landfill gas by investigating the use of the low energy vacuum swing adsorption (VSA) process, a lesser known variant of pressure swing adsorption, to remove CO_2, thereby enhancing the Btu content of the product gas. Researchers were also hoping that such a system could be used to remove nitrogen, the most predominant impurity in low Btu landfill gas.

The research team designed and built two single blower, single adsorption bed systems, each operating 180 degrees out of phase with the other. The two systems were intended to cycle so that feed could be continually processed: while one bed was in adsorption mode, the other bed was in desorption mode. Figure 18 shows a picture of a single adsorption bed system. The green colored motor drives the yellow colored blower to deliver feed landfill gas to the white cylindrical adsorption bed. After a set period of time the flow is reversed and the blower pulls suction on the adsorption bed, removing impurities from the bed. Both adsorption bed systems are now ready for field testing at a landfill site, a follow-on phase to this project.

Figure 18: Single Blower, Single Bed Prototype

Researchers performed experiments using eight different adsorbents in a laboratory environment. Figure 19 shows a picture of the test stand that was used for the research work.

Figure 19: Test Stand

Laboratory test results indicated that this concept has the potential of enhancing the energy content of low Btu gas and purifying it to a level that is suitable for electricity generation in a more cost effective manner compared to other alternatives. Quantitative experiments on lithium exchanged LSX and magnesium (Mg) molecular sieving zeolite demonstrated that the methane (CH_4) content of low Btu gas could be increased from 33 percent to greater than 40 percent, an improvement of more than 21 percent. In addition, experiments on both these materials demonstrated that the VSA process can also increase the methane content in a 55/45 CH_4/CO_2 mixture to greater than 98 percent.

Additionally, the researchers attempted to determine whether the use of carbon molecular sieves, along with two types of molecular sieving zeolites which favor the removal of nitrogen (N_2) in a N_2/CH_4 stream, were able to remove significant amounts of nitrogen from the landfill gas. The research team discovered that the use of carbon molecular sieves was not able to remove significant amounts of nitrogen from the landfill gas.

The use of VSA could reduce equipment capital costs. In addition, it consumes less power/energy compared with other separation processes including the well-known pressure swing adsorption process. Researchers estimated that the manufacturing cost to build a large biogas conversion plant that produces 1288 kilowatts (kW) at 35 percent gas-to-energy efficiency was approximately $466/kW. The life cycle cost per kilowatt of electric power produced for a large scale 1288 kW plant was estimated to be $1284/kW, assuming system life of

10 years and average electricity price of $0.10 per kWh. This includes parasitic electric load of approximately 120 kW.

The next step is to field test the concept at a landfill site to validate laboratory results and fine tune system design.

2.16.3 Objectives

The goal of this project was to enhance methane concentration in low Btu landfill gas by investigating use of the low energy vacuum swing adsorption (VSA) process (a lesser known variant of pressure swing adsorption) to remove CO_2, thereby enhancing the Btu content of the product gas. The researchers established the following project objectives:

1. Determine location of trace impurity adsorbent relative to blower.
2. Determine appropriate materials for siloxane, hydrogen sulfide, water vapor, carbon dioxide, and nitrogen removal.
3. Determine inlet gas system that comprises less than 35 percent methane.
4. Develop prototype.
5. Demonstrate measurement of post-heat exchanger temperature, pressures at the inlet and outlet of the adsorbent bed, product flow rate, the inlet and product methane concentrations, and system power usage.
6. Execute test plan.
7. Demonstrate methane content in product to be greater than 40 percent.
8. Calculate the manufacturing cost per kilowatt electricity produced for a proposed large scale system.
9. Calculate the life cycle cost per kilowatt electricity produced for a proposed large scale system.

2.16.4 Outcomes

1. The researchers identified two possible locations for trace impurity adsorbent depending on design conditions:
    - Place trace impurity adsorbent in the same bed used to remove more significant impurities such as CO_2 and N_2. This option is especially suitable for trace impurities that are more likely to be reversibly desorbed (perhaps H_2S).
    - Place trace impurity adsorbent in a small separate bed. This option is more suited for trace impurities that are more likely to be irreversibly adsorbed (perhaps siloxanes), thus requiring future bed replacement.
2. Several materials were used to remove specified impurities, including activated alumina, 13X zeolite, lithium exchanged LSX, 5A zeolite, two different carbon molecular sieves, a molecular sieving zeolite, a Mg exchanged form of the molecular sieving zeolite, and 4A zeolite.

3. The researchers produced gas with less than 35 percent methane in the laboratory for the experiments.
4. Researchers built two single blower, single adsorption bed systems which could also be used for field testing at a landfill site.
5. The researchers constructed an R&D test stand in the absence of a local landfill test site. The test stand replicated a two-bed vacuum swing adsorption process.
6. The researchers fully executed the test plan.
7. All experiments resulted in methane product concentrations greater than 40 percent and as high as 83 percent.
8. The manufacturing cost estimate for a large scale system that produces 1288 kW was $466 per kW.
9. The life cycle cost per kilowatt of electric power produced for a large scale 1288 kW plant was estimated to be $1284/kW.

2.16.5 Conclusions

1. Location of trace impurity adsorbent relative to blower depends on trace impurities that need to be removed for a particular application by reversible desorption or irreversible adsorption.
2. The outcomes show that 13X zeolite and lithium-exchanged LSX are the best materials for carbon dioxide removal.
3. Researchers were able to replicate landfill gas as a feedstock in a lab environment for purposes of this study.
4. Both single blower, single adsorption bed systems fabricated for this project are ready for further testing and validation at an actual landfill site.
5. The test stand fabricated by researchers successfully replicated the performance of a two bed vacuum swing adsorption process.
6. The test bed worked as designed.
7. Methane content level can be enhanced by removing CO_2 using VSA technology.
8. The manufacturing cost estimate of the proposed scaled-up version of the system appears to be reasonable.
9. The life cycle cost (per kilowatt of electric power produced) for a large scale plant appears to be reasonable.

Researchers were able to successfully demonstrate that the energy content of low Btu gas can be enhanced and purified to a level that is suitable for electricity generation using a VSA process. Quantitative experiments using various adsorbents showed that the methane (CH_4) content of low Btu gas could be increased from 33 percent to greater than 40 percent, an improvement of more than 21 percent. The research team was able to demonstrate that the VSA process can increase the methane content in a 55/45 CH_4/CO_2 mixture to greater than 98 percent. Capital and operating costs of the proposed concept are favorable compared to other separation processes such as the well=known pressure swing adsorption process. Finally,

researchers could not demonstrate that carbon molecular sieves can remove significant amounts of nitrogen.

The research team demonstrated that a vacuum swing adsorption (VSA) process could enhance the methane content in simulated low Btu landfill gas so that it can be used to produce clean, renewable electric power.

2.16.6 Recommendations

Researchers built a pilot scale unit that is now ready for demonstration at an actual landfill, but they found that many landfill operators are hesitant to explore new technology solutions. Low Btu gas is typically flared to meet air quality regulatory requirements. However there is growing interest in capturing low Btu gas and either converting it into electricity or injecting it into the natural gas pipeline system. To overcome some of the market barriers, the Program Administrator recommends the following actions:

- Complete a competitive analysis of other technologies such as thermal oxidation. The market analysis should also compare the merits of producing on-site electricity versus injecting conditioned gas into the natural gas pipeline system.
- Estimate the cost of a pilot test project at an actual landfill site and gain the cooperation of a landfill operator who is willing to explore advanced technology options as an alternative to flaring low Btu gas.
- Improve CH_4 recovery and N_2/CH_4 separation, possibly in collaboration with another scientist considered to be a leading expert in the field of N_2/CH_4 adsorptive separation activity.
- Conduct field testing to validate the performance and reliability of the technology in a real world working environment.
- Optimize system design and performance based on field testing.
- Develop a business/marketing plan to verify the market potential for this product and ensure that it compares favorably with other devices in the market.
- Perform a market study to determine the quantities of California landfill gases by Btu content. If most of the low Btu fuel targeted exists around 30—35 percent, then the approach taken here is complete. But if most is below 30 percent, the results shown here are not sufficient.
- Compare the cost of the new technology to simply enriching the low Btu gas stream by mixing in pure natural gas. This would be a simple calculation to demonstrate if the potential benefits are better or worse than a simple alternate option.
- Address the potential complications with trace impurities (siloxane, H_2S) found in real landfill gases.
- Develop a flow design with real operating parameters that will ensure maximum methane recovery with the highest Btu content.

After taking into consideration (a) research findings in the grant project, (b) overall development status, and (c) relevance of the technology to California and the PIER program, the Program Administrator has determined that the proposed technology should be considered for subsequent funding within the PIER program.

Receiving subsequent funding ultimately depends upon (a) availability of funds, (b) submission of a proposal in response to an invitation or solicitation, and (c) successful evaluation of the proposal.

2.16.7 Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the ratepayer from this research is reduced environmental impacts of the California electricity supply or transmission or distribution system.

California's three largest utilities (Southern California Edison, Pacific Gas and Electric, and San Diego Gas and Electric) collectively provided 18 percent of their 2010 retail electricity sales with renewable power. California utilities plan to provide 33 percent of all retail electricity sales from renewable power sources by 2020.[51] Researchers have estimated that this technology combined with on-site generation could produce up to 76.7 million kWh/year by enhancing the energy content of low Btu landfill gas in California. The market opportunity is quite large if the technology proves to be cost effective and landfill operators are willing to adopt a new technology with incremental revenue potential.

The proposed concept can help enhance the production of electricity from a largely untapped renewable resource, low Btu landfill gas that is normally flared because its CH_4 concentration level is not adequate to produce electric power. A 2005 report from the Center for Clean Air Policy estimates that California landfill methane emissions amount to 10.1 million metric tons CO_2 equivalent or about 481 gigagrams/year (in the year 2002).[52] The research team estimated that approximately 3.56 percent of total landfill methane emissions (about 17.1 gigagrams/year) could be classified as low BTU gas that is typically flared. The research team calculated that if the energy content of flared landfill gas could be concentrated to a level of 83.0 percent CH_4 recovery, a total of 7.67×10^7 kWh/year could be produced using internal combustion engine

51 Former California Governor Arnold Schwarzenegger signed Executive Order (EO) S-21-09 on September 15, 2009, directing the California Air Resources Board (CARB) to adopt regulations requiring 33 percent of electricity sold in the state come from renewable energy by 2020.

52 www.ccap.org/domestic/State/CCAP percent20- percent20methane.pdf

technology with an electric generating efficiency of 35 percent. The California Energy Commission (CEC) reported a per capita electricity usage of 6,732 kWh for 2003 in California.[53] Therefore low Btu landfill gas has the potential to meet the electricity needs of 11,393 people in California.

Another option for landfill operators to consider is injection of the enhanced conditioned gas into the natural gas pipeline system where it can then be subscribed for use by large combined cycle electric generating plants. This option is attractive because the electric generating efficiency of a large combined cycle plant is much higher (55 percent) than producing the electricity on-site (35 percent).

2.16.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Marke

The market opportunity is quite large if the technology proves to be cost effective and landfill operators are willing to adopt a new technology with incremental revenue potential. The researchers claim that lack of internal cash reserves and unclear market definition may lead landfill operators into cost share agreements with customers.

Engineering/Technical

Various design changes may be necessary for the technology to comply with all applicable codes and standards. The researchers speculated that any product resulting from this technology must be Class I, Div II compliant to satisfy some customers. The researchers stated that they could produce a small (30 scfm feed) demonstration unit in about one year for under $200,000.

Legal/Contractual

Researchers conducted a patent search and did not detect potential infringements on intellectual property. PCI has applied for one patent.

Environmental, Safety, Risk Assessments/ Quality Plans

The integrity of the system will need to be thoroughly tested to ensure it meets standard industry safety and permitting requirements.

Production Readiness/Commercialization

While the concept is not yet sufficiently developed for commercialization, PCI has in-house manufacturing capability to produce a product based on this technology. PCI has already built similar systems for other applications.

2.17 Undershot Impulse Jet Hydro-Turbine

Awardee: K.R. Broome and Associates

53 www.energy.ca.gov/electricity/us_percapita_electricity_2003.html (Appendix)

Principal Investigator: Kenneth R. Broome

2.17.1 Abstract

The purpose of this project was to physically verify the overall hydraulic/mechanical efficiency of a full-scale model of the Undershot Impulse Jet Hydro-Turbine (Hydro-Turbine), patented in 2009. This concept would make power generation feasible at smaller dams with a head of less than 15 feet, particularly on irrigation canals and rivers used for barge traffic. The researchers completed a full-scale verification testing program for three runner configurations at a test site located in Woodside, California, using recirculating water pumps.

The results of this test showed a much lower range of hydraulic/mechanical efficiency than was predicted by a computational fluid dynamic (CFD) model developed by the University of Iowa's Institute of Hydraulic Research. Actual efficiency measurements ranged from 12 percent to 21 percent, depending on the shape, depth, and number of vanes on the turbine runner, compared to projected efficiency levels of around 85 percent.

The researchers recognized the shortcomings of the University of Iowa's software and developed a more realistic CFD simulation model outside the scope of this project. With a better modeling tool in place, researchers plan to optimize the geometries of the turbine runner and nozzle orifice which shape the impulse jet and then validate the results by testing a two-foot diameter sub-scale model with adjustable geometry. The research team also plans to self-fund this incremental development work and to build a commercial scale 500 kW demonstration plant to validate the performance and reliability of the technology.

The researchers conducted a life cycle cost analysis that showed that this concept has the potential to deliver electrical power at a cost of $0.037 per kWh at 85 percent hydraulic efficiency. The cost would increase to $0.11 per kWh if only 20 percent efficiency were obtained. The market potential of low head hydropower applications in California is approximately 200 MW.

Keywords: Low head dams, irrigation canal drops, navigation lock dams, hydro-electric turbine, impulse jet, undershot, water level control

2.17.2 Introduction

California's three largest utilities–Southern California Edison, Pacific Gas and Electric, and San Diego Gas and Electric–collectively provided 18 percent of their 2010 retail electricity sales from renewable power. These utilities plan to provide 33 percent of all retail electricity sales from renewable power sources by 2020.[54] However, new cost effective renewable technologies and concepts are needed to minimize their incremental cost to ratepayers.

There are numerous potential sources of untapped renewable energy. One possibility is the generation of electricity by installing small modular water turbines in low head dams and irrigation canals. This concept has the potential to increase the supply of predictable, distributed, economical, and pollution free renewable energy to California ratepayers. The

54 Former California Governor Arnold Schwarzenegger signed Executive Order (EO) S-21-09 on September 15, 2009, directing the California Air Resources Board (CARB) to adopt regulations requiring 33percent of electricity sold in the state come from renewable energy by 2020.

estimated potential for generation of electricity at existing very low head dams on irrigation canals and water supply systems in California is 200 MW according to the National Inventory of Dams published by the U.S. Army Corp of Engineers in 1962, with no additional flooding of farmland or pollution of air or water resources.

The purpose of this project was to physically verify the overall hydraulic/mechanical efficiency of a full-scale model of the Undershot Impulse Jet Hydro-Turbine (Hydro-Turbine) that was patented in 2009. This concept has the potential to make power generation feasible at any navigation lock or small dam with a head of less than 15 feet.

The researchers formed a new business called Aquajet Lowhead Hydropower Co. (LLC) and registered it in California in April 2010. Aquajet is the sole U.S. licensee and manufacturer of the intellectual property related to the new Hydro-Turbine. Aquajet will market the Hydro-Turbine under the name of Broome Turbine. Aquajet performed all of the fabrication, inspection, and installation work needed to perform the verification test under contract to K.R. Broome and Associates.

To date there has been no significant deployment of small hydropower systems with less than 15 feet difference between upstream and downstream water levels on irrigation canals and navigable rivers. The primary reason is the lack of an efficient, cost effective, and reliable small water turbine. The traditional waterwheel is not economically viable for mass deployment because of its low capacity per foot of width, low efficiency, and consequent high cost per unit of output. Recently a few new concepts such the Banki or Crossflow Turbine have been introduced for developing power at low head dams. However these technologies require special intake and discharge channels to convey the water to and from the turbine, thereby increasing capital cost but still unable to use most of the available water. The majority of such installations are designed for more than 15 feet of head.

The researchers believed that the proposed Hydro-Turbine concept had the potential to be the most cost effective, reliable, and durable solution in the marketplace for the following reasons:

- The design enables almost all of the water in the river or canal. In addition, a given volume of water in a given unit of time can be directed at turbine vanes under a pressure head that is many times greater at a much higher velocity than the natural flow would be in an open channel.
- It uses durable mechanical components that can withstand harsh operating conditions.
- The unit can be pre-fabricated in the factory with the exception of the foundations, flow guide, and the orifice sole plate, which must be built on site.
- The turbine operation is self-regulated using a standard type of radial gate that is automatically controlled by an upstream water level monitor.

Researchers previously projected that the hydraulic mechanical potential efficiency of the

Hydro-Turbine could approach 85 percent over a wide range of discharge variables using a computational fluid dynamic (CFD) model developed by the University of Iowa. A water turbine matching this efficiency can produce power at a very competitive cost. Researchers proposed and conducted a full-scale verification testing program for three runner

configurations at a test site located in Woodside, California, using recirculating water pumps. See Figure 20.

Figure 20: Test Apparatus Constructed at Woodside, California

The researchers established test unit criteria based on the likely range of variables found at irrigation canal drops and river navigation locks/dams. They determined the likely range of head at both types of dams to be 5 to 15 feet. The runner design configurations to be tested were as follows:

- 16 vanes - 12 inches deep
- 16 vanes - 24 inches deep
- 8 vanes - 24 inches deep (configuration simulated in Iowa CFD model)

Test results are summarized in Table 5.

Table 5: Conditions at Maximum Calculated Efficiency

Conditions at Peak Efficiency						
Configuration	Flow CFS	Speed RPM	Torque ft-lb	Input Power kW	Output Power kW	Efficiency %
A	3.8	18	215	2.6	0.55	21
A	6.1	18	336	4.3	0.86	20
B	6	12.5	321	4.1	0.57	14
C	6.5	16	304	4.6	0.69	15
C	13.3	14.5	520	8.9	1.07	12

Test results clearly demonstrated a much lower hydraulic efficiency (range of 12 percent to 21 percent) compared to a predicted efficiency of 85 percent based on the University of Iowa's CFD simulation model. This discrepancy in system efficiency can be attributed to unrealistic assumptions and simulation parameters discovered by researchers.

Aquajet subsequently developed its own CFD model outside the scope of this project to more realistically predict actual hydraulic efficiency. Simulations from the new CFD model showed that predicted efficiencies are now within 15 percent to 25 percent of actual test results. With a better simulation model, the research team is now better equipped to optimize the design of the jet using various combinations of blade spacing, depth, and shape together with varying angles of approach. The research team plans to self-fund this incremental development work and to build a commercial scale 500 kW demonstration plant.

A promising candidate site for the demonstration plant is at the Thermalito Discharge Weir where water from the Oroville and Thermalito projects is returned to the Feather River near the town of Oroville. The research team believes that the time and expense required for obtaining an amendment to the existing FERC license for the Oroville/Thermalito project would be far less than requesting a new license from the FERC for a small hydroelectric project at a different site without an existing license. In addition, the research team believes that three more units could be added in the future for a total installed capacity of 2,000–2,400 kW.

The cost of electricity generated on either an irrigation canal drop or a navigable river lock/dam using the Hydro-Turbine could be as low as $0.03 to $0.05 per kWh, depending on equipment performance and site conditions. The researchers based this estimate on hydraulic efficiency in the range of 70 percent to 90 percent and system costs of less than $1,500 per kW. The market

potential for the Hydro-Turbine includes all dams and irrigation canal drops with a range of 5 to 15 feet of difference between upstream and downstream water surface elevations.

Researchers plan to commercialize the technology in the United States by means of licensing agreements based on geographic areas with small turbine manufacturers, steel fabricators, dam owners and small hydro developers interested in owning and operating profitable renewable energy projects. No such agreements can be made until a commercial sized unit (~500 kW) has been installed and operated for at least one year to prove the reliability and performance of the concept.

2.17.3 Objectives

The goal of this project was to physically verify the overall hydraulic/mechanical efficiency of a full scale model Undershot Impulse Jet Hydro-Turbine that was patented in 2009. The researchers established the following project objectives:

1. Inspect fabricated test unit for conformance with approved shop drawings and specifications before shipment.
2. Demonstrate stability and controllability of the test unit at various rates of water flow and radial gate openings.
3. Obtain trial readings of torque output at various gate openings, speeds of rotation, and brake settings.
4. Test data for various radial gate openings such as 20 percent to 100 percent.
5. Demonstrate 85 percent efficiency from 67—100 percent gate opening to match CFD analysis reports.
6. Show less than $0.05 per kWh potential for life cycle cost.

