



CALIFORNIA
ENERGY
COMMISSION

ENERGY INNOVATIONS SMALL GRANT PROGRAM
Renewable Energy Technologies

Development and Characterization of
Improved Solid State Dye-Sensitized
Nanocrystalline Solar Cells

FEASIBILITY ANALYSIS

March 2003
P500-03-016F



Gray Davis, Governor

CALIFORNIA ENERGY COMMISSION

Prepared By:

Hal Clark

Grant Program Administrator

San Diego State University Foundation

Prepared For:

California Energy Commission

Energy Innovations Small Grant Program

Researcher:

Jin Zhang

University of California Santa Cruz

Grant Number:

99-10

Philip Misemer

Grant Program Manager

Marwan Masri

Deputy Director

Technology Systems Division

Robert Therkelsen

Executive Director

LEGAL NOTICE

This report was prepared as a result of work sponsored by the California Energy Commission (Commission). It does not necessarily represent the views of the Commission, its employees, or the state of California. The Commission, the state of California, its employees, contractors, and subcontractors make no warranty, express or implied, and assume no legal liability for the information in this report; nor does any party represent that the use of this information will not infringe upon privately owned rights. This report has not been approved or disapproved by the Commission nor has the Commission passed upon the accuracy or adequacy of the information in this report.

PREFACE

The Public Interest Energy Research (PIER) Program 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 PIER Program, managed by the California Energy Commission (Commission), annually awards up to \$62 million of which \$2 million/year is allocated to the Energy Innovation Small Grant (EISG) Program for grants. The EISG Program is administered by the San Diego State University Foundation under contract to the California State University, which is under contract to the Commission.

The EISG Program conducts four solicitations a year and awards grants up to \$75,000 for promising proof-of-concept energy research.

PIER funding efforts are focused on the following six RD&D program areas:

- Residential and Commercial Building End-Use Energy Efficiency
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy Technologies
- Environmentally-Preferred Advanced Generation
- Energy-Related Environmental Research
- Strategic Energy Research

The EISG Program Administrator is required by contract to generate and deliver to the Commission a Feasibility Analysis Report (FAR) on all completed grant projects. The purpose of the FAR is to provide a concise summary and independent assessment of the grant project using the Stages and Gates methodology in order to provide the Commission and the general public with information that would assist in making follow-on funding decisions (as presented in the Independent Assessment section).

The FAR is organized into the following sections:

- Executive Summary
- Stages and Gates Methodology
- Independent Assessment
- Appendices
 - Appendix A: Final Report (under separate cover)
 - Appendix B: Awardee Rebuttal to Independent Assessment (Awardee option)

For more information on the EISG Program or to download a copy of the FAR, please visit the EISG program page on the Commission's Web site at:

<http://www.energy.ca.gov/research/innovations>

or contact the EISG Program Administrator at (619) 594-1049 or email

eisgp@energy.state.ca.us.

For more information on the overall PIER Program, please visit the Commission's Web site at

<http://www.energy.ca.gov/research/index.html>.

Executive Summary

Introduction

A research group at the Swiss Federal Institute of Technology in Lausanne, Switzerland has developed a potentially low cost solar cell based on “sensitized” organic dyes and titanium dioxide, (TiO₂, a material used in white paint). The Swiss technology has an experimentally determined, overall sunlight to electrical energy conversion efficiency of 7 -10 % under direct and diffuse sunlight. While this conversion efficiency is lower than the approximate 15 % of commercially available solar cell technology, the solar cell based on organic dyes and titanium dioxide offers advantages including environmentally friendly components, low temperature processing, and potentially lower costs to consumers. Calculations indicate that solar cells of at least 10 % efficiency could be realized at less than \$3 per Watt cost using the proposed technology. This may be competitive with conventional electricity generation in selected applications, and the approach could open up new markets in flexible solar cells used for consumer applications such as computers and cell phones, as well as in grid-connected distributed power generation. These markets are already over 100 Megawatts per year at a cost of approximately \$6 per watt. Patents for the new technology have been issued. To reach new markets the researchers may need to file additional claims for intellectual property protection.

