II.F.10 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, and Mark Vonderembse
University of Toledo
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) 586-9811
E-mail: Roxanne.Garland@ee.doe.gov

DOE Project Officer: Carolyn Elam
Phone: (303) 275-4953; Fax: (303) 275-4788
E-mail: Carolyn.Elam@go.doe.gov

Contract Number: DE-FG36-05GO85025

Subcontractors:
Bowling Green State University, Bowling Green, OH
Midwest Optoelectronics, LLC, Toledo, OH

Start Date: June 2005
Projected End Date: June 2007

*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, specifically, high-efficiency and low-cost production of hydrogen using photoelectrochemical methods.

Technical Barriers

This project addresses the following technical barriers from the Photoelectrochemical Hydrogen Production section (3.1.4.2.6) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(AP) Materials Efficiency
(AQ) Materials Durability
(AR) Bulk Materials Synthesis
(AS) 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.

Accomplishments

- Installed a 12 kW photovoltaic (PV) array for the generation of hydrogen.
- Studied six groups of materials (five groups of oxides and one polymer group) for use as transparent, conducting and corrosion-resistant layer for photoelectrodes.
- Studied two groups of oxide materials for use as photoactive semiconductor layers.
- Performed studies on the conversion of biomass derived wastes with the evaluation of steam and aqueous phase reforming.

Introduction

This project has two major components: 1) the demonstration of a PV-electrolysis system that has a separate PV system and electrolysis unit and the hydrogen generated is to be used to power a fuel cell vehicle; 2) the development of technologies for generation of hydrogen through a photoelectrochemical process and biomass derived resources. Development under this project could lead to the achievement of the DOE technical target 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 photoelectrochemical cells: 1) an immersion-type photoelectrochemical cell where the photoelectrode is immersed in electrolyte, and 2) a substrate-type photoelectrochemical cell where the photoelectrode is not in direct contact with electrolyte.

Approach

Five tasks are being carried out:

- Task 1. Integrated PV-Hydrogen-Fuel-Cell Facility
- 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
- Task 5. Cost and Performance Analysis of Integrated Hydrogen Systems

Results

Task 1. Integrated PV-Hydrogen-Fuel-Cell Facility

This is largely a demonstration of the integration of technologies cost-shared by the State of Ohio and the University of Toledo. The task includes:

- 12 kW PV array installation (first solar thin-film on glass modules).
- Integration of the solar array with a pressurized electrolyzer (or an integrated electrolyzer plus compressor), including pressurized hydrogen storage.
- DC voltage regulation system for direct PV-to-electrolyzer power feed.
- Retrofit of an electric vehicle with a Ballard 5 kW liquid-cooled fuel cell, including integration of all balance-of-plant components.

A 12 kW PV array of CdTe thin film panels, fabricated by First Solar, of Perrysburg, OH, was dedicated by Congresswoman Marcy Kaptur (Ninth District of Ohio), Tom Maves, (Ohio Department of Development Office of Energy Efficiency), and President Dan Johnson of the University of Toledo on September 30, 2005 (Figure 1a). The State of Ohio, through Ohio Department of Development, provided matching funds for the PV array. The University of Toledo provided the balance of the funds. The system was installed

FIGURE 1. (a) Rep. Marcy Kaptur speaking at the dedication of the 12 kW array, together with (L-R) Frank Calzonetti, Tom Maves, Dan Johnson, John Witte, and Al Compaan (b) Mark Tuttle and John Witte of ADG installing the CdTe panels

by Advanced Distributed Generation LLC (ADG) of Toledo, Ohio (Figure 1b). The array feeds power to the University of Toledo Research and Technology Building 1 (R1) where most of this project is being conducted. The PV power is fed through an underground conduit into the R1 building. Half of the power comes from 18 strings of six panels each series connected to provide ~360 V_{dc}. The 18 strings are connected in parallel to a Sunny Boy inverter tied into the 208 V_{ac} electrical system of the building. The other 6 kW of PV power is fed at 60 V directly into the building (with 108 panels wired in parallel). This power is currently being fed into a resistive load while the dc power control electronics are being designed and fabricated by Prof. Tom Stuart in UT's Electrical Engineering Department as part of this project. The power control system will be designed to match the operating characteristics of the electrolyzer that is soon to be acquired for the hydrogen generation.