2.17.4 Outcomes

1. The researchers found the test unit was in conformance with shop drawings and design requirements before shipment.
2. The researchers operated the test unit at various rates of water flow and radial gate openings without restraint from interference with the containment structure.
3. Researchers took trial readings of torque output at various gate openings, speeds of rotation, and brake settings.
4. Researchers recorded test data for three different configurations of vanes and at gate openings from 10 percent to 50 percent.
5. Maximum efficiency was only 21 percent.
6. A life cycle cost analysis resulted in an estimated cost of $0.11 per kWh at the demonstrated hydraulic efficiency of 21 percent, compared to $0.037 per kWh at the predicted hydraulic efficiency of 85 percent.

2.17.5 Conclusions

1. The test unit was consistent with shop drawings and thus was acceptable for this project.
2. Researchers were able to successfully vary water flow and gate openings to collect the necessary data without constraints from the containment structure. They found the test apparatus was durable and reliable and that it probably could be used for further testing.
3. The collection of test data was seamless and made possible by the durable, reliable test apparatus.
4. The test apparatus was flexible enough to enable testing of a wide range of water flow and gate opening configurations.
5. The researchers found the efficiency of the Hydro-Turbine was far less than anticipated.
6. The researchers found the life cycle cost of the Hydro-Turbine was much higher due to the fact that the demonstrated hydraulic efficiency of 21 percent was much lower than predicted.

Researchers were able to complete full-scale verification testing for three runner configurations as proposed. They completed testing at a location in Woodside using water recirculating pumps rather than at an irrigation canal drop structure due to time limitations imposed by the Turlock Irrigation District.

The researchers did not demonstrate feasibility of the proposed water turbine. Clearly, the demonstrated hydraulic efficiency was much lower than what the Iowa CFD model had predicted. Test results showed a much lower hydraulic efficiency range of 12 percent to 21 percent compared to the predicted 85 percent using the University of Iowa's CFD simulation model. This discrepancy in system efficiency can be attributed to unrealistic assumptions and simulation parameters.

The researchers discovered these unrealistic parameters through work they performed outside the scope of this project. Aquajet developed its own CFD simulation model using open source software that was able to predict simulated system efficiency within 15 percent to 25 percent of the results from physical tests. The research team recognized that additional work was needed on the actual formation of the shape of the jet; various combinations of blade spacing, depth, and shape, and varying angles of approach for the jet. It may be possible to optimize system performance using the newly developed CFD model prior to additional field testing. The research team plans to self-fund this incremental development work and to build a commercial scale demonstration project.

2.17.6 Recommendations

The Program Administrator recommends additional modeling work to optimize the vane configuration and approach angle of the jet to achieve a hydraulic efficiency that is economically competitive with or superior to other renewable electricity options. The researchers should determine why the two CFD programs produce seemingly different results. In determining why the programs diverge, the researchers may find valuable information for the design of their turbine. Once they have proven a high efficiency turbine in a laboratory, they should construct and operate a commercial scale demonstration unit for at least a year to test for performance and reliability before the concept can be considered for mass deployment. During the test the researchers should investigate environmental, safety, and other risk areas to assure

that the Hydro-Turbine can be permitted in California. Upon completion of that test the researchers should conduct a more detailed analysis of the economic competitiveness of the turbine.

The research team needs a formal business and sales plan to help guide its transition from a research effort to a full-scale commercial venture. As part of their business plan they need to determine how the FERC may license and regulate small hydro projects at existing dams on irrigations canals.

2.17.7 Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the ratepayer from this research is reduced environmental impacts of the California electricity supply or transmission or distribution system.

This concept has the potential to increase the supply of predictable, distributed, economical, and pollution free renewable energy to California ratepayers. The estimated potential for generation of electricity at existing very low head dams on irrigation canals and water supply systems in California is 200 MW, according to the National Inventory of Dams published by the U.S. Army Corp of Engineers in 1962, with no additional flooding of farmland or pollution of air or water resources.

The research team registered a new business in California called Aquajet Lowhead Hydropower Co. (LLC) to market the Hydro-Turbine under the name of the Broome Turbine. It estimated that this new business opportunity could create up to 100 new jobs in California. For instance, about 30 jobs would be needed to support marketing, engineering, purchasing, and project management activities of Broome turbines in California. An additional 50 jobs would be needed at one or two existing fabrication shops in the Central Valley to meet the goal of manufacturing and installing a total of two turbines per month. Finally, the research team estimated that an additional 20 jobs would be needed for on-going site operations, maintenance, and office administrative support.

The research team estimated that sales of generators, switchgear, and gear units to support this business could reach $5 million per year, a portion of which it expects would be provided by California suppliers.

2.17.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

Researchers plan to commercialize the turbine in the United States by means of licensing agreements based on geographic areas. Aquajet plans to market this product to owners of small dams and to private power developers who can contract with dam owners to use their dams. The research team eventually plans to negotiate license agreements with major turbine manufacturers such as Voith and Andritz to market the technology in countries outside of the U.S. with extensive irrigation canal resources (such as China, India, Vietnam, Egypt, and Brazil).

Engineering/Technical

Once a design with high efficiency has been achieved, Aquajet plans to build a 500 kW commercial demonstration project.

Legal/Contractual

The researchers have filed no new patents. The innovative aspects of the Hydro-Turbine are protected by existing intellectual property (U.S. Patent number 7,503,744 issued March 17, 2009). The researchers conducted an informal literature search and produced no evidence of potential infringement on existing patents or intellectual property. Aquajet plans to pursue intellectual property coverage in other countries that may find this technology concept to be of value.

Environmental, Safety, Risk Assessments/ Quality Plans

The researchers plan to test the integrity of the system and ensure that it meets standard industry safety and permitting requirements during the field test phase of their project.

Production Readiness/Commercialization

The concept is not yet sufficiently developed for commercialization.

2.18 Fully Printed All Inorganic Nanoparticle-Based Solar Cells

Awardee: University of California, Santa Cruz

Principal Investigator: Sue Carter

2.18.1 Abstract

This project demonstrated a new manufacturing approach for thin film photovoltaics. It tested ultrathin Schottky cadmium telluride (CdTe) solar cells fabricated using a largely print based process. The goal was to reduce costs significantly compared with other solar cell technologies. The researchers overcame substantial disadvantages of current CdTe thin film technologies. First, their use of a Schottky junction, rather than p/n junction structure, eliminated the chemical bath deposited cadmium sulfide (CdS) layer. CdS currently creates environmental and waste issues in CdTe solar cell fabrication. Second, the use of an ultrathin CdTe layer allowed the researchers to use one tenth the CdTe material used in current state of the art thin film CdTe cell manufacturing. Third, the researchers fabricated the solar cells using largely a print based manufacturing process that is compatible with lower material and energy usage and higher volumes. Taken together, the researchers estimated that these innovations could reduce production costs to $0.60/Wp, significantly below current production costs. The researchers achieved power efficiencies of 6.6 percent for all inorganic

nanoparticle based CdTe Schottky solar cells, which was below the project's target of 10 percent.

Keywords: CdTe, photovoltaics, solar cells, nanoparticles, quantum dots, Schottky

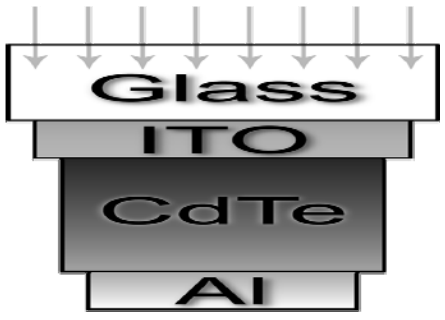
2.18.2 Introduction

Increasing the use of renewable energy sources remains a key component of California's electricity policy. Achieving greater use and complying with California's 33 percent renewable portfolio standard currently increases costs to consumers simply because renewable sources of electricity are more expensive than traditional sources. The increased consumer costs are associated with some degree of public opposition to renewables in general and renewable portfolio standards in particular. Achieving policy goals of increased renewable use along with public enthusiasm will require significant cost reductions through technology improvements.

One technology that shows promise is thin film photovoltaics. Thin films use less material than conventional photovoltaics and have largely supplanted crystalline and amorphous silicon in photovoltaic technology. The manufacture of thin films such as cadmium telluride (CdTE) remains expensive largely due to the complexity of cell manufacturing techniques, including vacuum deposition, thermal evaporation of cell material, and related factors. Similarly, the use of cadmium sulfide as a junction formation intermediary film has associated environmental and waste disposal issues.

In this project researchers investigated a novel method for producing CdTe based thin film photovoltaic cells. The major innovation was to use techniques that would allow printing of the cell material onto a substrate. In addition the researchers used a Schottky junction[55] rather than a more typical junction. The researchers printed colloidal mixtures of nanoparticle sized cadmium telluride onto the metallic aluminum substrate as illustrated in Figure 21. In Figure 21 ITO is the indium tin oxide electrode, CdTe is the cadmium telluride semiconductor, and Al is the aluminum (metallic) half of the Schottky junction. The glass is a transparent encapsulant and mechanical support.

Figure 21: Device Structure for a Typical CdTe Schottky Solar Cell



55 A Schottky junction is formed between a metal and a semiconductor, instead of a semiconductor–semiconductor junction as in conventional p/n junctions.

2.18.3 Objectives

The goal of this project was to determine the feasibility of using colloidal CdTe nanoparticles to fabricate fully printable Schottky solar cells with >10 percent power efficiency and one tenth the telluride material, enabling reduction in manufacturing costs from renewable energy sources to less than $0.60/Wp. This technology should be scalable to > 10 GW/year volumes using existing telluride materials and print based manufacturing lines in California. The researchers established the following objectives:

1. Demonstrate a CdTe ultrathin (< 500 nm) film with desirable PV properties, including low RMS roughness (< 3 nm), good adhesion, high resistivity (> 10 Ohm/cm), large grain growth (> 100 cm), and mobilities greater than 1 cm^2/Vs.
2. Demonstrate a Schottky junction capable of open circuit voltage above 0.7 V.
3. Obtain power efficiency greater than 10 percent on both glass and flexible substrates.
4. Verify manufacturing cost (materials and labor) for a fully printed CdTe nanoparticle (NP)[56] Schottky device of approximately $0.60/Wp.

2.18.4 Outcomes

1. The researchers fabricated 300 nanometer thick CdTe thin films by spin casting the CdTe quantum dot solution, pre-annealing the film for two minutes at 200° C, exposing the film to $CdCl_2$, and sintering it at 400° C for five minutes. The researchers achieved a smooth (< 3 nm RMS) film, good adhesion to glass, high resistivity (> 10 Ohm/cm), large grain growth (~100 nm), and mobilities greater than 1 cm^2/Vs. They measured electrical and physical properties using electrical and morphology. The researchers achieved this objective.
2. The researchers found that CdTe and indium tin oxide (ITO) electrodes resulted in open circuit voltage (V_{oc}) of 0.63 V. However, for devices with short circuit currents above 20 mA/cm^2, the highest V_{oc} the researchers obtained was 0.52 V. They did not achieve the objective of greater than 0.7 V_{oc}.
3. The researchers achieved a maximum power efficiency of 6.2 percent on glass substrates using ITO/CdTe/Al as the device structure and following the processing conditions identified in Outcome 1. This result was below the 10 percent objective but is representative of the failure to reach 0.7 V_{oc} in Objective 2. The researchers did not achieve this objective.
4. The researchers calculated a cost to manufacture solar cells using this technique. They assumed a 10 percent power efficiency was obtainable and calculated the costs to manufacture the CdTe NP Schottky solar cell at ~ $0.60/Wp, based on 50 percent cost reduction in materials, manufacturing tools, labor, and utilities. They compared this cost to First Solar's current CdTe thin film manufacturing process. First Solar claims its process costs ~$0.75/Wp.

56 Abbreviation NP for nanoparticle should not be confused with p/n junction type.

2.18.5 Conclusions

The researchers did not demonstrate the feasibility of using this technique to form low cost and high efficiency solar cells. However they did demonstrate that the technique shows promise to ultimately achieve breakthrough cost reduction. The electrical efficiency that the researchers obtained (6.6 percent) is the highest ever observed for an ultrathin (~300 nm) CdTe solar cell device or a Schottky solar cell fabricated from nanoparticle solutions. The device structure was not able to generate the voltage objective of 0.7 V_{oc}, nor efficiency of greater than 10 percent.

The researchers demonstrated that the CdTe thin films fabricated from printed sintered nanoparticles have properties similar to vacuum deposited CdTe films that are 10 times thicker. The nanoparticle films were very smooth so that the formation of shorts/shunts could be avoided depending on process quality control. Moreover, the short circuit currents of up to 25 mA/cm^2 were higher than traditional CdTe solar cells due to the lack of a CdS window layer, which absorbs the blue portion of the spectrum affecting efficiency. These results all indicate that the use of colloidal nanoparticle CdTe solutions could lead to substantial cost and material reductions without sacrificing performance compared to vacuum deposited CdTe.

The process investigated in this project uses significantly less CdTe than other cadmium telluride cell manufacturing techniques. To that extent, cost reductions and strategic benefits are of great interest to the solar industry and will find ready markets. Strategic benefits derive from the world market for tellurium (one of the lanthanides) whose production is increasingly shifting to China and Afghanistan along with other so-called rare earth elements.

2.18.6 Recommendations

The main engineering and technical issue will be to improve the efficiency from the current 6.6 percent to a commercially attractive 10 percent or better while insuring stability and durability. Only by achieving higher efficiency will the technology be of sufficient interest to the manufacturing sector of the solar industry. In addition, once efficiency is improved to minimally acceptable levels, engineering and manufacturing specifications will need to be developed, along with quality assurance plans.

The researchers should investigate the feasibility of p/n junctions using the same manufacturing technique to determine if higher V_{oc} and efficiencies are possible. They should investigate materials other than CdS in developing solar cells using p/n junctions using the spin casting technique and compare all relevant electrical and physical properties, as well as the impact on waste and disposal issues. The researchers should perform life cycle analysis of their technique compared to other manufacturing approaches. They should begin to develop encapsulation requirements or determine that existing encapsulation methods will provide for long life and high physical stability. They should evaluate the durability of spin cast ultrathin films to environmental stresses and begin to develop quality assurance needs for manufacturing processes.

After taking into consideration (a) research findings in the grant project, (b) overall development status, and (c) relevance of the technology to California and the PIER program, the Program Administrator has determined that the proposed technology should be considered for subsequent funding within the PIER program.

Receiving subsequent funding ultimately depends upon (a) availability of funds, (b) submission of a proposal in response to an invitation or solicitation, and (c) successful evaluation of the proposal.

2.18.7 Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the ratepayer from this research is increased affordability of electricity in California. A secondary, yet large and unquantified, benefit is from the reduced use of and importation of strategically important materials such as tellurium.

Assuming the cost projections developed by the researchers of ~$0.60/Wp, an approximate saving of approximately 20 percent could be achieved in the cost of the cells and lesser amounts in modules and system compared to current commercial technology. A 20 percent reduction in cell costs could easily translate into a 10 percent reduction in system costs, other things being equal, or about $0.20/Wp, or $200 kWp, providing a cost reduction of about $0.01/kWh. Further, assuming that 25 percent of the mandated renewable electricity in the year 2020 is provided by solar photovoltaics,[57] using this technology versus current state of the art would allow California residents to see a cost savings of approximately $273 million per year.[58]

2.18.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

The researchers have not pursued market connections. They have performed no market research.

Engineering/Technical

The researchers estimated that completion of technical work could require up to four years and require approximately $500,000. They plan to work with Colorado School of Mines to make structures based on p/n junctions.

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57 Solar fraction estimated at 24 billion kilowatt hours.

58 Note this is not an actual savings but a reduced cost to comply with the mandated renewable portfolio standard.

Legal/Contractual

The researchers have identified a patentable process technology but have not applied for a patent nor completed a patent search.

Environmental, Safety, Risk Assessments/ Quality Plans

There are no known environmental or safety risks unique to this technology. To the extent that the researchers choose and decide on pursuing p/n junction based cells and utilize CdS as a window, there could be waste and disposal issues, although that would not be unique to this fabrication approach.

Production Readiness/Commercialization

This technology is not ready for commercial production.

2.19 Closed Loop Tracking for Solar Thermal Heliostats Awardee Mark Convery

Principal Investigators: Mark Convery

2.19.1 Abstract

Reduced costs and higher production efficiencies in concentrating solar thermal power plants may be possible through faster, more precise, low cost systems for maintaining alignment of each mirror in the array. This research demonstrated a closed loop system for identifying the source and alignment of individual heliostats by inducing small mechanical vibrations on their surface using piezoelectric actuators. These time dependent vibrations in the reflected light were detected by photosensors arrayed around the receiver target. By creating a unique time/vibration frequency pair for each mirror, individual control and alignment were possible. A bench scale model using four mirrors proved capable of effectively identifying and maintaining their alignment with milliradian tracking accuracy. Scaling up this approach to commercial operation may be possible by following a number of identified items for further research and development.

Keywords: Concentrating solar power, CSP, solar, thermal, concentrated, heliostat, alignment, calibration, feedback, closed loop

2.19.2 Introduction

California's Renewable Energy Portfolio Standard requires 33 percent of energy sold in California to come from renewable sources by 2020. While significant progress is being made toward this goal, the present gap between the cost of electricity produced by renewable sources and conventional natural gas fueled generation alternatives hinders their development, delaying potential benefits to California electric customers.

One promising but relatively higher cost technology currently being developed at several sites in California is concentrating solar thermal power (CSP), which uses a field of hundreds of reflecting mirrors (heliostats) on moving mounts to direct sunlight onto a central receiver (power tower). The heat generated in the receiver is used to create steam and produce electricity in a conventional steam turbine. There are numerous opportunities to improve efficiency and reduce costs of this technology. One example is the cost of aligning each of the many mirrors to

focus precisely on the receiver and maintaining that alignment as the sun moves over days and months of operation. A more precise and lower cost method of alignment could reduce the time to commission/calibrate the plant, maintain the mirrors' focus on the tower, and improve thermal efficiency by ensuring that the full beam of reflected sunlight hits the tower receiver.

This project developed and demonstrated a closed loop mirror control system capable of providing alignment corrections for multiple heliostats simultaneously at bench scale. This was done by detecting light that is missing the tower using an array of light sensors surrounding it and identifying the source of each detected misaligned beam through an associated vibration frequency created through actuators on each mirror. These frequencies may be unique to each mirror or potentially to a group of mirrors that are vibrated at sequential times to create a unique frequency/time pair.

2.19.3 Objectives

The goal of this project was to determine the feasibility of using a vibrating mirror, closed loop tracking system for solar thermal heliostats to reduce their cost and hence the cost of power produced by CSP plants. The researchers established the following project objectives:

1. Build a single system for inducing vibrations on a mirror and detecting the frequency of those vibrations using reflected light. The additional cost for each mirror should be less than $10, and the cost for the detection system should be less than $10,000.
2. Build multiple copies of the above system and verify that the signals from several different mirrors, each vibrated at a different frequency, are simultaneously detectable. The Fourier peaks from each mirror should all be clearly above background noise and well separated from each other.
3. Build a motorized pointing system for controlling a small-scale mirror that uses the feedback signal to control it. Test that the feedback system can track the sun with an accuracy of one milliradian.
4. Build multiple copies of the motorized pointing system. Test that the feedback system can simultaneously control multiple mirrors and track the sun with an accuracy of one milliradian.

2.19.4 Outcomes

1. The researchers found that gluing small piezoelectric actuators (PA) to the back of the mirrors was an effective way to produce reliable and repeatable vibration amplitudes.[59] The required vibration detection system consisted of a diode laser reflecting off the vibrating mirror onto a photodiode, along with associated electronics to process the received signal for analysis. The cost of the PA was less than one dollar per mirror, whereas the cost of the required driver electronics was $60 per mirror. The cost of the detection system was roughly $2000 per mirror.