Liquid electrolytes are volatile. Solar cells produced with liquid electrolytes suffer from reduced reliability and lifetime. The purpose of this project was to prove the feasibility of a method to reduce these technical shortcomings. While the existing state of the art of the new technology holds the promise to reduce costs for solar generated electricity, the reduced reliability due to the volatile liquids limits potential application of this technology. This project involved replacing the liquid electrolyte with suitable solids.

The researcher chose conductive polymers as the replacement for the liquid, specifically, polythiophenes.

Objectives

The goal of this project was to determine the feasibility of replacing the volatile liquid in the dye sensitized nano-crystalline solar cell with conductive polymers. The following project objectives were established:

1. Determine if charge transfer can occur via the polythiophenes, and whether this material itself absorbs light.
2. If polythiophene does absorb light, determine if that absorption interferes and competes with light absorption by the dyes used in the state of the art device, and whether it can replace these dyes.
3. Measure the charge carrier dynamics of the dye, polymer, and TiO₂ suitable for this application. Construct an energy band diagram to better understand the functioning of solar cell with conductive polymers, and to optimize the solar cell output. Select an appropriate material based on these data.
4. Synthesize nano-crystalline TiO₂ films.
5. Fabricate, test and optimize solar cells using the materials exhibiting the best properties.

Outcomes

The following outcomes were achieved:

1. The researcher determined that polythiophenes could transfer charge and selected a hole-conducting polythiophene polymer. The researcher performed extensive tests on the absorption of light by the polythiophene and found that some polythiophenes can be both light absorbers and charge transporters.
2. One polymer, P3UBT, can act as a dye and a hole conductor possibly eliminating the need for a separate dye. This approach suffers from low mobility of charge carriers in the organic layer leading to low solar conversion efficiencies. For that reason, the grantee suggested using a separate dye and a separate transparent version of the polythiophene polymers along with porous TiO₂ in future work. A transparent polythiophene polymer will not interfere with light absorption by the dye.
3. This project measured charge carrier characteristics, constructed energy band diagrams and developed techniques to characterize materials suitable for the dye based solar cell. While specific polymer and dye combinations are recommended as a result of this work, the researcher recommends future work that will focus on materials with higher surface areas and therefore higher photocurrents.
4. The project synthesized TiO₂ films using sol gel depositing technique,
5. The researchers fabricated solar cells using sol gel deposited TiO₂ and the above polymer. They tested solar cell devices, and found that the junction properties are unique as well as efficient for the geometry selected. However the cells they created were single layer cells with an efficiency of only 0.032%. The grantee estimated that with 200 layers like the one reported, a solar cell with a solid electrolyte could be over 6% efficient. No further optimization work was reported.

Conclusions

The researcher utilized TiO₂ materials, together with solid polymers to fabricate solid-state solar cells. These devices produced encouraging results given the fact that only a thin layer of polymer and a single layer of TiO₂ were utilized. Current voltage characteristics of devices fabricated using this technique are consistent with the energetics of the components, and are encouraging when compared to existing technology based on sensitization mentioned above. The researcher obtained expected results from a single layer of sensitizer (polymer), and a flat TiO₂ surface given the energy band diagram, and spectroscopic characterization. With the techniques and materials developed in this project, the researcher measured voltages over 0.8 V and current densities of 100 micro-amps per square centimeter of active area with one sun of illumination. These results, reported for the model system, are not related to performance needed in a commercial device. There is no indication in the final report of the magnitude of improvement needed for commercial success.

