II.E.5 Production of Hydrogen for Clean and Renewable Sources of Energy for Fuel Cell Vehicles*

Xunming Deng (Primary Contact), Frank Calzonetti, Martin Abraham, Maria Coleman, Robert Collins, Alvin Compaan, Dean Giolando, A.H. Jayatissa, Thomas Stuart, Mark Vonderembse, and William B Ingler, Jr. University of Toledo (UT) 2801 W. Bancroft Street MS 111 Toledo, OH 43606 Phone: (419) 530-4782; Fax: (419) 530-2723 E-mail: dengx@physics.utoledo.edu

DOE Technology Development Manager: Roxanne Garland Phone: (202) 586-7260; Fax: (202) 586-2373 E-mail: Roxanne.Garland@ee.doe.gov

DOE Project Officer: David Peterson Phone: (303) 275-4956; Fax: (303) 275-4788 E-mail: David.Peterson@go.doe.gov

Contract Number: DE-FG36-05GO85025

Subcontractor: Bowling Green State University, Bowling Green, OH

Project Start Date: May 1, 2005 Project End Date: July 31, 2008

*Congressionally directed project

Objectives

- To expand research directed to the development of clean and renewable domestic methods of producing hydrogen. This project develops and evaluates methods of producing hydrogen in an environmentally sound manner to support the use of fuel cells in vehicles and at stationary locations.
- To address DOE program objectives in the general area of renewable hydrogen production. It addresses specifically high-efficiency and low-cost production of hydrogen using photoelectrochemical methods.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section (3.1.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (Y) Materials Efficiency
- (Z) Materials Durability
- (AB) Bulk Materials Synthesis
- (AC) Device Configuration Designs

Technical Targets

Solar power is an excellent source of renewable energy generated by the conversion of sunlight into electricity via solar cells. When solar cells produce electricity, the power they produce can split water into hydrogen and oxygen. This project includes two major components: 1) a research and demonstration project wherein photovoltaic electricity drives the production of hydrogen from water in a pressurized electrolyzer, which is then stored in gas cylinders for use in powering a fuel cell delivering traction power for a small utility vehicle, and 2) a research project wherein hydrogen is produced using renewable methods including photoelectrochemical (PEC) generation of hydrogen from water. DOE targets for PEC production of hydrogen for 2013 are:

- Solar to hydrogen (STH) Efficiency >8%
- Durability >1,000 hours
- Cost <\$2-3 gasoline gallon equivalent (gge)

Accomplishments

- Ballard 1.2 kW Nexa[®] Fuel Cell was installed in a GEM electric vehicle and was road tested with hydrogen usage gauged and measured (Figure 1).
- A second GEM vehicle is to be outfitted with a second fuel cell.
- Have completed an in-depth study of pulsed direct current (DC) electroplated nickel on nickel sheets to identify the best conditions for anode and cathode materials in substrate-type PEC cells (Figure 2).
- Patent being sought for electroplated nickel materials.
- Indium oxide-iron oxide developed as a transparent, conducting and corrosion-resistant (TCCR) material. Nitrogen titanium dioxide also being developed as a TCCR material (Figure 3).
- Development of the stable, active, inexpensive catalyst via platinum and cobalt on activated carbon was used for aqueous phase reforming (APR) of fermentation broth (Figure 4).



FIGURE 1. (a) Nexa[®]-Zahn Laboratory Test Setup for fuel cell optimization, and (b) the fuel cell attached to a GEM vehicle.



FIGURE 2. Prototype design used to electroplate nickel catalyst material on stainless steel substrate with a-Si triple junction on the reverse side.



FIGURE 3. The performance of the Pt-Co catalyst supported on activated carbon when exposed to different impurities.



FIGURE 4. Activity of the Different Catalysts for Hydrogen Production in APR of Ethanol



Introduction

This is a project that is focused on the development of technologies for generation of hydrogen through photoelectrochemical process and bio-mass derived resources. Development under this project could lead to the achievement of DOE technical targets related to PEC hydrogen production at low cost.

The PEC part of the project is focused on the development of photoelectrochemical hydrogen generation devices and systems using thin-film silicon based solar cells. Two approaches are taken for the development of efficient and durable PEC cells: 1) an immersion-type PEC cell (Task 3) where the photoelectrode is immersed in electrolyte, and 2) a substrate-type PEC cell (Task 2) where the photoelectrode is not in direct contact with electrolyte.

Approach

Four tasks are being carried out:

Task 1: Design and analysis of DC voltage regulation system for direct photovoltaic-to-electrolyzer power feed.

Task 2: Development of advanced materials for substrate-type PEC cells.

Task 3: Development of advanced materials for immersion-type PEC cells.

Task 4: Hydrogen production through conversion of biomass-derived wastes results.