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59 For a discussion of an approach to calculating the expected vibration amplitude for a given mirror/PA/voltage case, see R. L. Clark, M. R. Flemming, and C. R. Fuller, (1993), Piezoelectric Actuators for Distributed Vibration Excitation of Thin Plates: A Comparison between Theory and Experiment, *Journal of Vibration and Acoustics*, 115(3), 332. doi:10.1115/1.2930353

2. The researchers built additional copies of the actuator/mirror from Objective 1 above for a total test system of four mirrors, including four copies of the analog circuitry developed in the first objective. A commercially available data acquisition system and laptop computer software drove the test modules and analyzed the resulting vibration signal. Testing confirmed that the unique vibration signals from each mirror striking the same photodiode could be simultaneously detected.

3. A commercial motorized telescope mount controlled by laptop software designed by the researchers was able to track sun movement using feedback signals from the photodiodes. Closed loop feedback tests yielded tracking accuracy within one milliradian.

4. Outdoor testing of a four-mirror system confirmed simultaneous tracking within one milliradian for all mirrors.

5. The researchers included an additional task to test application of the system to commercial scale mirrors. A three-foot square mirror produced detectable signals with both a laser and sunlight source at reasonable PA excitation voltages.

2.19.5 Conclusions

This project met its objective of demonstrating a detection and tracking system for heliostats at bench scale. The design, testing, and documentation for the project were all successful and clearly identified a path for further research leading toward commercial scale application.

1. The first part of this objective was met through building a single mirror vibrating/sensing system. The finding that the amplitude of the vibration was extremely small (roughly 1 micron) supported a conclusion that in commercial scale it would be unlikely to cause any of the reflected beam to miss the receiver. The second part of the objective was only partially met, since the cost for the PA driver electronics was considerably above expectations, bringing the cost of the PA/electronics package well above the targeted $10 per mirror. The researchers' suggestion that at commercial scale this cost would approach the target is plausible but would need to be validated through further research. On balance, the $2,000 cost of the detection system was well below its targeted $10,000.

2. This objective was met through demonstration of successful detection of vibration frequencies from four mirrors. There appears to be no reason why the system could not be successfully scaled up to accommodate many more mirrors.

3. The telescope mount and controls proved capable of precise tracking. An unexpected beneficial outcome was that required signal acquisition time proved to be very small, approaching 100 milliseconds. In a commercial system this should allow identification of an individual heliostat based on the time stamp of its vibration signal in addition to its intended vibration frequency. This would allow many heliostats to share the same vibration frequency and to be vibrated in sequence, rather than requiring an individual frequency to be set for every mirror in the array, thereby reducing complexity.

4. This objective was met, with results similar to those for Objective 3.

5. The preliminary results for the larger mirror suggest this approach can work at commercial scale, assuming the required hardware can be developed for application under field conditions.

2.19.6 Recommendations

The success of this project at bench scale suggests several directions for further research and development. These include identifying solar thermal developers with whom further research could be conducted, evaluating the commercial scale economics of this approach, and refining technical and engineering parameters such as those listed below:

1. Since the actuators and sensors used in this project are not capable of withstanding the much higher temperatures in a commercial system (possibly 100 suns and 500° C), a new approach must be found.
2. The use of both time and vibration frequency to identify individual heliostats should be tested further, including refinement of the software for signal generation and synchronization.
3. Quantification of the tracking resolution improvement should be further refined with emphasis on likely results for typical commercial scale heliostat installations.

   After taking into consideration (a) research findings in the grant project, (b) overall development status, and (c) relevance of the technology to California and the PIER program, the Program Administrator has determined that the proposed technology should be considered for subsequent funding within the PIER program.

Receiving subsequent funding ultimately depends upon (a) availability of funds, (b) submission of a proposal in response to an invitation or solicitation, and (c) successful evaluation of the proposal.

2.19.7 Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the ratepayer from this research would be increased affordability of electricity in California. Adoption of renewable technologies, including CSP, is being driven by California's aggressive Renewable Energy Portfolio Standard. The potentially increased efficiency and resultant cost reductions from more precise alignment of heliostats could help narrow the gap between power from CSP and traditional natural gas fueled generation.

This project offered a way to reduce heliostat cost and improve plant performance by improving the alignment accuracy of the heliostats and reducing associated costs. Gauging the

cost reduction that could be achieved by wide adoption of this project's technology is difficult. However one benchmark comes from the experience of the Solar Two project, which was carried out in the late 1990s in Barstow, CA.[60] In that project, 10—20 percent of the reflected sunlight was lost due to poorly aligned heliostats. The technology developed in this project would correct those problems at a cost of less than 1.0 percent of the total plant cost, thereby achieving cost reductions of as much as 20 percent. Another benchmark comes from the eSolar pilot plant, which was recently constructed in Lancaster, CA.[61] In that plant, with a custom built alignment system, the operators of the plant were able to align the heliostats and achieve excellent tracking resolution. However the alignment procedure took 20 good weather days for the relatively small 5 MW plant. The costs associated with this due to lost operation time, as well as to the need for highly experienced personnel, were not disclosed by eSolar. However it is likely they are equivalent to at least a few percent of the total cost of the plant. Saving this time and the costs associated with the eSolar alignment system would be very valuable and would more than pay for the cost of the closed loop system.

2.19.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

According to the researchers, presentation of the research results at two solar energy conferences led to significant commercial interest. Several utility scale CSP plants are underway in California, and others are in development nationwide, indicating that a market for improved heliostat alignment and tracking exists.

Engineering/Technical

The researchers plan to develop a method of light sensing capable of withstanding 100 suns of radiation. This is a necessary step prior to commercialization. They plan to accomplish this task along with refinements in actuation hardware and detection software in approximately one year at a cost of $500,000.

Legal/Contractual

The researchers have completed a patent search and application and have not identified any significant infringement issues.

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60 K. W. Stone, H. Beach, and S. A. Jones, S. A. (1999), Analysis of Solar Two Heliostat Tracking Error Sources, *Sandia Report SAND99-0239C*.

61 S. Schell, (2011), Design and Evaluation of eSolar's Heliostat Fields, *Solar Energy*, *85*(4), 614-619.

Environmental, Safety, Risk Assessments/ Quality Plans

The researchers did not bring up any significant environmental or safety related issues that could require further evaluation. As a commercial scale prototype system is developed, quality/reliability testing will be extremely important, particularly with respect to the ability of available heliostat mounting/rotating hardware to match the precision alignment signals available from the system.

Production Readiness/Commercialization

Potential partners for development and application to a commercial CSP plant could include BrightSource Energy, eSolar, Solar Millennium, Solar Reserve, and others. The researchers indicated partnership negotiations were underway, although they did not provide further details.

2.20 Osprey: Ultra Efficient Mass Microalgae Culturing and Harvesting Device

Awardee: Green Reactions LLC

Principal Investigators: Matthew P. Huber

2.20.1 Abstract

Microalgae are a promising source of biomass for the production of biofuels, but cultivation and harvesting is energy intensive. This project focused on proving the feasibility of culturing and harvesting microalgae in raceway ponds with a novel airlift pump in place of the more traditional paddle wheel. The primary goal of this project was to demonstrate that the new airlift pump could combine the three tasks of water locomotion, gas exchange, and harvesting into a single device. The tested pond system could reach velocities over 50 cm/s, could keep dissolved oxygen levels below 20 mg/L, and could dissolve a supply of atmospheric carbon great enough to supply photosynthetic demand. The ponds were used to grow and harvest green algae, *Nannochloropsis*, and a pinnate diatom. The researchers used foam formation to harvest the algae, adding a water treatment coagulant to produce harvestable foam. Using this chemical technique, the researchers concentrated the *Nannochloropsis* biomass from 0.4 g/L to 70 g/L. The pinnate diatom self-harvested, building up extraordinary foam without the use of a coagulant. In a diatom culture having a biomass concentration of 0.35 g/L dry weight, the foam reached 60 g/L. A second equally important goal of the project related to the energy consumption of the device. Although the cost to operate the airlift was 100 percent to 400 percent higher than the paddle wheel, the capital and maintenance costs were 10 percent to 50 percent less than traditional systems.

Keywords: Microalgae, airlift pump, biofuel, paddlewheel, pond

2.20.2 Introduction

Algae are among the fastest growing organisms on the planet. They contain high energy density, can form lipids that can be converted to standard transportation fuels, and are a sink for CO_2 in the atmosphere. If algae biomass can be produced in a process with a net positive energy gain and is economically viable, algae could be a major resource for transportation fuels.

Previous reports have shown energy densities of algae to be 22,000 kJ/kg.[62] The researchers in this project claimed to have seen proprietary information from companies growing algae that contain energy densities reaching 32,000 kJ/kg. This is nearly the same energy density of coal, 35,000 kJ/kg.[63]

Liquid fuels are being extracted from algae biomass to make transportation fuels today. The major research area is to produce commercial fuels from algae at a cost comparable to traditional fuels. Fuel production from algae has been demonstrated by Solix, Solazyme, Sapphire, Synthetic Genomics, Aurora Algae Products, and many others.

The researchers proposed a system that combined water motion, gas exchange (O_2 and CO_2), and algae harvesting. They used an airlift pump for the water motion and the gas exchange. Harvesting was accomplished by skimming foam created by the algae. Figure 22 is a photo of one of the test ponds used in this project.

The researchers claimed their device would perform the same functions as others but at a significantly lower capital cost. Photosynthetic organisms in mass culture consume volumes of CO_2 in excess of what can diffuse into the media from the atmosphere. Currently the basic philosophy is to locate the algae farm next to a CO_2 source such as a fossil fuel burning power plant or cement manufacture. The gas is then transported from the source and into the farm where it is dissolved into the media. Each of these steps is costly. At the farm a second large capital cost is incurred in the equipment to dissolve the gasses into the pond media. For a small farm of a few acres the CO_2 supply from a waste source could cost from $50,000 to $200,000, depending on regulatory rules, engineering, and motivation of the parties involved. Water locomotion is a little more direct. A simple paddle wheel pond can cost between $70,000 and $150,000 per acre of pond. In addition there is the cost of the harvesting system. The cost of a traditional system can be $200,000 per acre. The researchers in this project claimed to be able to build their system for a capital cost of less than $40 K per acre of pond.

Figure 22: A Test Pond

62 Cebula,J, S. Kowalski, M Bodzek, K. Loska (1995) *Thermal Decomposition of Algae Bloom Biomass*. Journal of Thermal Analysis and Calorimetry Vol. 46 Issue 5. pp. 1467-1471.

63 Lindner, E. *Chemie Fur Ingenieure* Lindner Verlag Karlsruhe, S. p. 158.

2.20.3 Objectives

The goal of this project was to determine the feasibility of combining several independent processes for microalgae mass culture into a single device and demonstrate that it is more energy efficient than baseline paddle wheel designs. To prove feasibility the researchers provided the following objectives:

1. Build first test system. System is to have water flow of 0 cm to 50 cm per second. Maintain gas exchange at 20 mg/L O_2 and > 50 ppm CO_2.
2. Build two small demonstration ponds. System is to have water flow of 0 cm to 50 cm per second. Maintain gas exchange at 20 mg/L O_2 and > 50 ppm CO_2.
3. Conduct performance tests. System is to have water flow of 0 cm to 50 cm per second. Maintain gas exchange at 20 mg/L O_2 and > 50 ppm CO_2. Demonstrate biomass concentration of 50 times. Measure electricity consumption.
4. Build and test a large demonstration pond. System is to have water flow of 0 cm to 50 cm per second. Maintain gas exchange at 20 mg/L O_2 and > 50 ppm CO_2. Demonstrate biomass concentration of 50 times. Measure electricity consumption.
5. Conduct cost and energy analyses: water motion is to be 0.015 kWh $m^{-2}d^{-1}$, gas harvesting is to be 0.015 kWh $m^{-2}d^{-1}$, gas exchange is to be 0.342 kWh $m^{-2}d^{-1}$, electricity consumption is to be 3 kWh to 4.5 kWh per day per acre, and manufacturing cost is to be $25,000 per acre.

2.20.4 Outcomes

1. The researchers built the initial demonstration ponds, including one pond with a traditional paddle wheel circulation device. Growth and gas exchange in the airlift and the control paddle wheel systems were comparable.
2. The large $10m^2$ pond was constructed but ruptured after 30 minutes of testing. Because of lack of resources, it was not rebuilt.
3. The researchers observed no foam formation (needed for harvesting) in some of the algae species. They added chemicals that are commonly used in water treatment as flocculants and coagulants. Some chemicals formed small clumps of algae that sank to the bottom of the pond. Others formed thick, dense foam. The researchers selected the second method for harvesting the algae.
4. The researchers measured energy consumption of 6 to 15 Wh per acre day.
5. The researchers estimated capital costs at ~$25,000 per acre of pond.

2.20.5 Conclusions

1. The researchers generally met their goals of building and testing small test ponds.
2. They did not meet the goal of building and testing a $10m^2$ pond.
3. Harvesting results were good. Foam concentrated the algae biomass by over 100 times. Certain strains were able to build foam without the addition of water treatment coagulants, while others were not.

4. Energy consumption did not meet the goal and in fact was higher than that of the paddle wheel system.
5. The researchers met their goal of showing capital costs to be considerably less than that of the paddle wheel system.
6. In both the energy consumption and capital cost goals, full-scale tests are necessary to verify results. Either measure may not scale well.

The researchers demonstrated that the concept is feasible, but they have not yet demonstrated that it is practical. Large-scale production of algae derived transportation fuels is far in the future, perhaps a decade or more. Numerous technical and commercial hurdles remain.

2.20.6 Recommendations

The Program Administrator recommends that the researchers:

- Evaluate the current state of algae processing for transportation fuels. This field of knowledge is growing fast and the status should be evaluated before embarking on additional research.
- Evaluate and score the technical features of each algae handling system currently being evaluated by competitors.
- Prepare a draft design of a complete commercial algae processing plant using the researchers' technology.
- Test the draft design with national experts. Seek input and analysis.
- Seek companies that may wish to partner with the researchers.
- Perform a true life cycle cost analysis.
- Perform an energy balance for the entire system.

2.20.7 Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit of the results of this research is reduced environmental impacts of the California electricity supply or transmission or distribution system. Algae derived fuel can be produced in a manner that is essentially carbon neutral. The regulated emission of vehicles using algae derived fuels is not known at this time. If properly formulated, those fuels should exhibit emissions similar to conventional fuels.

Transportation fuels derived from algae have a large potential to benefit California ratepayers. The algae could be grown, harvested, and converted to fuel within California. This would lead to the creation of many jobs. Sourcing fuel in California would also improve the balance of payment for both the state and the country.

It is too early to assign a number to the financial or air quality benefits of this technology.

2.20.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

The researchers have performed an informal market study. They identified the following potential markets for this technology: commercial energy production, solid fuels, liquid fuels, wastewater cleanup, animal feed production, pigment manufacture, and chemical manufacture.

Engineering/Technical

The researchers plan to focus research on scaling the technology to commercial size ponds. They estimate a cost of $4 million to $10 million to develop and test a full size pond with at least 800 m^3 of volume.

Legal/Contractual

The researchers claim to have obtained a patent.

Environmental, Safety, Risk Assessments/ Quality Plans

The researchers recognize the need to develop these plans. They anticipate the following regulatory barriers: ground water contamination and invasive species propagation.

Production Readiness/Commercialization

The researchers need a business plan. They anticipate the need to form a partnership with a large construction company or a large algae producing company.

2.21 Module Level Power Converters for Parallel Connected Photovoltaic Arrays

Awardee: Missouri University of Science and Technology

Principal Investigators: Jonathan Kimball

2.21.1 Abstract

The goal of this project was to establish a new solar energy technology with the capability to increase array level power production. The new dc optimizers were dc-dc converters with high fixed voltage gain that were integrated within each photovoltaic panel. Therefore the outputs could be connected in parallel and directly connected to a grid tie inverter. This eliminated the need for connecting panels in series. In a parallel-connected array, each panel could produce nearly its individual maximum power without independent power trackers. Offline analysis validated this approach. The researchers tested power converters for a wide range of operating

conditions. Calculated performance indicated a theoretical increase in power ranging from 3.9 percent to 13.8 percent, depending on conditions and converter efficiency, with a material cost of $0.128/W. This improvement has the potential to offset 5 GWh per year of electric energy generation and 3300 tons/yr of CO_2 emissions. The researchers in this project showed experimental results with prototype converters. The proposed method does ensure that the modules operate near their individual maximum power points. However, additional work is needed to improve converter efficiency to achieve a net benefit. Significant challenges remain, primarily in transformer construction, to achieve efficiency above 98 percent.

Keywords: Photovoltaic, series parallel, dc-dc converter, dc optimizer, maximum power point, grid tie

2.21.2 Introduction

The most commonly used and fastest growing technology for residential scale solar energy is a series parallel array of photovoltaic (PV) panels connected to a central grid tie inverter. There are several reasons why this is the dominant technology:

- Wiring and installation practices are established.
- Cost of regulatory compliance is amortized over the power rating of the whole array.
- Efficiency goals are easier to reach at higher power levels.
- Reliability, while not as high as desired, is well known.

However these advantages come with one severe disadvantage: power production is disproportionately decreased if even one PV panel is shaded. Because panels are connected in series, they must all conduct the same current, and optimal current is largely determined by solar insolation. When insolation is non-uniform, some or all of the panels are operated away from their individual maximum power points.

One solution being considered by several companies is to use micro inverters. A micro inverter is functionally equivalent to a central grid tie inverter, but with a power rating compatible with a single panel. This allows maximum power point tracking (MPPT) at the individual panel level and provides inherent redundancy. However micro inverters are inherently difficult to design to be competitive with central inverters on cost, efficiency, and reliability. Some costs are fixed (control and monitoring for regulatory compliance) regardless of power rating. In addition, the environmental conditions on or near a PV panel are much harsher than the typical indoor conditions for a central inverter.

In this project the researchers proposed a middle solution, a dc optimizer. The primary reliability challenge for a single-phase grid tie inverter relates to the power ripple on the ac port, and the primary control challenge relates to regulatory compliance on the ac port. In an architecture with a dc optimizer, both of these problems are solved by a central inverter as in a conventional system. Each PV panel then has an integrated dc-dc converter that solves the problem of non-uniform insolation. This project studied an innovative dc optimizer technology.

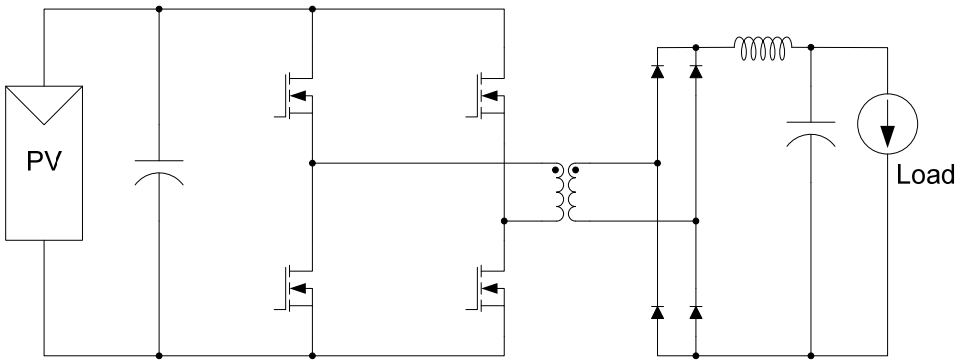
In one common dc optimizer system, each dc-dc converter performs MPPT, and its output is connected in series as in a conventional array. While this is attractive in principle, the assembly

of MPPT converters creates stability problems. In essence, each panel has constant power source characteristics, each with a different power capability. A constant power source has negative incremental impedance, so an assembly of constant power sources is inherently unstable. This is similar to the problem encountered in an input series output parallel (ISOP) dc-dc converter. The solution in the ISOP case is to force each converter to have positive incremental impedance. There are no directly equivalent solutions for dc optimizers.

In the new technology studied here, the dc optimizers are simpler fixed gain dc-dc converters. With a fixed gain there are no feedback control requirements, so the controller is much simpler than in an MPPT converter. The circuit topologies considered have a fixed gain with constant duty cycle and constant switching frequency, so the controller simply creates properly timed square waves. The converters have high gain (8.4 in the experimental results presented, perhaps as high as 12 in production units) so that their outputs can be connected directly to the input terminals of a grid tied inverter. Since the converters are connected in parallel, panels operate at nearly equal voltages. Since optimal panel voltage is largely determined by absolute temperature, the individual panels will be near their individual maximum power points even if insolation is non-uniform. If one panel is damaged and becomes non-functional, it does not inhibit the power production of the other panels.