The goal of this project was to determine the feasibility of replacing the volatile liquid in the dye sensitized nano-crystalline solar cell with conductive polymers. Based on results, commercial feasibility may be possible if the emphasis is now placed on utilizing porous or multi-layer materials. The most critical issue for future work will be the extension to higher surface area materials that can result in higher photocurrents. Specific performance criteria should be established before subsequent work is begun.

Benefits to California

At this point in the research, potential benefits to California can only be qualitatively estimated. The experimental results support the feasibility of replacing the liquid electrolyte with a conductive polymer. The long-term benefits to California ratepayers include lower cost solar cells. The cost of future cells produced with this technology is difficult to determine at this time. However, if the lower cost (\$3 per watt) is achieved, more ratepayers will install grid-connected solar power generators. These installations will help to diversify the California fuel portfolio. Increased utilization of solar energy to replace peaking power plants will greatly reduce the levels of CO₂ and NO_x in the atmosphere.

There are other solar cell technologies that promise similar benefits. Sharp Corporation recently announced a new solar cell that employs organic pigments to change light into electricity. Sharp succeeded in switching the necessary electrolyte in the organic solar cell from the liquid state to a solid-state material. Sharp estimates that this new innovation will cut the cost of solar cells by one half. Sharp did not report an absolute cost or price.

Stages and Gates Methodology

The California Energy Commission utilizes a stages and gates methodology for assessing a project’s level of development and for making project management decisions. For research and development projects to be successful they need to address several key activities in a coordinated fashion as they progress through the various stages of development. The activities of the stages and gates process are typically tailored to fit a specific industry and in the case of PIER the activities were tailored to be appropriate for a publicly funded energy research and development program. In total there are seven types of activities that are tracked across eight stages of development as represented in the matrix below.

Development Stage/Activity Matrix

	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6	Stage 7	Stage 8
Activity 1								
Activity 2								
Activity 3								
Activity 4								
Activity 5								
Activity 6								
Activity 7								

A description the PIER Stages and Gates approach may be found under "Active Award Document Resources" at: <http://www.energy.ca.gov/research/innovations> and are summarized here.

As the matrix implies, as a project progresses through the stages of development, the work activities associated with each stage needs to be advanced in a coordinated fashion. The EISG program primarily targets projects that seek to complete Stage 3 activities with the highest priority given to establishing technical feasibility. Shaded cells in the matrix above require no activity, assuming prior stage activity has been completed. The development stages and development activities are identified below.

Development Stages:	Development Activities:
Stage 1: Idea Generation & Work Statement Development	Activity 1: Marketing / Connection to Market
Stage 2: Technical and Market Analysis	Activity 2: Engineering / Technical
Stage 3: Research & Bench Scale Testing	Activity 3: Legal / Contractual
Stage 4: Technology Development and Field Experiments	Activity 4: Environmental, Safety, and Other Risk Assessments / Quality Plans
Stage 5: Product Development and Field Testing	Activity 5: Strategic Planning / PIER Fit - Critical Path Analysis
Stage 6: Demonstration and Full-Scale Testing	Activity 6: Production Readiness / Commercialization
Stage 7: Market Transformation	Activity 7: Public Benefits / Cost
Stage 8: Commercialization	

Independent Assessment

For the research under evaluation, the Program Administrator assessed the level of development for each activity tracked by the Stages and Gates methodology. This assessment is summarized in the Development Assessment Matrix below. Shaded bars are used to represent the assessed level of development for each activity as related to the development stages. Our assessment is based entirely on the information provided in the course of this project, and the final report. Hence it is only accurate to the extent that all current and past work related to the development activities are reported.

Development Assessment Matrix

Stages	1 Idea Generation	2 Technical & Market Analysis	3 Research	4 Technology Develop- ment	5 Product Develop- ment	6 Demon- stration	7 Market Transfor- mation	8 Commer- cialization
Marketing								
Engineering / Technical								
Legal/ Contractual								
Risk Assess/ Quality Plans								
Strategic								
Production. Readiness/								
Public Benefits/ Cost								

The Program Administrator’s assessment was based on the following supporting details:

Marketing/Connection to the Market.