Results

Task 1 of this project was driven towards the development of a fuel cell and electrolyzer that could be integrated into a GEM vehicle. Through the additional support of other state and federal grants this project was taken to fruition and a fuel cell was developed and attached to a GEM vehicle. A second GEM vehicle is being set up with a second variation of the fuel cell set-up. This task was changed from its original project description; however, this part of the task was completed as outlined in the statement of project objectives and the project description.

Task 2 of this project is for the development of materials that will be used as anode and cathode materials for a substrate module being developed under a separate grant (DE-FG36-05GO15028) at Midwest Optoelectronics. The material development at UT has produced several nickel-based materials that can successfully be integrated into a substrate-type PEC system. The material development on this project has met and exceeded the initial goals set for in the statement of project objectives.

Task 3 of the project is for the development of materials for an immersion-type PEC system. There were two paths that were outlined in the project description. The development of materials under this task has been lacking as the physical barriers that are needed to be attained have thus proven to be a difficult barrier to overcome. The main barriers have been conductivity, transmission, chemical and electrochemical stability, and it must be done at 250°C. Discounting the temperature barrier the task is already a difficult task to research and develop materials that can be deposited on a-Si surfaces. With the temperature barrier added it has been difficult to find chemically stable oxides using titanium and iron as the base materials. There have been some limited successes in indium iron oxide but the photocurrent is low, and polymer nanocomposite ATO-Flexbond but long-term stability is questionable. On the basis of numerous discussions with the hydrogen working group, material development will proceed down new paths to look into alternative solutions.

Task 4 of this project looked at the development of hydrogen production through conversion of biomass wastes. As outlined on the statement of project objectives and the project description this project was able to be completed successfully. Efforts were made to develop catalyst materials using less expensive materials. Nanofiltration was added to the system in order to remove sulfur contamination from the biomass source that was contaminating the catalyst. The addition of nanofiltration was able to stabilize the system and hydrogen was able to be produced at a constant rate.

Conclusions and Future Directions

This project has ended; however, these materials under Tasks 2 and 3 will continue to be developed further on a sub-contract from Midwest Optoelectronics, LLC during Phase 2 of grant DE-FG36-05GO15028.

FY 2008 Publications/Presentations

1. Xiesen Yang, Xianbo Liao, Wenhui Du, Xinmin Cao, Dinesh Attygalle, Xianbi Xiang, Nirupama Adiga, Xunming Deng, "Theoretical Analysis and Modeling of Light Trapping in a-Si based Thin Film Solar Cells", presentation at 2008 IEEE 33rd Photovoltaic Specialists Conference, Manchester Grand Hyatt, San Diego, CA, May 11-16, 2008.

2. Wenhui Du, Xianbo Liao, Xiesen Yang, Xinmin Cao, Nirupama Adiga, Xianbi Xiang, Dinesh Attygalle, Xunming Deng, "Study of Amorphous Silicon Germanium Solar Cells with i-layer Deposited at High Rates using RF-PECVD", presentation at 2008 IEEE 33rd Photovoltaic Specialists Conference, Manchester Grand Hyatt, San Diego, CA, May 11-16, 2008.

3. Jason A. Stoke, Lila R. Dahal, Jian Li, Nik J Podraza, Xinmin Cao, Xunming Deng, Robert W. Collins, "Optimization of Si:H Multijunction n-i-p Solar Cells through the Development of Deposition Phase Diagrams", presentation at 2008 IEEE 33rd Photovoltaic Specialists Conference, Manchester Grand Hyatt, San Diego, CA, May 11-16, 2008.

4. Swami, S. M.; Abraham, M. A. "Investigation of catalyst deactivation mechanism for hydrogen production from fermentation broth", 2007 AIChE Annual Meeting, Salt Lake City, UT, Nov, 4-9, 2007.

5. Swami, S. M; Ayyappan, P.; Abraham, M. A. "Production of hydrogen from biomass: Integrated biological and thermo-chemical approach", ACS 234th national meeting and Exposition, Boston, MA, Aug, 19-23, 2007.

6. Swami, S. M.; Ayyappan, P.; Abraham, M. A. "An integrated approach for production of hydrogen from biomass", 3rd International Conference on Green and Sustainable Chemistry, Delft, The Netherlands, July, 1-5, 2007.

7. Swami, S. M.; Abraham, M. A. "Production of hydrogen from biomass: Integrated biological and thermo-chemical approach", North American Catalysis Society, 20th North American Meeting, Houston, TX, June, 17-22, 2007.

8. Swami, S. M.; Vaibhav C.; Kim Dong-Shik; Sim S. J.; Abraham, M. A., Production of Hydrogen from Glucose as Biomass Simulant: Integrated Biological and Thermochemical Approach, *Ind. & Eng. Chem. Res.* (In Press).

9. Swami, S. M.; Ayyappan, P.; Abraham, M. A. Preprints of symposia-American Chemical Society, Division of Fuel Chemistry, 2007, 52 (2), 360-361.