The primary challenge was achieving high gain with high efficiency. The main topology studied in this project was a full bridge converter, a buck derived isolated converter (Figure 23). The transformer provided the voltage gain. The duty ratio of the primary side switches determined the output voltage, as in a conventional buck converter. The effective duty ratio was fixed at approximately 84 percent. With improved gate drivers, this duty ratio could approach 100 percent. Therefore, a small output inductor could ensure continuous conduction mode (CCM) operation. The researchers found this topology to be effective, although design and construction of an effective transformer proved to be a limiting factor.

Figure 23: Full Bridge Converter Topology Used in This Project



The researchers continued outdoor testing of a small PV array (two panels with integrated converters) after the completion of this project. Preliminary results indicated that, despite any differences that occur near open circuit, panels do operate near their individual maximum power points when the array is at its combined maximum power point.

2.21.3 Objectives

The goal of this project was to determine the feasibility of simple integrated power converters to improve the total power output of a photovoltaic array. To prove feasibility the researchers established the following objectives:

1. Quantify the advantage of a parallel connected array.
2. Design a power converter suitable for integration with a 24 V-class, 200 W PV panel, with projected efficiency of 98 percent and prototype cost of $2/W.
3. Construct and test a power converter in a laboratory environment. Verify efficiency of 97 percent, load regulation of 2 percent, source regulation of 2 percent, and transient settling time of 10 ms.
4. Design an improved power converter with predicted efficiency of 98 percent and material cost (in volume production) of $0.15/W.
5. Operate two panels each within 5 percent of individual maximum power points with 50 percent insolation variation.
6. Demonstrate predicted mean time before failure (MTBF) > 20 years.

2.21.4 Outcomes

1. The researchers concluded that the parallel connected topology produces more power than a series connected topology in all cases, with the advantage ranging from 3.9 percent to 13.8 percent, even after accounting for the efficiency penalty of the converter.
2. The projected efficiency of the power converter was 98.0 percent. The prototype cost was $0.452/W.
3. The measured efficiency was a maximum of 93.0 percent and an average of 92.0 percent. Load regulation was 8.5 percent over most of the load range. Source regulation was 4.6 percent. Transient settling time was 8.8 ms.
4. The re-designed power converter had a predicted efficiency of 98.0 percent and a projected material cost in volume of $0.128/W.
5. For a test case where one panel received full sun and the other received 50 percent sun, the unshaded panel operated within 1.7 percent of its maximum power point and the shaded panel operated within 6.7 percent of its maximum power point. The weighted deviation from maximum power was 3.4 percent.
6. The researchers computed MTBF to be 29.01 years using MIL-HDBK-217F2.

2.21.5 Conclusions

Overall the researchers did not demonstrate feasibility.

1. They met this objective.
2. They met this objective.
3. The measured efficiency and load regulation deviated considerably from the objectives.

4. The outcome of this objective was unclear. First, the power converter must be redesigned to meet the efficiency and regulation goals. It is hard to estimate the cost of this undesigned component. Second, electronic products generally retail for three times the parts (material) cost. Using the researchers' volume material cost number, the retail cost of the power converter could be close to $0.4/W.
5. The researchers met this objective.
6. The researchers met this objective.

However, the design approach does result in improved power output when a panel encounters partial shading. If the researchers had access to an efficient dc-dc converter to achieve the high voltage gain, the new approach could have substantial impact, perhaps an 8 percent increase in average energy production for a typical PV array.

The key limitation is the transformer design and construction. With the manufacturing technology available at Missouri S&T, the researchers were unable to construct a transformer with an effective foil winding. As a result, they used round wire windings that suffered from high proximity effect losses. With improved assembly techniques, the proposed power converter may be capable of meeting the design goals.

The challenge is to develop this technology fast enough to avoid being crowded out of the market. To develop an effective product, the researchers must resolve technical challenges (primarily efficiency, but also packaging). Then they must identify a viable path to market. The most logical approach is for Missouri S&T to partner with either an established company or a start-up company working in the PV power converter space. This would leverage an existing system of logistics (manufacturing, marketing, distribution). Just as micro inverters will have the most impact as integrated PVAC modules, the technology proposed in this project could have the most impact as an integrated high voltage PVDC module

2.21.6 Recommendations

The Program Administrator recommends the researchers develop a working relationship with one or more transformer manufacturers to design a practical transformer compatible with the design objectives of the new technology. Any new transformer must be packaged and deployed for extended periods of time to establish field reliability data.

The first major step is to investigate alternative transformer construction techniques. Improved transformer construction could enhance both this technology and competing technologies and could be licensed to dc optimizer or micro inverter companies. With good transformers, new high efficiency power converters can be designed and tested.

In addition, the Program Administrator recommends the following additional steps be taken by the researchers:

1. Investigate voltage gain calibration (for a range of panels), adding MPPT, and using hybrid topologies.
2. Develop packaging techniques to integrate the power converters within the PV panels.

3. Develop a relationship with a commercial company to take the project technology to market.

4. Identify and patent applicable intellectual property.

2.21.7 Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the ratepayer from this research is increased affordability of electricity in California.

The proposed technology could increase PV array output by 8 percent. According to an analysis of the California Solar Initiative, 92.1 MW of residential PV systems were installed in 2010.[64] Considering the growth rates, this may grow to 191 MW by 2014.[65] If this product can be commercialized by that time and achieve 15 percent market penetration, the total extra power capacity would be 2.3 MW.

The proposed technology could increase PV output by 5 GWh/yr. The retail price of electricity in California in January 2011 for residential users was 15.3 ¢/kWh.[66] Assuming that the PV energy displaces electricity that would have been purchased, California residential electricity consumers could avoid a cost of $765,000 per year.

Furthermore, PV generated electricity mostly displaces natural gas. Therefore, CO_2 emissions would decrease. Natural gas generators produce 1.321 lbs CO_2 per kWh of electricity.[67] The proposed technology would decrease emissions by 3300 tons of CO_2 per year.

These savings come at a cost. If the converters could be sold for $0.25/W, the cost to install converters on 15 percent of the 191 MW installed in 2014 would be $7.2 M. With simple payback, the converters could pay for themselves in less than 10 years. This time could be shorter if electricity prices increase or if regulatory costs are applied to CO_2 emissions. Many people consider a 10 year payback too long.

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64 Zero Net Energy Solutions, *The U.S. PV Market: A tale of David vs. Goliath?*, accessed on 5/29/2011, http://zeronet-energy.com/solar-energy-blog/the-u-s-pv-market-a-tale-of-david-vs-goliath/298/.

65 Solarbuzz, *Solar Energy Market Growth,* accessed on 5/29/2011, http://solarbuzz.com/node/42.

66 U.S. Energy Information Administration, *Average Retail Price of Electricity to Ultimate Customers by End-Use Sector, by State,* accessed on 5/31/2011, http://www.eia.gov/cneaf/electricity/epm/table5_6_a.html.

67 Department of Energy and Environmental Protection Agency, *Carbon Dioxide Emissions from the Generation of Electric Power in the United States,* Washington, DC, July 2000.

2.21.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

The researchers had not performed any market analysis during the project. If the researchers complete the development of their technology, they plan to license or collaborate with established companies in the photovoltaic industry.

Engineering/Technical

The researchers plan to focus on high efficiency, high frequency transformer design and construction. Only when that technology area is developed will they continue with the technology in this project.

Legal/Contractual

The researchers did not identify any patentable intellectual property during the performance of this project. They did find an existing patent that may block patents of the concept developed in this project.

Environmental, Safety, Risk Assessments/ Quality Plans

This technology may be subject to location specific permitting under local environmental or safety regulations.

Production Readiness/Commercialization

The technology is not ready for full-scale demonstration. Development of the transformer and the manufacturing methods for that transformer will be key to production readiness.

2.22 Low Cost Dye Sensitized Solar Cells

Awardee: Torrey Hills Technologies LLC

Principal Investigators: Ken Kuang

2.22.1 Abstract

Torrey Hills Technologies LLC (THT) undertook a project to reduce the cost of dye sensitized solar cells (DSC). The researchers identified seven natural dyes from a population of 25 candidates with potential to replace synthetic ruthenium based dyes. The seven potential replacements have lower cost and higher raw material availability. However all of them are inferior to the standard N719 dye in terms of solar performance: saturation currents, conversion efficiencies, and chemical stability. THT completed the development of a U-shaped assembly line and tested the concept. The new assembly approach appeared to be effective in reducing labor costs by 20 percent to 60 percent, depending on the scale of production. Finally THT constructed and tested a DSC backed security light prototype. The prototype has the capability to work in a very low light environment where conventional solar cells do not. Cost remains the most significant single factor that affects the marketability of DSC products.

Keywords: DSC, dye, solar cells, security light

2.22.2 Introduction

California's Renewable Portfolio Standard requires utilities to supply an increasing portion of their energy mix from renewable energy sources. California is blessed with significant renewable resources, remains a global leader in the application of these technologies, and has long had policies encouraging their use. However most of the renewable resources and their development have high associated costs. This is especially true for solar photovoltaic (PV).

Existing solutions of solar cells that generate electricity are made either of silicon or from thin film second generation semiconductors. At the beginning of this project the limited supply of crystalline silicon kept the price of silicon based solar cells high. Until recently the price of silicon cells exceeded $4.50 per peak watt. Even at that price those cells had a distinct advantage over thin film technology due to their higher level of efficiency. By January 2012 the prices for crystalline silicon (c-Si) solar photovoltaic (PV) cells had fallen below $1/W for the first time. This was caused by new silicon foundries coming on line, reducing the cost of silicon from about $800/kg to around $30/kg.

Dye sensitized solar cells, a third generation PV technology, employ relatively inexpensive construction materials, including glass and titania powder. The major cost comes from the dye required to absorb light, currently ruthenium based, and expensive electrolytes. Dye sensitized solar technology currently remains expensive for this reason.

This project sought to verify manufacturing feasibility of dye sensitized solar cells (DSC) at a cost of below $1.0/W by using low cost materials (i.e., substitutes for the ruthenium based dye and electrode materials), high volume microelectronics manufacturing methods, and lean manufacturing based design.

2.22.3 Objectives

The goal of this project was to verify manufacturing feasibility of dye sensitized solar cells (DSC) at low cost, below $1.0/W, by using novel low cost materials, high volume microelectronics manufacturing methods, and lean manufacturing based design. To meet these goals, the project established several objectives:

1. Search for and determine extraction methods for organic/natural dyes with potential cost of $100/g or lower. The current ruthenium based dye costs over $1000/g.
2. Replace expensive platinum metal with nickel-iron based catalysts with 75 percent conversion efficiency.
3. Demonstrate the materials cost less than $1.0/W at low volume and $0.5/W at high volume.
4. Evaluate the feasibility of the projected manufacturing cost for DSC of $0.70/W at high volume.

2.22.4 Outcomes

1. The research team tested 25 organic/natural dyes. The team identified seven of the 25 as potential candidates to be manufactured with cost below $100/g. The research team

found three dyes, HC-1, Dye-H3, and BTS, to be most promising in terms of output current and voltage. However their inherent chemical instability resulted in quick performance degradation. Although the fabrication cost could be reduced by using substitute organic dyes, the substitution of N719 with organic dyes resulted in significant reduction of saturation currents, conversion efficiencies, and chemical stability which reduced the overall conversion efficiency by 37 percent compared to the standard N719 dye.

2. When using nickel, the team measured chemical reactivity similar to that of platinum. Nickel is many times cheaper than platinum. The team also found that replacing Pt with Ni resulted in a loss of output power by more than 50 percent, as shown in Table 3. The efficiency of platinum and three nickel electrodes is shown in bold type.

Table 6: DSC Cell Performance with Ni Electrode Replacing the Pt Electrode

Anode	Dye	Light source	J_{sc} (mA/cm^{-2})	V_{oc} (V)	FF (%)	**η (%)**	Plating batch cost ($)	Metal cost ($/coat)
Pt	N719	AM1.5	4.34	0.66	0.72	**4.72**	$40.50	$15.00
Ni-1	N719	AM1.5	1.62	0.393	0.502	**1.8**	$20.00	$0.06
Ni-2	N719	AM1.5	1.87	0.358	0.519	**1.92**	$20.00	$0.06
Ni-3	N719	AM1.5	1.7	0.39	0.47	**1.87**	$20.00	$0.06

3. The research team did not report material costs using the various substitute dyes.

4. The team estimated the final cost of cells could range from $2/W to $5/W under different scenarios of economies of scale.

2.22.5 Conclusions

1. The researchers identified seven organic dyes as low cost substitutes for N719. They found three of them demonstrated comparable J_{SC} values, but chemical instability caused quick performance degradation. Therefore the organic dyes examined in this work were unsuitable for replacing N719. The research team did not meet this project objective.

2. Nickel plating of electrodes has potential to reduce material cost compared to platinum, but only at the loss of cell performance. In this research the loss was nearly 60 percent of conversion efficiency. Replacing Pt with Ni significantly reduced the photocurrent and output voltage, which resulted in a loss of 55 percent of power output. The research team did not meet this project objective.

3. The researchers did not report estimation of material costs alone, except for the electrode metal choice. In the case of electrode costs, there was a reduction from $15 to $0.06 when changing from platinum to nickel. The lack of overall material cost estimates was

consistent with the research findings of dramatic loss of performance. The researchers did not achieve this objective.

4. The research team did not accomplish the goal of developing a cell manufacturing cost of $1/W or less. The team achieved estimates of $2/W to $5/W. However it was successful in lowering estimated production costs using the U-shaped production layout.

5. The dyes tested showed a narrow absorption spectrum in the visible range, understandable given the nature of dyes. That absorption reduced their overall performance.

This research led to a more complete understanding of dye sensitized solar cells, but it did not verify manufacturing feasibility of the dye sensitized solar cells (DSC) at cost below $1.0/W. The current glut of poly silicon has driven the price of that material to as low as $30/kg from a high of $800/kg to $1000/kg a few years ago. Chinese manufactured crystalline silicon solar cells are being sold commercially below $1/W in mid 2012. This makes it more difficult for DSC to compete in this market.

2.22.6 Recommendations

The Program Administrator recommends the researchers should:

- Investigate mixtures of multiple dyes to improve the absorption spectra of the dye sensitized solar cells, which should lead to increased conversion efficiency.

- Investigate the ability to design and formulate dyes and dye systems with the requisite properties, in addition to searching for existing dyes with the requisite properties. Modern chemical formulation techniques may greatly simplify the task of obtaining a dye or dye system with both low cost and high performance.

- Evaluate alloys and plated electrodes (e.g., a thin layer of Pt on a base metal) or metal/ceramic composites,[68] to reduce electrode metal (Pt) requirements while enhancing electrode performance.

- Investigate the cost versus performance tradeoffs of using other electrode metals (gold, palladium, or silver) in place of Pt for the electrodes. While gold has a slightly higher price than platinum, it also has easier alloying properties. Palladium currently has a price about 30 percent of platinum while the price of silver is 2 percent of platinum.

- Conduct an extensive literature search on evaluations done by others before embarking on physical evaluation of alternative electrodes.

68 Metal/ceramic electrodes have been evaluated for use in more rigorous environments such as high temperature solid oxide fuel cells, as described in *Novel Composite Materials for SOFC Cathode Cathode-Interconnect Contact*, J. H. Zhu, Z.G. Lu, and D. A. Ballard, Department of Mechanical Engineering, Tennessee Technological University, Cookeville, TN. Presented at UCR Contractors Review Conference, Pittsburgh, PA, June 5-6, 2007.

2.22.7 Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit of the results of this research is increased affordability of electricity in California, given the otherwise increased cost of meeting the renewable portfolio standard requirements. While the project did not directly provide for lower cost solar photovoltaic systems and consequently will not provide benefits to California ratepayers per se, it did add to the scientific understanding of dye sensitive solar cell photochemical behavior. This may ultimately advance DSSC technology. The research did provide unquantifiable benefits for lowering production costs through the U-shaped assembly configuration and a useable DSC for use in low ambient light conditions.

2.22.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

The project team is evaluating market potential, determining marketing approaches, and developing a commercialization plan. 3G Solar has expressed interest in assisting in commercial development of the technology.

Engineering/Technical

The project team is developing engineering requirements for products using this technology.

Legal/Contractual

The research team has not applied for a patent but has non-disclosure agreements with all principals.

Environmental, Safety, Risk Assessments/ Quality Plans

There are no known environment or safety risks, although any devices made using these technologies will need to get UL testing and labeling.

Production Readiness/Commercialization

The technology and system are not yet ready for production or commercialization, except for use in limited niche markets.

2.23 High Efficiency, Compact SiC-Based Solar Inverter

Awardee: Aegis Technology Inc.

Principal Investigators: Timothy Lin

2.23.1 Abstract

The goal of this project was to determine the feasibility of producing a high efficiency, high reliability, and compact solar inverter using commercially available silicon carbide (SiC) power devices and to analyze the benefits of such a SiC-based solar inverter. Current commercial inverters are based on silicon (Si) power electronics but suffer from poor lifetimes and inefficiencies. They comprise the second largest cost component of PV systems, second only to the panels themselves. In this project researchers designed a more efficient and reliable solar inverter. They used a simulation model of the power module and inverter to model the power module performance and fabricated power modules using commercial SiC devices. They fabricated a 5 kVA solar inverter prototype and tested it in a laboratory scale PV system. They demonstrated the technical feasibility of a high efficiency, high reliability solar inverter based on commercially available silicon carbide power devices.

Keywords: SiC, power module, solar (PV) inverter, high efficiency, high reliability

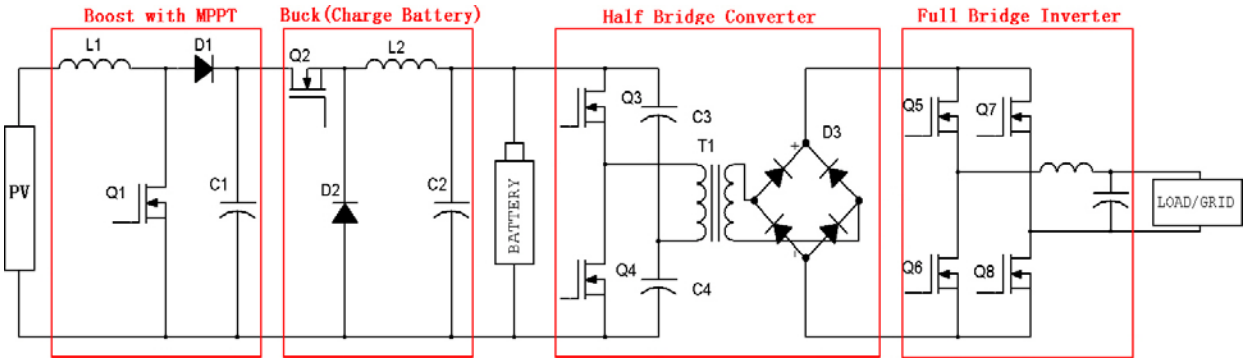
2.23.2 Introduction

Solar energy has been a policy preference in California since the 1970s. Solar electric photovoltaic (PV) systems produce direct current and must include an inverter to convert their output to alternating current for connection to the electric grid. One key component of the entire solar energy system, the inverter, currently is a high cost component with a relatively short mean time between failures (MTBF). They typically must be replaced after 7 years to 10 years, and they represent a large (10 percent to 25 percent) part of system costs. The cost of inverters has taken on even greater importance with the recent price drops of solar panels themselves. With rapid advances in solar cell technology and arrays, inverter reliability has become even more important to the overall economics and customer satisfaction with solar PV.

Commercial solar inverters that are predominantly based on silicon (Si) power devices are quite mature, and increases in reliability and energy efficiency appear limited. Silicon carbide (SiC) semiconductors have been recently investigated for use in power devices, because such devices offer potentially outstanding power conversion capabilities. Compared with Si-based devices, SiC-based power devices have the capability of operating at higher junction temperatures, higher power densities, and higher frequencies. Several technical challenges exist that are hampering the integration of SiC power devices for SiC power converters and inverters, including circuit design, modeling, and high junction temperature packaging.

In this project the researchers demonstrated the technical possibility of developing SiC-based solar inverters with commercially available SiC devices. They demonstrated a prototype SiC solar inverter as functional. A system diagram of an inverter is shown in Figure 24. If further development is successful, SiC-based PV inverters may be fabricated into a new generation of solar energy systems with improved energy efficiency and reliability.