Task 2. Development of Advanced Materials for Substrate-Type PEC Cells

In such a PEC cell, a triple-junction amorphous silicon photoelectrode deposited on a conducting substrate is integrated into a PEC cell in which the hydrogen and oxygen compartments are both behind the photoelectrode and are separated by a membrane. Areas of research activities include encapsulation materials and process, grid configuration and installation process, effect of various cell dimensions in the oxidation and reduction compartments, improved membrane holder to prevent hydrogen and oxygen from intermixing, and electrolyte inlet and gas/electrolyte outlet configurations. During the current phase, the UT team has explored electroplating of porous Ni on stainless steel to be used as the counter electrode in the substrate-type PEC cell and obtained low-cost Ni coating with high current density for water electrolysis.

Task 3. Development of Advanced Materials for Immersion-Type PEC Cells

3-1. The objective of this subtask is to develop a transparent, conducting and corrosion-resistant material that can be made at low temperature (below 250°C) using a low-cost thin-film deposition technique, and in addition has the following properties: high optical transmission in the visible wavelength range, high electrochemical stability in the electrolyte, and sufficient conductivity for transport of charge carriers such that an ohmic contact is formed with both the electrolyte and the topmost layer of the amorphous silicon (a-Si) solar cell.

3-2. The objective of the task is to develop a photoactive semiconductor material that: 1) is stable in electrolyte both in the dark and under illumination, 2) forms a high-quality rectifying junction with electrolyte and an ohmic contact with the thin film silicon (tf-Si) layer underneath, 3) generates at least 7.5 mA/cm^2 current so that it can be matched with the middle and bottom component solar cells in an a-Si-based triple-junction stack, and 4) is deposited at low temperature ($< 250^{o}$C) using a low-cost deposition method.

3-3. This subtask includes effort on real-time characterization of corrosion resistance using Mueller matrix ellipsometry and modeling of PEC photoelectrode.

As highlights of work carried out under this Task, we have:

- Studied the deposition of Co-doped TiO_2 using rf co-sputtering of Cobalt and TiO_2 in an O_2/Ar environment at the deposition temperature less than 250°C. Results show excellent stability; however, the current density is lower than that required for photoelectrode applications (Figure 2).
- Studied the deposition of zirconium seed layer and then deposition of TiO_2. The seed layers show crystal formation with films of minimal thicknesses around 70 to 100 nm.
- Studied reactive sputtering of Ti to form TiO_2 for improved stability, control and reproducibility.
- Studied the deposition of Co_3O_4 using rf sputtered by cobalt in an O_2/Ar atmosphere at 200 and 250°C. The films were found to be highly stable with excellent current density but that the absorption is poor at 75%. NiO addition improved the current density further; however, it is still not yet sufficient for use in efficient PEC cells.
- Studied the deposition of Fe_2O_3 by rf sputtering of Fe_2O_3 in an O_2/Ar atmosphere up to 400°C that produced the best results. The films, ~200 to 300 nm thick, are approximately 80% transparent and show approximately 0.2 mA/cm^2 photocurrent (Figure 3).
- Studied the deposition of $InFe_2O_4$ by rf co-sputtering of Fe_2O_3 and In in an O_2/Ar atmosphere with the best films made at 200°C, but the photocurrents are only at 0.03 mA/cm^2.
- Studied the deposition of WO_3 by rf sputtering of W in an O_2/Ar atmosphere. The films are made at 200°C and have demonstrated 50 mA/cm^2 at 3 V.
- Studied Flexbond brand polymer with the addition of antimony tin oxide to improve conductivity as a transparent, conducting and corrosion-resistant layer on solar cells with a 30% by volume addition. The polymer coating shows excellent stability as an anode but no stability as a cathode. The polymer on a solar cell generated gas after 3 minutes and ran continuously for up to 2 hours before delaminating from the solar cell.