A marketing analysis as well as a business plan has been completed by Dr. Michael Graetzel of the EPFL. He has enlisted the aid of several companies as license holders to the technology involving the liquid based junction. The configuration described in this report represents significant improvements to the technology. Therefore, this plan would need to be suitably modified and updated for Stage 4 PIER development. In addition, other markets including low power and low cost consumer power sources need to be considered and an alternative development path formulated that utilizes the device's promise as a light detector. Industrial partners need to be identified and included in a commercialization team.

Engineering/Technical

During this EISG study, the research proved the feasibility of replacing liquid electrolytes with solid polymers. This work reduces the risk for the technology and advances the development of a potentially low cost PV solar cell. Further research is needed to extend this result to TiO₂ with higher surface areas to increase the cell efficiency to at least 8%. Additional work is recommended to determine realistic production costs for a solid-state dye-sensitized nano-crystalline solar cell with efficiencies in the range of 8 to 10%.

Legal/Contractual

U.S. Patents 5,084,365 (Graetzel et al, 1992) and 4,927,721 (Graetzel et al, 1990) have been issued, as well as World Patent WO 91/16719 (Graetzel et al, 1991). Development of additional Intellectual Property is possible through the research described in this report, since it potentially extends the usefulness of the above invention.

Environmental, Safety, Risk Assessment/Quality Plans.

A Quality Plan needs to be developed that meets ISO 9004 Quality Management and ISO 9001 Quality Assurance criteria. The Quality Plan will specify quality control criteria including technical performance, safety and environmental performance, in accordance with ASME, AWS, ASTM, IEEE standards, California and federal regulations. Selected elements of the Quality Plan will minimize risks by applying risk reduction techniques with safety analysis methods.

Environmental and Safety issues in the configuration could represent substantial improvements over state of the art PV devices. A full assessment of this aspect has yet to be completed.

A preliminary life cycle cost analysis is given in Appendix V of Appendix A to this report. Any updates of this would be made in accordance with Commission requirements and in close collaboration with PIER staff.

Strategic

Development of the technology has been linked to PIER policy objectives. This project does not appear to impact other PIER projects at this time, but a full assessment of the projects is necessary, as the findings of this study are relevant to the development of both solar cells and light detectors. These detectors may have applications in other PIER projects. This project is not critically dependent on other projects under development within PIER or elsewhere. The results of this project must be compared with recent commercial developments in dye-sensitized solar cells when the data are available.

Production Readiness/Commercialization.

This research is not ready for the production stage. However, as shown in Appendix A and in its appendices, production techniques that meet the goals outlined in the lifecycle analysis and cost estimate have been considered throughout the research. If this research continues, this aspect will be one of the central issues to be considered. Several PV companies have been contacted, and a literature search completed. Information gained from these processes will serve as a reference as the development process advances. The researcher will have to show that his proposed solar cells will be less costly and/or more efficient than the solar cells that Sharp Corporation and others are beginning to commercialize.

Public Benefits.

Public benefits derived from PIER research and development 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 rate-payer from this research is to make electrical energy more affordable in California. This will be accomplished by reducing the cost per kW of power generated.

At this point in the research, only potential benefits to California can be qualitatively estimated. Using the results from this study, a researcher could further optimize dye-sensitized solar cells. Additional improvements can yet be made with the fundamental knowledge gained during this study. It is possible that the resulting devices could be cost and performance competitive with existing solar cell materials such as Silicon (Si) and Cadmium Telluride (CdTe).

The long term benefits of diversifying our energy portfolio include stabilization of CO₂ levels in the atmosphere, decreased pollution and environmental degradation, and economic benefits to both the United States and to California due to use of resources available within California.

Appendix A: Final Report (under separate cover)

Appendix B: Awardee Rebuttal to Independent Assessment (none submitted)