Figure 24: Systematic Design of a PV (Solar) Inverter Incorporating Energy Storage



2.23.3 Objectives

The goal of this project was to demonstrate the technical feasibility of a novel type of solar inverter using commercially available SiC devices. The researchers had the following objectives:

1. Design a highly efficient and highly reliable solar inverter. This includes power module, packaging, heat sink, and electrical interconnection.
2. Perform system modeling, including power module and inverter performance, and compare power loss and weight to a silicon-based inverter.
3. Fabricate the power module and package using commercially available SiC power electronic components. Test and conduct reliability assessment.
4. Develop suitable gate drive systems. Fabricate and characterize a prototype inverter.
5. Analyze technical costs and benefits, and survey potential customers.

2.23.4 Outcomes

1. The researchers designed a solar inverter based on commercially available SiC components. The output voltage of the PV inverter, with regulation by a high frequency transformer, was adjustable to 200 V and 120 VAC.
2. The researchers developed a loss model of the power module and compared the power loss, size, and weight of the SiC inverter with a Si-based inverter. The simulation results are shown in Table 4.

Table 7: Primary Simulation Results in the Discharging State of Battery System

Inverter	JFET/IGBT Temperature Rise (°C)	Diode Temperature Rise (°C)	Total Power Losses (W)	Efficiency (%)	Power Loss Percentage (%)	Heatsink (in^3) Natural Convection
	Peak (Ave.)	Peak (Ave.)	Peak (Ave.)	Lowest (Ave.)	Largest (Ave.)	Thermaflo E1353
Si	109 (101)	125 (116)	311 (288)	95.6 (95.9)	4.6 (4.1)	140.1
SiC	123 (110)	121 (108)	175 (153)	97.6 (97.8)	2.4 (2.2)	25.4

3. The researchers fabricated two types of power modules using commercial SiC power devices: an H bridge (four packed) and a three-phase (six packed) power module. They performed preliminary tests. They did not report any reliability assessment.
4. The researchers designed and fabricated gate drivers for both normally off and normally on SiC JFET[69] devices and power modules. After substitution of transistors with MOSFET,[70] the researchers demonstrated the gate drivers function with the inverter prototypes.
5. The researchers fabricated a 5 kVA inverter prototype and tested it by integrating power modules, gate driver board, and other components. Using this inverter, the researchers constructed a laboratory test setup for a complete solar energy system. Preliminary testing showed an improvement in conversion efficiency of 97.5 percent compared to Si-based systems at 93 percent.

2.23.5 Conclusions

1. The incorporation of commercially available SiC power devices into solar inverters is possible and could provide advantages compared to existing Si-based inverters. The researchers completed this objective to design a SiC-based inverter.
2. The simulation modeling of SiC-based inverters compared favorably to Si-based inverters with respect to temperature and efficiency. The researchers completed this objective.
3. Preliminary testing reported by the researchers was inconclusive and inadequate to determine reliability of the SiC-based inverter. The researchers did not complete this objective.

69 JFET= junction gate field effect transistor

70 MOSFET= metal–oxide–semiconductor field effect transistor

4. Further development work focused on gate drivers is needed before any advantages offered by SiC power devices can be achieved. The gate drivers developed so far demonstrate only that such devices are possible. The researchers completed this objective to design and fabricate gate drivers.

5. Laboratory scale testing indicated that SiC-based inverters provide efficiency and power loss advantages compared to mature Si-based inverters. The researchers completed this objective.

The researchers successfully demonstrated that SiC-based inverters are feasible using commercially available SiC components. Significant work remains before such inverters can be considered practical.

2.23.6 Recommendations

The Program Administrator recommends that the researchers:

- Focus on improving gate drivers, reduce or eliminate electrical noise and harmonics in produced wave forms, and improve overall performance of the SiC-based inverter.
- Test and fully document performance, including at different solar panel output in terms of watts and amperage (e.g., such as that produced at different times of day).
- Undertake a comprehensive life cycle cost analysis and compare results to commercial Si-based inverters.
- Ensure there are no grid synchronization issues as they ultimately strive for interconnection certification under California's Rule 21.
- Continue working with firms able to commercialize and integrate the inverter into complete solar packages and begin work with firms making other DC devices such as fuel cells.
- Determine mean time between failure (MTBF) and failure modes for the device (e.g., slow persistent degradation over time or outright failure).

After taking into consideration (a) research findings in the grant project, (b) overall development status, and (c) relevance of the technology to California and the PIER program, the Program Administrator has determined that the proposed technology should be considered for subsequent funding within the PIER program.

Receiving subsequent funding ultimately depends upon (a) availability of funds, (b) submission of a proposal in response to an invitation or solicitation, and (c) successful evaluation of the proposal.

2.23.7 Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system

- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit of the results of this research is increased affordability of electricity in California. According to the National Renewable Energy Lab, residential PV systems cost about $3.20/Watt (depending on application), with inverters representing about 42 cents of that or 13 percent.[71] However inverter lifetimes do not match panel and BOS lifetimes and generally only last only 7 years to 10 years. Even at the optimistic end of that range, inverters need to be replaced fully twice during the lifetime of the solar panel, adding effectively 26 percent to the system cost, assuming replacement costs rise with general inflation or zero in real dollar terms. If the longer lives promised by SiC-based inverters can be achieved, an effective cost saving for PV systems of about 26 percent would result. The California Solar Initiative and New Solar Homes Partnership have a goal of 2300 MW of solar electricity, with another 700 MW goal by various publicly owned utilities.[72] Assuming that 25 percent of the installations were to make use of the SiC-based inverters, and further assuming that they are successfully advanced, a saving of about $625 million dollars would accrue to Californians compared to current Si-based inverters.

2.23.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

Green Power has expressed interest by a letter and will provide a commercialization path for Aegis Technology's inverter technology for solar energy applications.

Engineering/Technical

The researchers are developing technical requirements and continuing work on gate drive modules. Their next step is to develop SiC-based power modules followed by the development of various inverters/converters. They project commercial readiness in approximately two years at a cost of close to $2 million.

Legal/Contractual

The researchers have applied for patent protection, but patents have not yet been awarded. The researchers themselves performed a patent search and found no conflicting patents.

Environmental, Safety, Risk Assessments/ Quality Plans

There are no known environmental or safety risks associated with the new concept. Quality assurance plans will need to be developed and implemented once the concept is proven. The

71 http://www.nrel.gov/docs/fy12osti/53347.pdf

72 http://www.cpuc.ca.gov/puc/energy/solar/aboutsolar.htm

device will ultimately need to be certified by Underwriter Laboratories. If the device is to be grid connected, the electric utilities will need to approve.

Production Readiness/Commercialization

The device is not ready for production or commercialization. Aegis plans to license the technology and not commercialize the technology in house.

2.24 Direct Solid Oxide Fuel Cells

Awardee: University of California, San Diego (UCSD)

Principal Investigators: Nguyen Minh

2.24.1 Abstract

California policy encourages accelerated deployment of combined heat and power (CHP) systems to improve source efficiency, enhance the reliability of electricity supplied to customers, and reduce greenhouse gas (GHG) emissions.

The objective of this project was to determine the feasibility of using a direct solid oxide fuel cell (SOFC) incorporating novel cell and interconnect designs to generate electricity from a variety of fuels. The proposed concept had the potential of increasing the system efficiency of fuel cells resulting in lower operating costs and further reduction of GHG emissions. The proposed direct SOFC concept was based on a bi-functional bi-layer anode and prime surface interconnect design that was developed during the course of this project.

The results of this project are promising. Single cells and a single cell stack incorporating an impregnated cell and prime surface interconnects demonstrated excellent performance.

The research team first constructed and demonstrated high performance and stable operation of single cells. The team observed no evidence of carbon deposit during a short term (2.5 hour) testing period. Researchers then developed a unique, integrated interconnect design that was used to help assemble single cell stacks, incorporating impregnated cells. Testing of the fabricated single cell stacks demonstrated excellent peak performance and stable operation during a two-hour test cycle.

This project confirmed the feasibility of the direct SOFC concept. The research team recognizes the need for further development work to ensure multi-fuel capability of the fuel cell, optimize system design, and validate performance, durability, and reliability. A prototype will need to be fabricated and extensive testing conducted in the lab and field to ensure that the product is ready for the marketplace. Finally, a commercialization plan will help identify markets, sales targets, and product distribution channels. In the immediate future the research team is considering the possibility of pursuing a patent for the new interconnect design and licensing the technology to interested component suppliers and/or fuel cell manufacturers.

Keywords: Solid oxide fuel cell, bi-functional bi-layer anode, impregnation, prime surface interconnect, direct ethanol utilization

2.24.2 Introduction

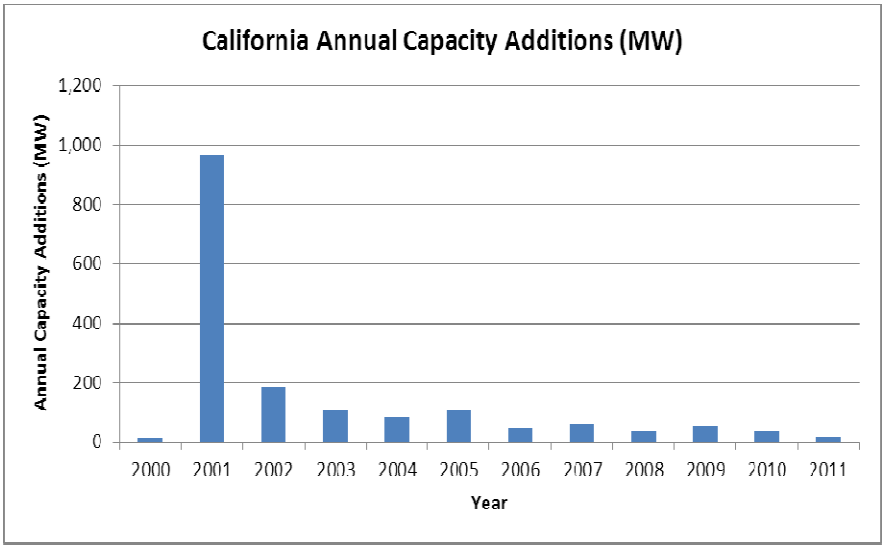
California residents consumed approximately 272,300 gigawatt hours (GWh) of electricity in 2010. Electricity consumption is forecasted to grow at a rate of 1.32 percent per year between 2010 and 2020 in the mid-case scenario. In California electricity produces about 21 percent of the state's GHG emissions, about half of which comes from imported electricity.

There is a need in the marketplace for more cost effective, clean, efficient, and reliable power generation systems. Direct solid oxide fuel cells (SOFC) have the potential to serve a variety of applications and markets including grid power, portable power, transportation, and auxiliary power units (APU). Perhaps the most immediate and compelling application is CHP. The technical market potential for CHP in California is approximately 18.4 gigawatts (GW).

According to the California Energy Commission (CEC), California's main challenge is to ensure adequate electricity supplies while reducing greenhouse gas emissions as directed by Assembly Bill 32 (AB 32). California policy supports increased adoption of combined heat and power (CHP) systems to further reduce greenhouse gas (GHG) emissions and increase source energy efficiency. In its 2008 Climate Change Scoping Plan developed pursuant to AB 32, the California Air Resources Board (CARB) identified CHP as the third most significant source for GHG emissions reductions and called for 4,000 megawatts (MW) of new CHP capacity, which would result in 6.7 million metric tons (MMT) of GHG reductions.

Over the past several years, however, the addition of new CHP capacity has fallen flat (Figure 25). Incremental CHP capacity in California increased only by an average of about 40 MW per year from 2007 to 2011, equivalent to approximately 10 percent of the current goal (roughly 400 MW per year). Clearly, more cost effective product solutions and business models are needed for California to have any chance at meeting its CHP goals.

Figure 25: Incremental CHP Capacity Trends in California



Solid oxide fuel cells (SOFC) can serve as a potential clean and efficient distributed generation technology to support California's current and future energy needs. The attributes of the SOFC

for power generation include higher fuel-to-electricity conversion efficiency (40—60 percent), near zero emissions, fuel flexibility, modularity, and multiple operation options including possible integration with internal combustion engines to further reduce engine emissions. SOFC products can operate on a number of conventional and renewable fuels and can be used as an on-site distributed generation device or configured as a CHP system. Certain fuel cell products also produce a small quantity of water as a by-product, an increasingly valued resource in California. Further development and commercialization of cost effective SOFC products could help accelerate adoption of cost effective distributed generation solutions in the marketplace and help meet California's policy goals.

SOFC products can potentially be used for a variety of applications in the marketplace including portable power, transportation, and stationary power as follows:

- Portable: 10—100 watt military power systems
- Transportation: 10—50 kilowatt (kW) automobile and truck auxiliary power units (APU) and 500 kW APU for aircraft applications
- Stationary: 1 to 10 kW residential CHP systems, 100—1,000 kW CHP systems, 1 to 10 MW distributed generation (DG) units, and multi-MW base load power plants

Many of these applications have progressed to hardware demonstration and prototype stages, and several applications, especially those with large power outputs, are at the conceptual stage. At present SOFC technology is under study and/or development in at least 30 countries worldwide. In the U.S. the main SOFC development effort is the U.S. Department of Energy (USDOE) Solid State Energy Conversion Alliance (SECA) program. There are many technical and cost hurdles which need to be overcome prior to widespread adoption of SOFCs in the marketplace, including stack performance, system reliability, and durability. Fuel cell interconnects are a critical component to a high performing and reliable fuel cell stack. Fuel cells must be used in combination to generate enough voltage and current. This means that the cells need to be connected together and a mechanism for collection of electrical current needs to be provided, hence the need for interconnects. The interconnect functions as the electrical contact to the cathode while protecting it from the reducing atmosphere of the anode.

The focus of this project was to determine the feasibility of using a direct SOFC for clean and efficient generation of electricity from a broad spectrum of fuels without the need for a separate reformer or fuel processor. Researchers incorporated two key configurations proposed for direct SOFCs: the bi-functional bi-layer anode and prime surface interconnect designs. The technology selected for this project was a planar stack of direct SOFC single cells connected in electrical series with prime-surface metallic interconnects. The researchers developed this design concept to address two critical issues facing current SOFC technology: relatively poor performance on direct utilization of practical fuels and high interconnect costs. The design of the single cell was based on the anode-supported configuration as shown in Figure 26. The operating temperature of the fuel cell was 800° C. The anode was a bi-functional bi-layer with the thicker outer layer that promoted hydrogen reforming/forming from ethanol and the thinner inner electro-active layer. The interconnect was based on the prime-surface design shown in Figure 27 using an egg carton shaped flow field.

Figure 26: Direct Ethanol SOFC Cell Configuration (not to scale)

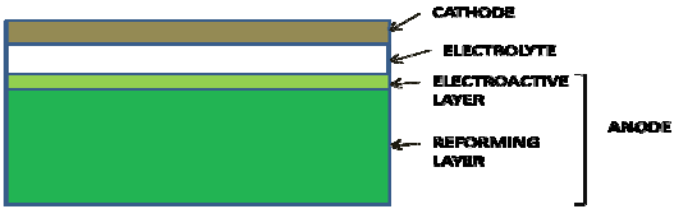
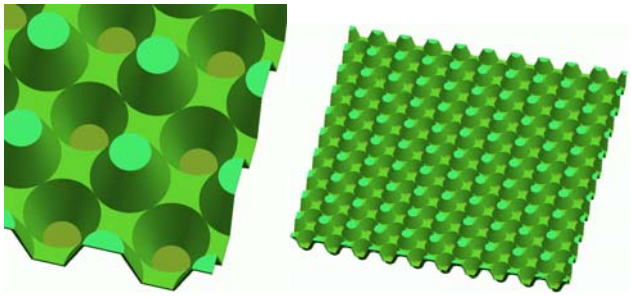


Figure 27: Egg Carton Shaped Prime Surface Interconnect Design. Full View Right, Detailed View Left (not to scale)



Excellent performance was achieved for both single cells and a single cell stack incorporating an impregnated cell and prime surface interconnects. The research team first constructed and demonstrated high performance and stable operation of single cells operating on ethanol using bilayer nitrogen/yttria-stabilized zirconia (Ni-YSZ) anodes impregnated with copper-ceria. Researchers obtained peak power density of about 404 milliwatts per square centimeter (mW/cm2) at 800° C with 7.3 percent ethanol balanced by helium. They observed no evidence of carbon deposit during the short term (2.5 hour) testing period. Researchers then developed a unique, integrated interconnect design that was used to help assemble single cell stacks, incorporating impregnated cells. Testing of the fabricated single cell stacks demonstrated peak power density of about 300 mW/cm2 at 800° C with stable performance during a two hour test cycle running on 7.3 percent ethanol that was balanced by helium.

The results of this project demonstrated the feasibility of the bi-functional bi-layer anode concept, the prime surface interconnect design, and operation of direct SOFCs on ethanol fuel without carbon deposition in short term tests. The direct SOFC concept evaluated in this project is a significant advancement in SOFC technology compared with conventional designs. Its clean and efficient direct operation on various types of fuels at a lower cost has the potential to overcome key barriers facing current fuel cell technologies and facilitate the use of this technology in the marketplace. The research team identified several remaining technical and cost issues which need to be addressed before this technology is ready for the marketplace, including:

- Durability testing of direct SOFC cells and stacks under practical operating conditions such as higher ethanol concentrations and longer test times.

- Development of new material compositions and system optimization to enable operation with different practical fuels such as natural gas, syngas from coal, biofuels, diesel, etc.
- Documentation of detailed specifications for various cell configurations, cell preparation methods, operating parameters, and cell performance maps.
- Optimization of prime surface interconnect designs, selection of suitable materials, and design of fabrication processes, including manufacturing scale-up.
- Demonstration of long-term operation of cells, interconnects, and stacks to meet system durability requirements for commercial products. Causes for performance losses during long-term operation if any are identified to develop approaches to mitigate performance degradation.
- Investigation of technology/product reliability.
- Analysis of cost effectiveness.

Upon completion of this development work, the researchers will then need to fabricate a prototype and conduct extensive testing in the lab and field to help ensure that the product is ready for the marketplace. A commercialization plan is also required to identify markets, sales targets, and product distribution channels. In the immediate future, the research team is considering the possibility of pursuing a patent for the new interconnect design and licensing the technology to interested component suppliers and/or fuel cell manufacturers.

2.24.3 Objectives

The goal of this project was to determine the feasibility of using a so-called direct SOFC for clean and efficient generation of electricity from a broad spectrum of fuels. The researchers established the following project objectives:

1. Determine material compositions for bi-functional bi-layer anodes in direct SOFCs with a target concentration of catalyst in the reforming layer of less than 5 percent of total weight.
2. Demonstrate fabrication of direct SOFC prime surface interconnects as confirmed by measurements within plus or minus (±) 5 percent of dimension specifications.
3. Demonstrate direct oxidation of ethanol on bi-functional bi-layer anodes with minimal carbon deposition as confirmed by optical and microscopic observations and/or chemical analysis.
4. Demonstrate a direct SOFC single cell stack operating on ethanol fuel with the target power density of greater than 100 milliwatts per square centimeter (mW/cm^2).

2.24.4 Outcomes

1. The researchers developed an anode configuration consisting of two nitrogen-yttria stabilized zirconia (Ni-YSZ) layers impregnated with copper-ceria for direct ethanol SOFC single cells. No catalyst was needed for this anode composition.

2. The researchers successfully fabricated interconnect samples based on the integrated prime surface design conceived in this project. Characterization of as fabricated interconnects indicated that dimensions such width, length, and holes were within 5 percent tolerance of the dimension design. On the other hand, flatness showed about 9.2 percent offset.

3. Researchers were able to successfully demonstrate operation of single cells using ethanol as a fuel source with impregnated bi-functional bi-layer anodes. Power densities as high as 404 mW/cm2 were obtained at 800° C with fuel containing 7.3 percent ethanol balanced by helium. Constant current duration testing and examination of tested anodes indicated no carbon deposition under the testing conditions.

4. Researchers operated a direct SOFC single cell stack at 800° C with 7.3 percent ethanol balanced by helium. The peak power density achieved was about 300 mW/cm^2.

2.24.5 Conclusions

1. Impregnated anodes operated directly on ethanol fuel without addition of catalysts.

2. The researchers invented a new interconnect design referred to as integrated prime surface design in this project. They fabricated metallic interconnects based on the new design within stated acceptable tolerances.

3. The researchers demonstrated excellent performance for single cells with impregnated anodes with a peak power density that is the highest reported to date at this concentration of ethanol. Single cells showed stable performance with no evidence of carbon deposition during short-term (2.5 hour) duration.

4. The researchers assembled and tested with ethanol fuel the single cell stack incorporating an impregnated cell and prime surface interconnects. It produced excellent performance results.