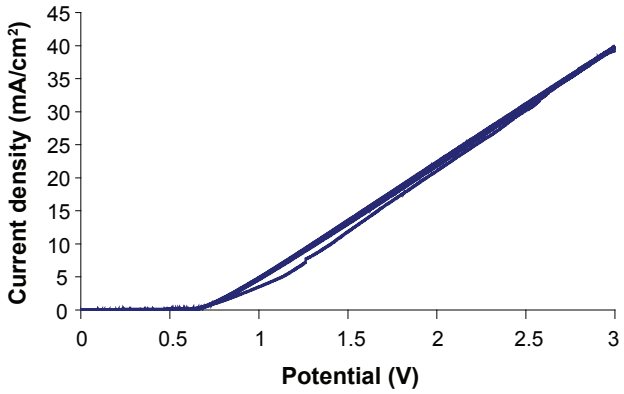

FIGURE 2. Current Density (mA/cm^2) versus Voltage (V) for Cobalt-Doped TiO_2

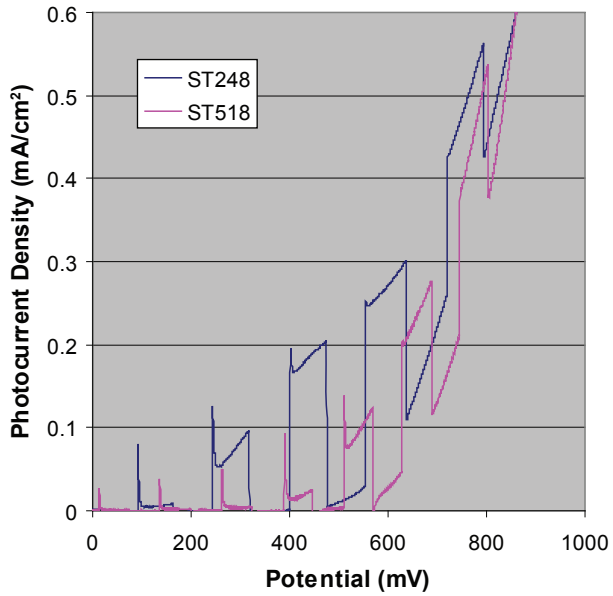

FIGURE 3. Photo- and Dark-Current Densities (mA/cm^2) for Fe_2O_3 Deposited Using Magnetron Sputtering

- Used real time Mueller matrix spectro-ellipsometry for modification of ZnO electrodes as a model system analysis of roughness evolution on three in-plane scales.

Task 4. Hydrogen Production through Conversion of Biomass-Derived Wastes

The objective of this task is to demonstrate conversion of biomass-derived resources into hydrogen of sufficient purity for use in conjunction with PEM fuel cells. Specific work activities include evaluation of fermentation options to convert solid biomass to liquid products, investigation of performance characteristics for aqueous phase reforming, and continued analysis of hydrogen separation options developed from modified polymer membranes.

Hydrogen production from: 1) steam reforming of glycerol using different catalysts supported on a commercially available alumina-based support, and 2) a flow reactor during aqueous phase reforming of ethanol was studied. These activities have demonstrated the potential for hydrogen production from biomass-derived molecules. Additional work is ongoing to improve the performance of the catalyst for the steam reforming system, and to improve the performance of the reactor when operating under aqueous phase reforming conditions.

Task 5. Cost and Performance Analysis of Integrated Hydrogen Systems

The objective of this task is to assess performance, cost, efficiency, and reliabilities related to hydrogen generation using a photoelectrochemical method. Currently, a team consisting of faculty and students in the College of Business and the College of Engineering has been formed to work on this task.

Conclusions and Future Directions

Major progress has been made under this project. This includes:

- A demonstration of a 12 kW PV system designated for the generation of hydrogen using an electrolysis process.
- A comprehensive study of six groups of materials: TiO_2, In-TiO_2, WO_3, Co_3O_4, NiO_x-Co_3O_4 and Flexbond coating, for use as transparent, conducting and corrosion-resistant coating for triple-junction thin-film silicon based photoelectrodes.
- A comprehensive study of Fe_2O_3 and In-Fe_2O_3 as photoactive semiconductor layers for use with double-junction thin-film silicon based solar cells as photoelectrodes.

FY 2006 Publications/Presentations

1. A presentation regarding the overall project status was given at the DOE Annual Merit Review Meeting (May 2006).

2. Presentation, "Sputter Deposition of Fe_2O_3 Films for Photoelectrochemical Hydrogen Production", 208th Meeting of the Electrochemical Society, Los Angeles, CA, October 16-21, 2005.