These results demonstrated the feasibility of the bi-functional bilayer anode concept, the prime surface interconnect design, and operation of direct SOFCs on ethanol fuel without carbon deposition in short term (up to 2.5 hours) and low ethanol concentration tests (up to 17.6 percent ethanol). Direct SOFC technology based on these design concepts is thus attractive and suitable for further development to move the technology toward commercial viability.

2.24.6 Recommendations

This project demonstrated the feasibility of the direct SOFC concept incorporating single cells with bi-functional bi-layer anodes and prime surface interconnects. Researchers identified several critical issues that need to be addressed before this technology can achieve commercial viability, including durability testing and the development of new material compositions to enable operation with different fuels.

The Program Administrator recommends the follow-on activities listed below:

1. Demonstrate the durability of this technology under practical operating conditions. Extend test time to weeks, months, and years.

2. Conduct a market assessment.

3. Contact SOFC manufacturers to assess potential for collaboration.
4. Evaluate and demonstrate multi-fuel capability.
5. Develop complete engineering specification of cell configurations, cell preparation methods, and operating parameters.
6. Develop cell performance maps.
7. Design and test balance of system design and components.
8. Develop and demonstrate large-scale fabrication processes.
9. Conduct a thorough reliability analysis.
10. Conduct a cost study to determine cost effectiveness of the technology.
11. Develop a commercialization plan to identify beachhead markets, sales targets, and product distribution channels.

In addition, detailed specifications are needed for various cell configurations, cell preparation methods, operating parameters, and cell performance maps. Further optimization is needed for prime surface interconnect designs, along with demonstration of long term operation of cells, interconnects, and stacks to meet system durability requirements for commercial products. Upon completion of this development work, the researchers will need to fabricate a prototype and conduct extensive testing in the lab and field to help ensure that the product is ready for the marketplace. In the immediate future, the research team is considering the possibility of pursuing a patent for the new interconnect design and licensing the technology to interested component suppliers and/or fuel cell manufacturers.

After taking into consideration (a) research findings in the grant project, (b) overall development status, and (c) relevance of the technology to California and the PIER program, the Program Administrator has determined that the proposed technology should be considered for subsequent funding within the PIER program.

Receiving subsequent funding ultimately depends upon (a) availability of funds, (b) submission of a proposal in response to an invitation or solicitation, and (c) successful evaluation of the proposal.

2.24.7 Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the ratepayer from this research is reduced environmental impacts of the California electricity supply or transmission or distribution system. In this project the specific benefit lies in reduced environmental impacts of the California electricity supply.

Successful development and widespread deployment of direct SOFCs have the potential to reduce electricity consumption, lower electricity costs supplied to customers, and reduce GHG emissions as detailed below:

- Reduce electricity consumption. Researchers estimate that successful development and commercialization of direct SOFCs can reduce electricity consumption in California by about 2,150 GWh per year beginning in 2017. This estimate is based on an assumed 20 percent market penetration of direct SOFCs in the residential and commercial markets, which currently consume about 215,000 GWh per year, and that such customers would realize an overall efficiency improvement of 5 percent. SOFCs could potentially provide enormous benefits to California ratepayers if cost effective units could be developed and successfully deployed.
- Lower electricity costs. Presently California utility customers pay an average of about 13 cents per kWh. Experts project costs to climb to 16—17 cents/kWh in 2017. The researchers estimated that successful deployment of direct SOFCs throughout the electric utility grid could result in 20 percent lower electricity costs compared with conventional technology, thus lowering the overall cost of electricity supplied by the grid. With low cost natural gas for fuel and high efficiency combined cycle gas turbines (about 60 percent efficient) currently available, the SOFC has a formidable challenge to achieve lower cost electricity. Combined heat and power units achieve about 75 percent efficiency with current technology. The cost advantage for SOFC may occur in smaller capacity units, perhaps under one MW.
- Reduce GHG emissions. In general, fuel cells produce little or no oxides of nitrogen (NOx), sulfur oxide (SOx), or carbon monoxide (CO) emissions. Fuel cells also enable a reduction in carbon dioxide (CO_2) emissions (1200 lb/MWh) compared with fossil fired plants (2000 lb/MWh). Use of biofuels can enable further reductions in GHG emissions by more than 50 percent.

In addition, direct SOFCs can improve energy supply reliability of the electric grid with rapid deployment where required. SOFCs can also be used in a combined heat and power (CHP) configuration, providing customers with additional energy options to help increase source energy efficiency, lower operating costs, and reduce GHG emissions. Finally, SOFCs can be used for remote customers without access to the electric grid or for backup power purposes.

2.24.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

This technology concept was derived at UCSD and eventually needs to be transferred to an industrial company for further development and product commercialization. Researchers

signed a non-disclosure agreement (NDA) with a venture capital company which expressed interest in the intellectual property related to the new prime surface interconnect design. The researchers had not conducted a market survey nor had they contacted potential customers/users of this technology by the end of this project.

Engineering/Technical

Further technology development work is needed before this concept can be considered ready for commercial deployment. The research team estimates that this technology development and demonstration work can be completed in the next two to three years at an additional cost of approximately $5 million.

Legal/Contractual

The researchers submitted an invention disclosure on the interconnect design to the UCSD Technology Transfer Office. There is no evidence that the researchers conducted a patent search.

Environmental, Safety, Risk Assessments/ Quality Plans

Because of the early stage of development, the researchers had not addressed these plans as of the end of their project.

Production Readiness/Commercialization

The concept was not sufficiently developed for commercialization at the end of this project.

2.25 Petcoke Fueled SOFC Power Generator for On-Site Application

Awardee: Materials and Systems Research Inc

Principal Investigators: Greg Gege Tao

2.25.1 Abstract

The objective of this project was to prove the feasibility of a power generator capable of efficiently converting petroleum coke chemical energy directly into electricity. To fulfill this objective, the researchers designed and built partial oxidation (POX) reactors similar to simplified fixed bed coal gasifiers. These reactors incorporated improved reaction enhancement and thermal management features. The researchers coupled the reactors with solid oxide fuel cell (SOFC) modules to directly convert the petcoke producer gas into electrical energy.

In the POX process, petroleum shot coke was partially oxidized to produce a gas consisting of a relatively stable 60 percent CO. This hot producer gas was fed directly to an SOFC module anode which electrochemically oxidized it with a cathode air stream to generate electricity.

The researchers fabricated anode supported SOFCs using their proprietary cell materials. They evaluated both button cells and tubular cells with per cell active areas of 2 cm^2 and 24 cm^2, respectively, using bottled gases as a baseline. The bottled gas simulated producer gas compositions ranging from 50/50 percent to 90/10 percent CO/CO_2 by weight. Proof of concept testing performed on multiple three-cell (100 cm^2 per cell active area) SOFC modules using the petcoke producer gas showed the value of this technology by demonstrating levels of performance on par with that delivered through the use of bottled gases.

The cost of commercial units based on this technology appears moderate to high at this point. Cost of the SOFC modules is the biggest unknown.

Keywords: Solid oxide fuel cell, petroleum coke, partial oxidation, opportunity fuel utilization

2.25.2 Introduction

California has the third largest petroleum refining capacity in the nation and produced over 26,887 short tons of petroleum coke (petcoke) daily as a byproduct in 2010. The energy content of this material is sufficient to potentially generate 27.72 billion kWh of electricity yearly, or nearly 10 percent of California's current annual power consumption. Instead of exporting over 80 percent of this petcoke overseas, the energy of this opportunity fuel produced in California can be utilized for power generation.

Southern California Edison is one example of the interest in petcoke. In 2009 Southern California Edison with partner BP Alternative Energy won California Public Utilities Commission (CPUC) approval to build a plant near Bakersfield to gasify petroleum coke for producing hydrogen and carbon dioxide. The hydrogen would be burned at a nearby facility to produce 250 MW of electricity while the carbon dioxide would be captured for enhancing oilfield production.

The partially oxidized petcoke can, instead of being used in relatively dirty and low yield conventional power plants, be oxidized electrochemically using fuel cell technologies. Unlike heat engines or gas/steam turbines, fuel cell efficiency is not limited by the Carnot efficiency. Therefore efficiency potential of a fuel cell based system is increased significantly, and fuel selectivity is low, particularly for a solid oxide fuel call (SOFC). Some fuel cell systems require fuel processors that reform and purify hydrocarbon fuels into pure hydrogen, adding significant costs to power generation systems, particularly for the polymer electrolyte membrane (PEM) based fuel cells. However, SOFCs operate at 750° C to 1000° C on flexible fuels, including gaseous or gasifiable hydrocarbon fuels, either directly or indirectly, with minimal processing. This can significantly reduce capital costs.

Coupling the two technologies, solid oxide fuel cells and petcoke partial oxidation, provides a means to leverage the abundant supply of petcoke into an opportunity fuel with significant energy potential for electricity. This can be realized without serious environmental cost and with a scalable capital cost. The use of this fuel would also increase the extracted energy value of every barrel of imported oil.

Fuel cells are electrochemical devices that generate electricity from a broad range of fuels. The solid oxide fuel cell (SOFC) typically operates at 750—1000° C on a variety of gaseous or gasifiable hydrocarbon fuels, either directly or indirectly, with minimal processing. An SOFC consists of electrolyte, anode, and cathode in the form of electrolyte supported, cathode supported, or anode supported architecture. A mixture of Ni and yttria stabilized zirconia (YSZ) is commonly used as the anode, thanks to excellent catalytic characteristics. Extensive analyses have shown that advanced power plants adopting combined SOFC and gas turbine technologies have the potential to achieve system efficiencies greater than 70 percent. Though an SOFC offers better fuel flexibility, fuel feedstock to the SOFC based power generator typically is hydrogen, light hydrocarbon fuels, natural gas, or coal derived syngas with a well-controlled steam/carbon ratio to avoid carbon deposition issues. Carbon monoxide, like

hydrogen or hydrocarbon fuels, can also be used as a feedstock to the SOFC for power generation, but it is less investigated. In addition to CO, the petcoke producer gas also contains a certain amount of sulfur compounds that may poison the nickel based anode substrates.

Figure 28: Integrated SOFC-POX Reactor Test Bed Complete with Enclosure

2.25.3 Objectives

The goal of this project was to determine the feasibility of developing a highly efficient and environmentally benign power generation system using SOFCs operating directly on a petcoke derived gas for on-site power generation applications. The petcoke generator consisted of a partial oxidation reactor (POX) integrated with a SOFC stack (Figure 28). Petcoke was partially oxidized by oxygen in the POX reactor, forming a producer gas. Specific objectives identified as key in the proposed work were:

1. Fabricate two sizes of planar cells with 2 cm^2 and 100 cm^2 active areas per cell.
    a. Control the electrolyte thickness to approximately 10 μm.
    b. Fabricate tubular SOFCs with 24 cm^2 per cell active area.
2. Demonstrate a petcoke conversion rate greater than 90 percent in a temperature range of 850° C to 950° C.
3. Prove the concept of power generation directly using petcoke in a SOFC module in the temperature range of 800° C to 850° C.
    a. Demonstrate power density of button cells greater than 1 W/cm^2 when operating on a mixture of bottled gases.
    b. Demonstrate the power density of a three-cell stack (100 cm^2 per cell areas) greater than 0.3W/cm^2.

c. Demonstrate the degradation of a three-cell stack at less than 2 percent in 200 hours.

d. Demonstrate ~75W generated from a petcoke fueled SOFC module.

4. Confirm that the on-site application of the generators with existing petroleum refining facilities is technically viable and cost effective. Show that the cost of the power generation system is less than $700/kW.

5. Determine possible causes of degradation or damage.

2.25.4 Outcomes

1. The researchers built two identical POX reactors similar to a simplified fixed bed coal gasifier. They added reaction enhancement and thermal management improvement features.

   a. The researchers did not comment on the electrolyte thickness.

   b. They manufactured tubular SOFCs with per cell active areas of 24 cm^2 and evaluated them under various testing conditions including different types of fuels.

2. The researchers did not indicate that they had demonstrated a petcoke conversion rate greater than 90 percent. They evaluated POX reactors with shot coke at 850° C to 950° C. Characterizations of the producer gas-by-gas chromatography demonstrated a production rate of 60 percent CO over a 2.5 hour run. CO concentration reached as high as 65 percent, accompanied by ~3 percent hydrogen for the initial 20 minutes of operation. The researchers performed experimental evaluations of individual button cells and tubular cells.

3. The researchers measured power density directly.

   a. At 800° C the power density of button cells reached 0.294 W/cm^2 at 0.7 V when operating on a simulated producer gas. The researchers investigated effects of fuel and air utilizations on SOFCs on tubular cells. When a simulated producer gas with 90 percent CO and 10 percent CO_2 was used as a fuel at 800° C and 0.7 V power, densities of 0.32 W/cm^2 and 0.3 W/cm^2 were achieved at fuel utilizations of 20 percent and 80 percent, respectively. The effect of CO concentration on the tubular cells showed that a CO rich gas was more desirable for SOFC performance. The researchers also performed tests of tubular SOFCs fed with the producer gas directly from the petcoke POX reactor. At 0.7 V SOFCs generated 6.0 W (0.25 W/cm^2) and 4.4 W (0.183 W/cm^2) power corresponding to the O_2 flow rate to the POX reactor at 0.2 SLPM and 0.3 SLPM, respectively.

   b. Proof of concept demonstration tests of multiple three cell (100 cm^2 per cell) SOFC modules directly operating on the petcoke producer gas showed the development value of this technology by demonstrating levels of performance on par with that delivered through the use of bottled gases.

   c. Long term stability tests showed that in-reactor oxygen distribution must be improved to prevent temperature mal-distribution and oscillation.

d. The stack operating on bottled gas produced 61.75 W; the stack operating directly on the producer gas generated 57.33 W, a 7 percent reduction.

4. The researchers projected a total system capital cost of $1250 per kWe. They did not address the technical and economic viability of this technology in existing petroleum refining facilities.

5. The researchers observed SOFC module damage intermittently through the testing and demonstration process. Damage was characterized as re-oxidation of anode substrates and carbon deposition on fuel manifolds. Such events were attributed to irregularities in the POX output. Researchers stated that further work must be done to regulate and monitor output gas properties to prevent damaging electrochemical modules.

2.25.5 Conclusions

1. The researchers were able to construct the facilities necessary to test their concept.

2. The researchers did not demonstrate 90 percent conversion rate over the designated temperature range.

3. Power densities fell short of the anticipated levels. In addition, the stack produced about 60 W rather than the 75 W expected.

4. At this stage of development it is difficult to assign a cost to this technology. The biggest unknown is the cost of the SOFC built with the researchers' technology. The projected cost of $1250 per kWe, if true, is not unreasonable.

5. Many issues need to be evaluated to test the robustness of the proposed concept. Obviously the researchers did not have enough time or funds to evaluate them. They observed carbon deposition after tests. The effects of sulfur compounds must also be addressed

Overall the researchers came close to meeting their objectives. However many questions remain unanswered.

2.25.6 Recommendations

Based on the project outcomes, the Program Administrator recommends that the researchers:

- Build a prototype POX reactor to validate at benchtop scale flow of a petcoke producer gas with desired fuel compositions. The researchers should consider a petcoke feeding mechanism and ash removal system. Real time regulation and monitoring the producer gas properties (compositions and flow rate) are also needed to prevent damaging electrochemical modules.

- Improve the long term stability of SOFC operations and thus increase the SOFC based power generator life. Researchers should focus on possible degradation mechanisms such as carbon deposition and sulfur poisoning.

- Build a complete system for proof of concept demonstration at a system level once subcomponent issues are resolved.

- Reduce the capital cost of the petcoke fueled SOFC generator to meet competitive prices.

- Protect all intellectual property before disclosure at conferences.
- Monitor the operational results of the Southern California Edison petcoke power plant.

After taking into consideration (a) research findings in the grant project, (b) overall development status, and (c) relevance of the technology to California and the PIER program, the Program Administrator has determined that the proposed technology should be considered for subsequent funding within the PIER program.

Receiving subsequent funding ultimately depends upon (a) availability of funds, (b) submission of a proposal in response to an invitation or solicitation, and (c) successful evaluation of the proposal.

2.25.7 Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the ratepayer from this research is reduced environmental impacts of the California electricity supply or transmission or distribution system.

California has the third largest petroleum refining capacity in the nation. In 2010 California had 12 major refineries with petcoke production capacity concentrated primarily in three areas. California refineries produced more than 26,887 short tons of petcoke daily in 2010. The energy content of that petcoke is sufficient to generate up to 27.72 billion kWh of electricity annually, equivalent to nearly 10 percent of California's power consumption in 2010. Consequently, implementing petcoke fueled SOFC generators could supplement electricity supplies in California. In addition, refineries currently export most of the petcoke to areas of the world with less stringent emission rules. The ships transporting the petcoke and the end uses of the petcoke can have a major effect on worldwide air emissions, especially CO_2. Clean conversion of petcoke into electricity in California could reduce air emissions while providing a higher level of energy output from every barrel of oil used in the state. Any CO_2 stripped out of the producer or exhaust gases could be used for enhanced oil recovery if the economics were favorable.

2.25.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

At the conclusion of the project the researchers had not yet surveyed any potential customers nor had they performed a market analysis.

Engineering/Technical

The researchers estimate that product development and demonstration will require four to five years and approximately $2.5 million. The two primary tasks will be the design of a POX reactor with subsystems for petcoke feeding and another for ash removal and demonstration of long term stability of the SOFC.

Legal/Contractual

The researchers performed a patent search and found no directly relevant patent. They had not applied for any patents by the end of the project. They planned to disclose their invention in journal articles and at conferences.

Environmental, Safety, Risk Assessments/ Quality Plans

The researchers did not address these issues. A licensee of the technology must address these issues in the future.

Production Readiness/Commercialization

MSRI will not commercialize this technology directly. The researchers plan to license the technology.

2.26 Development of High Efficiency and Cost Effective Micro Wind Turbines

Awardee: Iowa State University

Principal Investigators: Xinwei Wang

2.26.1 Abstract

The goal of this project was to develop a new type of micro wind turbine with a proposed diffuser technology for significant efficiency improvements and initial capital cost reductions. The researchers used a 3D printer to produce wind turbine blades of varying shapes, lengths, widths, twist angles, and tip angles. Testing of these blades in a wind tunnel allowed the researchers to identify the highest performance, which was obtained from a blade with a 37 degree twist angle, 0 degree tip twist angle, 6 cm mid-cord length, and 30 mm tip width (blade 3-37-6cm-30 mm). Operating at 14 m/s, the theoretical output peak power for this blade was 9.69 W. Experimental results yielded an output peak power of 1.5 W, resulting in an efficiency of 15.48 percent. Although the researchers demonstrated higher efficiencies with smaller blades, the additional turbines required to capture the same wind area would be cost prohibitive. The researchers were able to improve efficiency of this blade by experimenting with brush and brushless DC motors and demonstrated 27 percent efficiency with the 1100206 brush DC motor from Maxon operating at 8 m/s. The researchers introduced additional efficiency gains through the use of a diffuser. Experiments performed with varying diffuser inclination angles were able to demonstrate that a diffuser with a 3.9 percent inclination angle could achieve an efficiency of 55 percent, which was more than a 100 percent improvement over the micro turbine without the diffuser.

Keywords: Wind energy, blade design, diffuser, twist angle, wind tunnel

2.26.2 Introduction

California now demands that utilities provide 33 percent of their energy from renewable energy sources by 2020. In 2011 the California Energy Commission reported that wind energy provided 5.1 percent[73] of the State of California's electricity supply. The Center for Sustainable Energy has noted that costs for wind energy capture have decreased fourfold since 1980 and could easily contribute 20 percent of California's electricity supply by 2020.[74]

To meet these goals California must develop methods to harness wind energy at more than the few sites currently developed as wind farms. While California has several sites where the wind resource is great enough to employ wind turbines of greater than 300 feet in tower height and generator capacities of over 2 MW, California will need to develop machines where it is not practical to install 300 foot towers. Distributed rooftop wind generators with capacities of 2 kW to 25 kW may be one answer to this challenge.

However, smaller wind generators face several obstacles that have impeded widespread adoption. Wind is turbulent, and wind speeds vary tremendously near the ground and around buildings. Wind turbines offer their peak efficiency within a narrow range of wind speeds. Wind speeds below about 4 m/s are insufficient to drive the turbine, and speeds above 15 m/s or turbulent wind may cause damage to the turbine blades. The peak efficiency of small wind turbines is in the range of 25 percent to 30 percent for wind speeds ranging from 10 m/s to 13.5 m/s. Efficiency drops to less than 5 percent under low wind conditions.

In this project the researchers sought to design a micro wind turbine that would be suitable for residential installations and would be capable of operating in a wide range of wind speeds with a higher efficiency than commercially available wind turbines. Their innovation was to add a shroud or diffuser around the bladed area. The researchers constructed prototype blades using a 3D printer and tested them in a wind tunnel for output power, using a brush DC motor from Portescap with a no load speed of 7600 rpm and output power of 4.5 W at wind speeds varying from 7 m/s to 16 m/s. The researchers iterated blade shape, lengths, widths, twist angles, and tip angle to identify the most efficient configuration. They obtained the best performance with the prototype blade having a 37 degree twist angle, 0 degree tip twist angle, 6 cm mid-cord length, and 30 mm tip width (Figure 29). The researchers assumed 0.5 maximum rotor efficiency and calculated the theoretical peak power of 9.69 W at 14 m/s. Comparing the experimentally measured output peak power of 1.5 W to the theoretical maximum value resulted in an efficiency of about 15 percent. The researchers measured efficiencies in excess of 30 percent for a smaller blade that produced half of the output peak power. Although the efficiency was greater, it would require twice as many turbines to produce the same amount of power, leading to significantly greater capital costs. The researchers tested the blade with alternate

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73 California Energy Commission (2011), Total Electricity System Power. http://energyalmanac.ca.gov/electricity/total_system_power.html

74 Center for Sustainable Energy (2012), Wind Turbines, http://energycenter.org/index.php/technical-assistance/renewables/wind-turbines?gclid=CLCtzO2J6LECFWYZQgodIB8AQA

motor/generators. They demonstrated a 27 percent efficiency using a Maxon 110206 brush DC motor operating at 8 m/s.

Although experimental efficiency measurements of the micro wind turbines were within the range of commercially available small wind turbines, the researchers were able to demonstrate more than 100 percent improvement by adding a diffuser to the turbine system. They added diffusers with inclination angles of 3.9, 5, and 6 degrees to the system to increase the wind capture area and improve efficiency. Measured efficiency using the 3.9 degree inclination diffuser was 55 percent, a 100 percent improvement over the system without the diffuser. Efficiency increased slightly with the 5 percent inclination and had no additional effect by increasing inclination to 6 degrees. Therefore the researchers determined the optimal inclination to be 5 degrees, as shown in Figure 30.

The proposed technology could be used in arrays in residential and other small-scale settings. A major feature of this proposal was an array of small shrouded wind turbines. The researchers suggested that an array of micro wind turbines could be installed for $0.80 per watt. However experiments did not extend to the performance of the micro turbines in an arrayed configuration and did not include cost analyses to confirm the initial capital costs. The shroud itself may cause sufficient turbulence that the efficiency of an array of these turbines would exhibit poor performance.

Figure 29: Prototype of Blade 3-37-6cm-30mm Created Using a 3D Printer

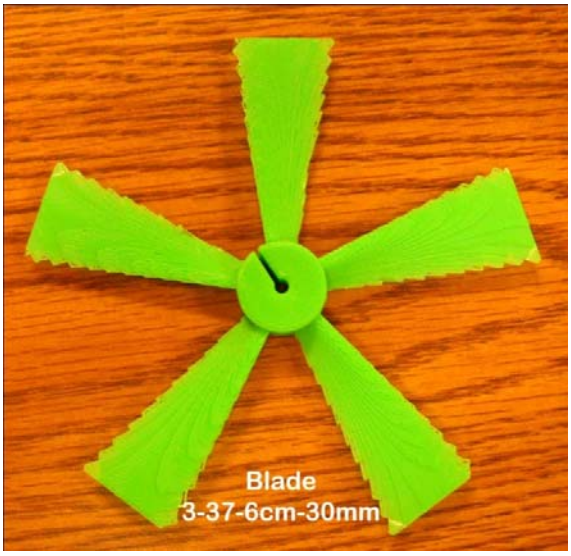
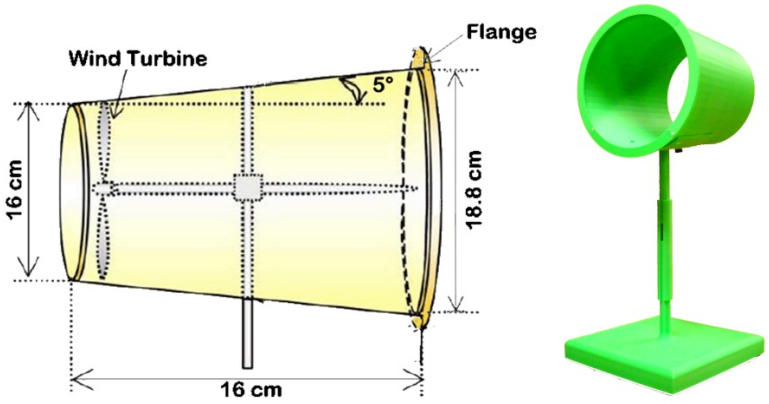


Figure 30: Prototype of Diffuser 2 with a 5 Degree Inclination Angle Created Using a 3D Printer



The researchers anticipated that if 25 percent of California families installed a 2 kW system, the savings would total $180.81 million each year. Additionally, this would result in more than 728,820 tons of reduced CO_2 emissions each year through reduced dependence on power plants with coal fuel. However, it is not clear if 25 percent of all household sites have sufficient wind power to drive these turbines for enough hours to provide economic payback.

2.26.3 Objectives

The goal of this project was to prove the feasibility of a new type of micro wind turbine with a diffuser (shrouded blades) to obtain significant efficiency improvements and initial capital cost reductions. The researchers established the following project objectives:

1. Demonstrate that the wind annulus nozzle distributor (WAND) structure can collect more wind and distribute it uniformly to an annulus region.
2. Confirm the WAND structure can reduce the cost of the wind turbine to $0.8/watt.
3. Design blades for the micro wind turbine. Achieve high efficiency (50 percent) for micro wind turbines.
4. Demonstrate that the new micro wind turbines can operate under wider wind conditions (2 m/s to 30 m/s).
5. Evaluate performance of a single WAND based micro wind turbine. Demonstrate the efficiency of the micro wind turbine can be significantly higher than that of normal wind turbines (efficiency 50 percent).
6. Optimize the design of micro wind turbine arrays to significantly reduce the initial capital cost to $0.8/watt.

2.26.4 Outcomes

The researchers produced three diffusers (WANDs) with inclination angles of 3.9, 5, and 6 percent using a 3D printer. They did not measure wind capture and uniformity of distribution to the annulus region.

The researchers produced all prototype diffusers and blades using a 3D printer. The project proposal noted that fabrication would ultimately include fiber embedded materials to achieve

lightweight, extremely high mechanical strength, and sound flexibility. The researchers did not discuss fabrication materials and costs in their final report.

Using an iterative approach and varying blade shape, lengths, widths, twist angles, and tip angles, the researchers selected the blade configuration that demonstrated the most efficient configuration. They obtained the best performance with the prototype blade having a 37 degree twist angle, 0 degree tip twist angle, 6 cm mid-cord length, and 30 mm tip width. This blade had a measured efficiency of 15.48 percent at a wind speed of 14 m/s using the Portescap motor. The overall efficiency was increased to 27 percent by changing to the Maxon motor operating at 8 m/s. Without the diffuser assembly, the maximum efficiency of any blade tested was 30.99 percent.

The researchers selected blade shape using experiments with wind speeds varying from 6.65 m/s to 16.00 m/s. Once the shape was selected, they conducted additional experiments to select twist angle, tip twist angle, and blade dimensions under wind speeds varying from approximately 7.5 m/s to 14 m/s.

The researchers added prototype diffusers (Objective 1) to the optimal blade (Objective 3). Addition of the 3.9 degree inclination diffuser further increased efficiency to 55 percent.

The researchers did not conduct experiments, analyze performance, or evaluate costs of micro wind turbines in an arrayed configuration.

2.26.5 Conclusions

1. The researchers did not meet the goal to demonstrate that the WAND could collect more wind and distribute it uniformly to the annulus region. Wind turbulence is one of the primary causes of reduced efficiency and potential damage in wind turbines. The researchers acknowledged that addition of the diffuser to a single turbine introduced disturbance to the air flow nearby and also that diffusers sustaining too much force/stress from wind could lead to material failure. They used a literature review to determine a recommended ratio of the inlet area to the outlet area of 0.781, but did not provide the reasoning behind this recommendation. The diffuser with an inclination angle of 3.9 degrees was closest to the recommended ratio (with a ratio of 0.773), yet exhibited the worst performance of the three tested. Rather, the diffusers with ratios of 0.724 (5 degree inclination) and 0.680 (6 degree inclination) performed better. These results did not confirm the relevance or benefit of the ratio selected from the literature review. Indirectly the researchers showed that the addition of the diffuser was beneficial to the system (see Outcome 3), and intuitively it is logical that the diffuser would have a larger capture area. However, the effect of the diffuser on the capture area or distribution uniformity for a single wind turbine was neither analyzed nor quantified.

2. The researchers did not meet the goal to confirm that the cost of the WAND structure could reduce the cost of the wind turbine to $0.8/watt. The researchers created all prototypes using a 3D printing polymer, which would not be suitable for use in production. There was no discussion of proposed fabrication materials or their associated costs. Because the researchers did not support the cost estimates presented in the project proposal, the benefits of the technology were generalized rather than quantified in the final report.

3. The researchers did not meet the objective to achieve greater than 50 percent efficiency for the micro wind turbine without the use of the diffuser assembly. According to Betz's law, the maximum efficiency achievable by a standard bladed wind turbine is 59.3 percent. This law does not apply to wind turbines that are enhanced with a diffuser. Nevertheless it would be unrealistic to approach the theoretical maximum without the use of a diffuser. Objective 5 addresses efficiency with the diffuser assembly addition. In addition, the researchers spent considerable effort on motor selection rather than efforts to improve the turbine and diffuser.
4. The researchers did not meet the objective to demonstrate that the micro wind turbines could operate under wind conditions ranging from 2 m/s to 30 m/s. The maximum range in wind speeds tested was 6.65 m/s to 16 m/s. The researchers determined peak efficiencies in the range of 8 m/s to 14 m/s, but they did not investigate the effect of low or high wind speeds on efficiency. Additionally, they did not address the stability of the prototype and its ability to resist mechanical failure at high wind speeds.
5. The researchers met the objective to achieve greater than 50 percent efficiency for the micro wind turbine with the diffuser assembly.
6. The researchers did not meet the objective to design, test, or analyze micro wind turbines in an arrayed configuration. They did not present cost estimates.

The researchers were successful in demonstrating efficiency improvements for one configuration of a micro wind turbine with a diffuser, but they did not show cost reductions achievable through this technology.

2.26.6 Recommendations

The researchers plan to continue development of the proposed technology through to commercialization. As part of continued development of this technology, the Program Administrator recommends that the following tasks be completed:

1. Complete testing for the proposed objectives, including testing at a wider range of wind speeds and turbulent flow analysis.
2. Evaluate the impact of wind speed on efficiency. Evaluate the wind resource at the targeted sites for installation. Measure both wind speed and duration.
3. Determine how a wind turbine(s) on a single-family residence would be integrated with the local electric utility at typical locations around the state.
4. Determine roof stresses induced by the wind turbine and determine if additional bracing would be needed on a typical family house.
5. Evaluate the impact of airflow disturbance on turbines in an arrayed configuration.
6. Identify suitable fabrication materials and perform failure analyses at various wind speeds.
7. Perform a complete cost analysis and compare to alternative technologies including rooftop solar PV.

8. Present a life cycle cost analysis.
9. Perform a detailed market analysis and pursue commercialization.

2.26.7 Benefits to California

Public benefits derived from PIER research and development projects are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the public from this research is increased affordability of electricity in California. The researchers suggested in the project proposal that an array of micro wind turbines could be installed for $0.80 per watt. However, the experiments did not extend to the performance of the micro turbines in an arrayed configuration and did not include cost analyses to confirm the initial capital costs. The researchers anticipate that if 25 percent of California families installed a 2 kW system, the savings would total $180.81 million each year. Additionally, the researchers stated that this would result in more than 728,820 tons of reduced CO_2 emissions each year through reduced dependence on coal power plants. Since California does not produce or buy electricity produced by burning coal, the CO_2 reduction would be considerably less.

2.26.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

The researchers have not performed a market analysis. This technology is applicable to residential and small-scale commercial installations.

Engineering/Technical

The primary technical challenge will be to select and test low cost UV resistant materials and to develop a low cost power inverter needed to integrate into existing power systems.

Legal/Contractual

The researchers have not performed a patent search for this technology. Although it may be possible to obtain a patent for the identified blade and diffuser, the concept of this technology is not novel. Numerous similar products have been developed and are widely available for use in residential and small-scale commercial installations.

Environmental, Safety, Risk Assessments/ Quality Plans

These plans have not yet been developed. The researchers do not anticipate negative effects with regard to public safety or the environment aside from potential nuisance noise generation.

Production Readiness/Commercialization

The researchers have developed a preliminary commercialization plan and will not need support to pursue commercialization.

2.27 Flywheel Hybrid with Switch Mode Continuously Variable Transmission

Awardee: Worcester Polytechnic Institute

Principal Investigators: James Van de Ven

2.27.1 Abstract

This project evaluated the technical feasibility of a novel solution of an on/off switch mode, continuously variable transmission (CVT) to transmit torque from a flywheel to a torsion spring and to the output shaft for hybrid vehicle applications. By varying the duty cycle of the clutch, the torque to the output shaft was controlled. Flywheel energy storage combined high energy density with high power density.

The researchers designed and tested two torsion springs and a custom clutch to meet the component requirements determined from undertaking a system analysis. They separately evaluated these components on individual test fixtures to evaluate their efficiency and dynamic behavior. They then integrated these components into a system prototype and tested it. The component tests demonstrated technical functionality, but the integrated system had excessive energy loss due to friction.

The project demonstrated the functionality of the switch mode CVT from an analytical and experimental perspective, but it did not demonstrate technical feasibility due to the limited nature of the test conditions. Future work is required to further study and optimize components before performing a detailed system redesign to demonstrate the performance potential in more real world conditions.

Keywords: Continuously variable transmission, CVT, switch mode circuit, clutch design, torsion spring design, flywheel hybrid vehicle

2.27.2 Introduction

Transportation consumes the most fuel in California and is responsible for the largest share of air pollution and greenhouse gas emissions. Most conventional modes of transportation are relatively inefficient in terms of fuel use. Improvement in transportation fuel use efficiency has long been a major policy goal in California.

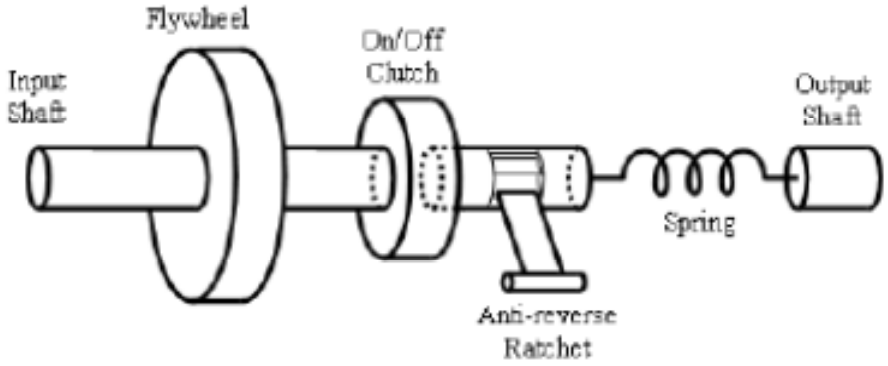
Hybrid power trains can improve fuel efficiency in transportation applications by utilizing two sources of power: an internal combustion engine and a second power source that is capable of recovering, storing, and then releasing energy. A wide variety of auxiliary hybrid power sources and energy storage devices have been previously explored for hybrid vehicles.

Flywheel energy storage provides one potential high energy density option with power density limited only by the torque capabilities of mechanical components.

One challenge that has hindered flywheel energy storage in vehicles is lack of a transmission capable of coupling the high-speed flywheel, typically rotating at 20,000 to 50,000 RPM, with the wheels. The transmission for this application must be efficient, continuously variable, and have a very large rotational speed reduction ratio. Previous work in this field has proposed continuously variable transmissions using hydraulics, belt drives, and toroidal drives, all with marginal success.

The novel solution studied in this work is the switch mode continuously variable transmission (CVT) that uses rapid engagement and disengagement of a clutch to transmit power. This transmission uses a single clutch, a flywheel, and a spring to provide a digitally controlled continuously variable transmission with significant energy storage capability. Because the switch mode CVT directly controls the output torque, it achieves large rotational speed reductions. This solution combines high energy density, high power density, and efficient energy transfer, creating a superior hybrid power system. Figure 31 illustrates the concept.

Figure 31: Basic Architecture of the Switch Mode Continuously Variable Transmission



2.27.3 Objectives

The goal of this project was to determine the feasibility of applying switch mode control to a rotating mechanical system to create an efficient, continuously variable transmission to enable flywheel energy storage use in a hybrid vehicle. The researchers established the following project objectives:

1. Design a custom clutch capable of operating at frequencies up to 50 Hz and having an engagement time of less than 20 percent of the switching period. The researchers added this objective after work began.
2. Design a custom torsion spring capable of 180 degrees of rotation, a linear spring rate, in a scalable design. The researchers added this objective after work began.
3. Demonstrate that the test stand was capable of measuring the torque applied to and the angular position of the flywheel within an error of +/- 2.0 percent.

4. Demonstrate a sufficient number of factor level combinations and trials to capture the significant factors with statistical significance with regard to the torsion spring experiments.
5. Demonstrate the significance of the individual factors and their interaction on the damping coefficient of the torsion spring.
6. Demonstrate that the test stand was capable of measuring the angular position of the flywheels within an error of +/- 2.0 percent. The purpose of this objective was to validate the measurement accuracy of the clutch test stand.
7. Demonstrate a sufficient number of factor level combinations and trials to capture the significant factors with statistical significance with regard to the clutch experiments. The purpose of this objective was to assure that the experiment design provided sufficient trials and factor levels to achieve statistical significance of the results.
8. Demonstrate the significance of the individual factors and their interaction on the engagement profile and engagement time of the clutch.
9. Demonstrate through the analytical model that the average continuously variable transmission efficiency can reach 80 percent, the response time < 0.5 second, and the torque ripple < 5 percent of the output torque. This roundtrip efficiency target was set as a means of improving existing hydraulic hybrids capable of reaching 70 percent roundtrip efficiency. The targets for the response time and torque ripple were based on human factors data of acceptable response and vibration.
10. Demonstrate that the system test stand was capable of measuring the angular positions, input torque, and output power within an error of +/- 2.0 percent. The purpose of this objective was to validate the measurement accuracy of the system test stand.
11. Demonstrate that the performance criteria of the bench top prototype test plan are evaluated.
12. Demonstrate on the prototype system that the average efficiency exceeds 80 percent on the EPA Urban Dynamometer Driving Schedule (UDDS).
    - Demonstrate the response time < 0.5 s.
    - Demonstrate the torque ripple < 5.0 percent.

2.27.4 Outcomes

1. The researchers designed and built a custom clutch that was actuated by an axial cam on the flywheel. When the flywheel was operating at 1000 RPM, the clutch engaged and disengaged three times per revolution, providing a switching frequency of 50 Hz. The rise and fall period of the cam profile occurred across 15° of flywheel rotation, resulting in 12.5 percent of the switching period utilized for engagement.
2. The researchers also designed and fabricated a cable wrap torsion spring. They demonstrated the spring capable of static deflection up to 360°. The researchers measured the spring rate using a load cell on a linear actuator and found the spring rate

to be linear. The researchers believe the spring design is scalable from the 33 Newton meters per radian (N*m/rad) of deflection of the prototype up to higher rates appropriate for a full-size vehicle. Despite these positive results from a static analysis, when the spring was cycled multiple times, the cables passing through the input shaft quickly became frayed. For this reason, the researchers halted further dynamic testing of the cable wrap spring. The researchers demonstrated that the custom cam torsion spring could achieve static and dynamic deflection of up to 180°. They verified that the constant slope of the cam surface resulted in a linear spring rate in the same manner as for the cable wrap spring. The researchers believed the design was scalable in terms of spring rate. The constructed prototype spring had a rate of 22.3 N*m/rad.

3. The researchers used US Digital HB6M-2500 encoders for the torsion spring test stand. The encoders had 2500 quadrature cycles per revolution, providing 10,000 pulses per revolution. This resolution allowed the researchers to determine the angular position of the input, intermediate, and output shafts within 0.036° of rotation. The researchers measured the static torsion spring rate of the springs by applying a force to a cable wrapped around a pulley of known diameter while measuring the angular deflection with the encoder. The load cell used to measure the force was an Omega LCR series load cell with an advertised accuracy of +/- 0.25 percent, which was less than the objective of +/- 2.0 percent.

4. The researchers varied several factors in the torsion spring experiment, including the duty cycle, switching frequency, and input flywheel angular velocity. Each of these factors was varied across the full range of system capabilities. The researchers tested the spring at duty cycles of 10 percent, 20 percent, and 50 percent; the switching frequency levels of 1 Hz, 2 Hz, 5 Hz, and 10 Hz; and the input flywheel speed varying from 200 to 1000 RPM in 200 RPM increments. The researchers performed three replications of each factor level combination.

5. The researchers measured the efficiency of the switch mode CVT system by comparing the energy content of the input and output flywheels at the beginning and the end of a test run. In tests the researchers achieved an efficiency of 65 percent with an increase in efficiency with higher angular velocity and higher duty cycle.

6. For the clutch test the researchers used US Digital HB6M-2500 encoders, which have 2500 quadrature cycles per revolution and provide 10,000 pulses per revolution. This resolution provided the angular position of the input and output within 0.036° of rotation.

7. The researchers determined clutch slippage as a function of angular velocity using a friction brake with torque varied from 10 N*m to 70 N*m in 10 N*m increments. The initial angular velocity of the flywheel was varied from 200 RPM to 1000 RPM in 100 RPM increments. At higher levels of friction brake torque, particularly over 30 N*m, the output shaft velocity did not meet the input shaft velocity during the clutch engagement due to clutch slippage.

8. The researchers used an analytical model to estimate performance requirements of the components necessary to achieve system performance outcomes. They calculated the

torque pulsations created by the spring deflection to be approximately 3.75 N*m at a total magnitude of 100 N*m, for a torque ripple of < 4.0 percent. During an acceleration event from 0 to 13.4 m/s (30 mph), the end point kinetic energy was 134 kJ while simulated energy transferred through the system was 164 kJ, resulting in a calculated efficiency of 82 percent.

9. The researchers fabricated the system test stand by combining the torsion spring test fixture and the clutch test fixture. They continued use of US Digital HB6M-2500 encoders.

10. The researchers used closed loop control of the clutch duty cycle to simulate an acceleration profile of the EPA Urban Dynamometer Driving Schedule (UDDS).

11. The researchers assembled the prototype systems using both the cable wrap spring and the cam spring. The cable wrap spring demonstrated early failure of the cables under dynamic testing. The researchers also had problems with the cam spring when mounted in the full system due to binding in the clutch output shaft bearings.

2.27.5 Conclusions

1. When the flywheel was operating at 1000 RPM, the clutch engaged and disengaged three times per revolution, providing a switching frequency of 50 Hz. The researchers achieved this objective as defined. The clutch would have a very different and variable switching frequency at other flywheel rotational velocities.

2. The researchers successfully achieved the objective of designing and fabricating a torsion spring capable of static deflection up to 360°. The researchers confirmed the spring rate was linear.

3. The researchers achieved the objective of precision measurement of the angular position of the flywheel within +/- 0.01 percent, which was less than the objective of +/- 2.0 percent. The dynamic torque measured by the load cell had a precision of +/- 0.25 percent, which was less than the objective of +/- 2.0 percent.

4. The researchers completed three tests per combination of factors, the minimum number required for significance of results from the torsion spring experiments, successfully achieving this objective.

5. The efficiency increased with increased angular velocity and increased duty cycle until clutch slippage occurred at higher torque levels. The primary sources of energy loss in the system were slip in the clutch, bearing friction, aerodynamic drag on the flywheels, and damping in the spring. No conclusive results could be drawn about the significance of individual factors, in particular the torsion spring damping. The researchers did not achieve this objective.

6. The researchers achieved the objective of precision measurement of the angular position within +/- 0.01 percent, which was less than the objective of +/- 2.0 percent.

7. The researchers collected meaningful data only at low torque levels. Clutch slippage was encountered at torque levels of approximately 30 N*m. They did not achieve this objective.

8. The researchers determined that the dynamic torque necessary to accelerate the output shaft and brake rotor exceeded the torque capabilities of the clutch. The researchers did achieve this objective by demonstrating the significance of clutch slippage, an individual factor, as being a limiting factor.

9. The torque pulsations created by the spring deflection were calculated at approximately 3.75 N*m at a total magnitude of 100 N*m, for a torque ripple of < 4.0 percent. During an acceleration event from 0 m/s to 13.4 m/s (30 mph), the end point kinetic energy was 134 kJ, while simulated energy transferred through the system was 164 kJ, resulting in a calculated efficiency of 82 percent. The researchers achieved this objective.

10. The researchers achieved the objective of precision measurement in the combined test stand of the angular position of the flywheel within +/- 0.01 percent and dynamic torque within +/- 0.25 percent.

11. The researchers achieved the objective of evaluating the performance criteria under the test conditions specified. The test conditions did not meet the objective of establishing performance criteria of the bench top prototype representative of real world application.

12. The clutch actuator traversed from 0 percent to 50 percent (maximum) duty cycle in 2.0 seconds, which is slower than the objective of under 0.5 seconds. The initial energy content was 142 Joules and the final energy content was 93 Joules, for a system efficiency of 65 percent. The researchers did not achieve this objective.

The researchers proved technical functionality of applying switch mode control of a clutch on a rotating mechanical system to create a continuously variable transmission. They did not demonstrate technical feasibility of applying the switch mode clutch to create an efficient continuously variable transmission to enable flywheel energy storage in a hybrid vehicle.

2.27.6 Recommendations

The researchers should test the technology with more representative flywheel conditions. The tests performed so far used a flywheel with energy storage and rotational speeds far lower than would be used in actual vehicles. This is primarily a function of the low speed of the flywheel used in the test. Higher flywheel speeds may affect both friction losses and torque ripple. The first may further reduce the overall system efficiency, while the latter may negatively impact occupant satisfaction. Excessive torque ripple would give vehicle occupants a sensation of surging and simultaneously negatively affect efficiency. The researchers should test or evaluate the safety risks associated with a flywheel spinning at higher rotational speeds than used in their tests so far.

The researchers should test the capability of the on/off clutch to efficiently transfer torque under higher torque loading of the driven shaft while limiting clutch slippage and perceived torque ripple. This will be important to quality assurance as perceived by drivers. There may be maximum heat or wear issues on the clutch or other elements that prevent the system from ever being used in real vehicle. That is a safety and quality risk.

The torque ripple may be highly dependent upon speeds and loads, and those have not yet been identified. Final size and weight of whole package may be a risk to market feasibility.

The researchers will need to demonstrate clear benefits in both overall efficiency and occupant comfort and drivability to compete against alternative modes of energy transfer in flywheel based hybrids, such as electronically controlled motor/generators. The relative complexity of the system will need to be shown as robust, reliable, and easily maintained if the market is to accept the technology.

The researchers should also investigate the concept's capability to accommodate regenerative braking, a feature many hybrids incorporate for higher overall vehicle efficiency. Finally, the researchers should compare the overall efficiency and occupant sensation of their concept with an electric drive system, using, for example, electronically controlled motor generators as the clutch interface between the flywheel and the driven wheel.

The researchers should determine clutch material needs. The rapid and continuous engagement and disengagement of the clutch could lead to rapid wear of the clutch surface.

After taking into consideration (a) research findings in the grant project, (b) overall development status, and (c) relevance of the technology to California and the PIER program, the Program Administrator has determined that the proposed technology should be considered for subsequent funding within the PIER program.

Receiving subsequent funding ultimately depends upon (a) availability of funds, (b) submission of a proposal in response to an invitation or solicitation, and (c) successful evaluation of the proposal.

2.27.7 Benefits to California

Public benefits derived from PIER transportation research and development projects are assessed within the following context:

- Improved transportation energy efficiency
- Reduced greenhouse gas emissions or reduced health and environmental impacts from transportation associated air pollution related to electricity and NG production and use
- Increased the use of alternative fuels

The primary benefit to the ratepayer from this research is reduced greenhouse gas emissions from transportation and associated air pollution.

When operating on the EPA Urban Dynamometer Driving Schedule, a four-door passenger vehicle with an 80 percent regenerative efficiency series hybrid drive train has an estimated fuel consumption of 73 mpg, compared to 35 mpg using a conventional drive train. If the switch mode continuously variable transmission can reach the target goal of 80 percent efficiency, it would enable a flywheel hybrid drive train with approximately double the fuel economy compared to conventional drive train. If the technology were used in 5.0 percent of the vehicles in California, the State could achieve a reduction of just over 365 million gallons of gasoline per year or a decrease in CO_2 gas emissions of approximately 3.2 million metric tons. For

comparison, California emits about 475 million metric tons annually.[75] Because of the status of this technology and long introduction cycles in the automotive industry, it may take up to 10 years to realize these benefits.

2.27.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

The researchers had not conducted a market evaluation at the completion of this project nor had they written an engineering specification. There is no evidence that they had made connections with commercial players that could take this technology to market.

Engineering/Technical

The researchers recognized that significant design and performance improvements were required. They anticipated three years of engineering development and tests are required to complete product development.

Legal/Contractual

The researchers have applied for a patent, but they provided no pending patent numbers.

Environmental, Safety, Risk Assessments/ Quality Plans

Because of the immature status of this technology, none of these plans were completed during the term of this project.

Production Readiness/Commercialization

The researchers recognized that they required a commercialization partner but had not identified that partner by the end of this project.

2.28 Metallic Nanotubes as Low Cost and Durable Fuel Cell Catalysts

Awardee: University of California Riverside

Principal Investigators: Yushan Yan

2.28.1 Abstract

Researchers in this project worked to improve PEM fuel cell commercialization by reducing catalyst cost and increasing durability. Using platinum nanotubes (PtNT) with smaller and thinner wall thickness improved specific activity and should lead to reduced catalyst costs. However, durability compared to conventional catalysts suffered.

The researchers synthesized porous platinum nanotubes to increase the surface area and catalyst mass activity for oxygen reduction. They utilized palladium as an alternate substrate to

75 www.arb.ca.gov/cc/inventory/inventory.htm

increase the platinum normalized mass activity. Durability decreased, however, with decreases in the platinum content. The researchers attributed this to instability of the palladium substrate during potential cycling.

Researchers also examined copper as a more favorable substrate for platinum for oxygen reduction, thereby increasing the platinum nanotube specific activity. Platinum nanotubes synthesized from copper nanowires produced a specific activity approximately 50 percent greater than those synthesized from silver nanowires.

Researchers successfully demonstrated smaller and thinner platinum catalyst structures with good specific activity, but catalyst durability remained a significant concern.

Keywords: Oxygen reduction, platinum nanotubes, proton exchange membrane fuel cells

2.28.2 Introduction

Proton exchange membrane fuel cells (PEMFC) have long been a preferred technology in California because of their high efficiency and low emission characteristics. Although PEMFC can be utilized in stationary power devices, they also show promise for the transportation field and have been the subject of successful technical demonstrations in both types of applications. PEMFC are not fully commercialized yet due to high initial costs, largely the result of reliance on precious metal catalysts, in particular platinum, in the cathode.

Advancing PEMFC commercialization requires further catalyst improvement and cost reduction while maintaining durability. Electrocatalyst development for the oxygen reduction reaction (ORR) has narrowed to the development of improved platinum (Pt) based catalysts using nanotechnology. Pt nanoparticles of 2—3 nm on carbon (20 wt percent Pt, Pt/C) are the current state-of-the-art catalyst. High catalyst cost has led to the establishment of United States Department of Energy (DOE) benchmarks for oxygen reduction reaction mass and specific activity for Pt catalysts. DOE benchmarks for 2010—2015 have been set to a mass activity of 0.44 Amg^{-1} and 0.72 $mAcm^{-2}$ at 0.9 V versus a reversible hydrogen electrode (RHE).

In this project researchers modified the process by which platinum nanotubes (PtNT) are synthesized to develop a variety of electrocatalysts. In one approach they generated porous PtNT to increase specific surface area. In another approach they synthesized palladium (Pd) nanotubes (Pt/PdNT) with a single layer of platinum to reduce the overall amount of Pt and hence catalyst cost. Finally they coated copper nanowires (CuNW) with platinum nanotubes to improve the ORR specific activity. The researchers combined scanning and transmission electron microscope characterizations with electrochemical and durability testing of the new catalysts.

2.28.3 Objectives

The goal of this project was to prove the feasibility of a new class of fuel cell catalysts based on platinum nanotubes (PtNT}. The researchers established the following project objectives:

1. Reduce platinum wall thickness from 5 nm to 2 nm.
2. Increase the platinum specific activity from 20 m^2 per gram to 60 m^2 per gram.

3. Attempt to meet Department of Energy transportation targets for mass activity (0.44 Amg_{Pt}^{-1}) and specific activity (0.72 $mAcm_{Pt}^{-2}$).

4. Attempt to reach less than 20 percent surface area loss after 30,000 cycles from 0.6 to 1.1 V vs. RHE.

2.28.4 Outcomes

1. The researchers synthesized silver nanowires (AgNW) with a mean diameter of 60 nm and a length of 10—500 μm. They synthesized porous PtNT with a mean thickness of 5 nm and a length of 5—20 μm using the silver wires as substrates. The researchers also synthesized Pt/PdNT from AgNW with wire lengths of 5—20 μm and platinum wall thicknesses of approximately 0.7 nm, 0.5 nm, and 0.4 nm. Finally, the researchers synthesized Pt/PdNT from copper nanowires in place of silver. They measured the Pt wall thickness from copper nanowire synthesis at 13.0 nm for PtNT and 0.7 nm for Pt/PdNT.

2. The deposition of platinum on palladium nanotubes (from silver nanowires) resulted in an increase in platinum specific activity from 20 m^2g^{-1} to 157.0 m^2g^{-1}. The researchers measured the electrochemically active surface area (ECSA) values for porous PtNT and Pt/C to be 23.9 m^2 per gram and 70.4 m^2per gram, respectively.

3. The researchers developed polarization curves for porous PtNT, Pt/C, and bulk polycrystalline platinum (BP-Pt) catalysts. They measured the half-wave potential of PtNT, Pt/C, and BP-Pt electrodes at 0.889 V, 0.883 V, and 0.831 V, respectively. The researchers demonstrated that the PtNT had a slightly higher mass activity than Pt/C (PtNT was 0.088 $mA^{\mu g^{-1}}$ compared to Pt/C at 0.084 $mA^{\mu g^{-1}}$), but they demonstrated a specific activity of 0.369 $mA_{cm}^{Pt^{-2}}$, 3.1 times higher than that of Pt/C.

4. The researchers tested the catalyst's durability by cycling the applied potential 30,000 times in the range 0.6—1.1 V versus RHE. They took periodic voltammograms every 6,000 cycles to monitor the electrochemically active surface area. The electrochemically active surface area of Pt/C degraded 48.3 percent over the 30,000 cycles, while PtNT lost 23.5 percent of their surface area. See Table 5 for experimental results.

Table 8: Summary of Catalyst ORR Activity Following Durability Experiments

Catalyst	ECSA (m^2g^{-1})	$E_{1/2}$ (V)	j_k (Amg_{Metal}^{-1})	j_k (Amg_{Pt}^{-1})	j_k ($mAcm_{Metal}^{-2}$)
PtNTs	10.0	0.896	0.096	0.096	0.961
PtPd 20%	3.0	0.879	0.074	0.369	2.50
PtPd 15%	2.6	0.882	0.075	0.498	2.85
PtPd 10%	1.7	0.860	0.044	0.436	2.53
Pt/C	12.0	0.775	0.005	0.005	0.041

2.28.5 Conclusions

The researchers successfully reduced the size of PtNT thickness to less than 2 nm and increased the specific and mass activities. Surface area loss under durability testing was larger than the target limit and remains an impediment to ultimate success of this approach. The researchers

partially proved technical feasibility of an improved catalyst using reduced size platinum nanotubes. The new catalyst did not provide the projected durability. Although the researchers observed ECSA losses, ORR losses following durability testing confirmed improved durability characteristics compared to traditional catalysts for some, but not all, of the catalyst synthesis concepts. PtNT, PtCu 20 percent, and PtPd 10 percent lost 0.0 percent, 61.5 percent, and 97.5 percent of their ECSA, respectively, through durability testing, illustrating tradeoffs between specific activity and durability and cost. The catalysts with highest specific activity initially showed highest degradation under durability tests. The researchers did not meet DOE established activity and durability goals.

2.28.6 Recommendations

Researchers should investigate the electrochemical properties after thermal cycling, in addition to their completed electrical cycling tests. Thermal management of fuel cells remains an important aspect to their ultimate market adoption and attention should be paid to thermal management needs of both catalysts and complete fuel cells. The researchers should also investigate physical properties and durability using various mechanical stresses such as vibration, as this is especially important in transportation applications. The researchers should determine the comparative sensitivity of their catalyst concept to various poisoning agents typical of PEM fuel cell catalysts. Further, the researchers should determine the manufacturability in large-scale production of their novel yet precise catalysts. While there is a tradeoff between single layer platinum-on-palladium versus porous platinum nanotubes versus platinum-on-copper in terms of ECSA and durability, the researchers should investigate palladium with multiple layers (as opposed to monolayers) of platinum and other copper based approaches.

After taking into consideration (a) research findings in the grant project, (b) overall development status, and (c) relevance of the technology to California and the PIER program, the Program Administrator has determined that the proposed technology should be considered for subsequent funding within the PIER program.

Receiving subsequent funding ultimately depends upon (a) availability of funds, (b) submission of a proposal in response to an invitation or solicitation, and (c) successful evaluation of the proposal.

2.28.7 Benefits to California

Public benefits derived from PIER transportation research and development projects are assessed within the following context:

- Improved transportation energy efficiency
- Reduced greenhouse gas emissions or reduced health and environmental impacts from transportation associated air pollution related to electricity and natural gas production and use
- Increased the use of alternative fuels

The primary benefit from this research is reduced greenhouse gas emissions and environmental impacts from the use of natural gas derived hydrogen in fuel cells in transportation

applications. Secondary benefits would likely come from improved transportation energy efficiency. Additional benefits could accrue in the electricity supply system, given that PEMFC are also appropriate technologies in stationary application. Thermal cycling and management should be less problematic in stationary applications, as reject heat can be beneficially used and cycling would generally be less frequent.

The United States Department of Transportation and United States Department of Energy have estimated that automobiles using proton exchange membrane fuel cells and deriving hydrogen from reformulated fossil fuel could result in 42 percent less carbon emissions than hybrid-electric vehicles and 60 percent less carbon emissions than conventional internal combustion vehicles per mile traveled. California consumption of gasoline in 2007 was 15.6 billion gallons.[76] Assuming that 10 percent of that consumption could be displaced by economically competitive fuel cells, the savings would be 156 million gallons of gasoline. The California Air Resources Board estimates that CO_2 emissions from passenger vehicles were 128.51 million metric tons in 2008. Again assuming 10 percent penetration and the Federal DOT and DOE estimate of 60 percent reduction in carbon emissions, that figure could be reduced by 6.0 percent or 7.71 million metric tons per year. By way of comparison, the CARB Scoping Plan for implementing AB32 sets a goal of total greenhouse emissions of 427 million metric tons in 2020, a reduction of approximately 30 percent from a "business as usual" case in that year.[77] Economically competitive fuel cells could provide about 4.0 percent of the emission reductions required under the CARB Scoping Plan.

2.28.8 Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researchers' overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

The researchers stated that their university would have to partner with a private company to take this innovation to market. They also stated that they had received some interest in their technology from private companies.

Engineering/Technical

The researchers stated that they should be able to determine if they can meet DOE targets within two years if they secure sufficient funds to support two full-time postdoctoral researchers.

Legal/Contractual

The researchers previously applied for patent protection. They have received $600,000 from U.S. DOE for additional work to further develop the catalyst concept.

76 California Board of Equalization, Special Taxes Department Fuel Taxes Division, June 2008.

77 http://www.arb.ca.gov/cc/scopingplan/scopingplan.htm

Environmental, Safety, Risk Assessments/ Quality Plans

There are no known environmental or safety issues. Quality assurance plans for manufacturing process will be crucial in, and dependent on, resolution of durability issues.

Production Readiness/Commercialization

The technology is not yet ready for production or commercialization until durability issues are resolved.