II.G.6 Production of Hydrogen for Clean and Renewable Sources of Energy for Fuel Cell Vehicles*

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*Congressionally directed project

Objectives

- To expand research directed to the development of clean and renewable domestic methods of producing hydrogen. This program 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 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 activity 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 activity wherein hydrogen is produced using renewable methods including photoelectrochemical (PEC) generation of hydrogen from water. The goal is to achieve the DOE MYPP objective for Photoelectrochemical Production of Hydrogen for 2013:

- Solar-to-hydrogen (STH) efficiency >8%
- Durability >1,000 hours

Accomplishments

- Completed bench testing of the Ballard 1.2 kW Nexa Fuel Cell in preparation for installation on a Global Electric Motorcars (GEM) electric vehicle.
- Completed plans and work order for installation of utility connections for the solar driven 2 kW Avalence electrolyzer for producing hydrogen.
- Completed an in-depth study of pulsed DC electroplated nickel on nickel sheets to identify the best conditions for cathode materials in substrate-type photoelectrochemical (PEC) cells.
- Studied four groups of materials (three groups of oxides and one group of nanocomposite polymers) for use as transparent, conducting and corrosion-resistant layer for photoelectrodes.
- Studied two groups of oxide materials for use as photoactive semiconductor layers.
- Develop of a stable, active, inexpensive catalyst for aqueous phase reforming (APR) of fermentation broth.

Introduction

This is a two-year project that has two major components: 1) the demonstration of a photovoltaic (PV)-electrolysis system that has a separate PV system and electrolysis unit and the hydrogen generated used to power a fuel cell-based 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 DOE technical targets related to PEC hydrogen production at low cost.

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

Task 1 includes the demonstration of a fuel cell vehicle operating on hydrogen produced from solar power. This is largely a demonstration of the integration of technologies, funded using resources from the State of Ohio and the University of Toledo. The task includes:

- Demonstration of a solar-powered fuel cell vehicle.
- While this task involves some research elements, this is largely a demonstration of technologies.
- Matching funds were received from the Ohio Department of Development to support this demonstration activity.
- Complete bench testing of the Ballard 1.2 kW Nexa fuel cell in preparation for installation on a GEM electric vehicle.
- Determined satisfactory method for mounting two hydrogen tanks on the GEM.
- Initiated testing of the 2 kW Zahn DC-DC converter that interfaces the 26 V fuel cell with the 72 V battery on the GEM.
- Completed plans and work order for installation of utility connections for the solar driven 2 kW Avalence electrolyzer for producing hydrogen.
- This task was delayed because state matching funds were delayed until late FY 2007.

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

The DC power supply-based electroplated porous nickel electrodes prepared showed poor adherence to the nickel substrate in our earlier experiments (see Figure 1). Renewed efforts in the past year made significant advances. After a series of experiments run on a pulsed DC supply for applied frequencies varying from 5 to 200 kHz, optimization of electroplated samples was done on the basis of adhesion, current density, and reproducibility of results. Optimum electroplated electrodes were obtained at 20 kHz pulsed DC frequency, while higher frequencies produce poorly electrodeposited samples (see Figure 2). Also, the lowest cathodic over-potential of 88 mV was obtained. The detailed experiments were focused on the (i) effect of area at constant set of applied voltages at 1.8, 1.9 and 2.0 V, (ii) effect of dynamic cathodic over-potential (V_{cc}) at constant dynamic anodic over-potential (V_{ca}), and (iii) effect of anodic over-potential (V_{ac}) at constant dynamic

FIGURE 1. Pulsed DC Power Supply with Electroplating Bath for Electrodeposition of Porous Nickel

FIGURE 2. Pulsed DC Electroplated Porous Nickel Substrates at 10× Magnification of the Electrode Sample Prepared at 20 kHz

cathodic over-potential (V_{cc}). These experiments were done for small areas (1 to 10 cm^2 and 5 to 50 cm^2) porous electroplated cathodes with respect to large area platinum mesh anode of area 356 cm^2. The use of the porous catalyst as a cathode enables the operation of the unit in the range of 1.75 to 1.9 V in triple junction amorphous silicon based photoelectrochemical cells for efficient generation of solar hydrogen.

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

Highlights of work carried out under this Task include:

- 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. TiO_2 using radio frequency (rf) co-sputtering of Zr with TiO_2 in an O_2/Ar environment.
- Studied the deposition of Co_3O_4 using rf sputtering of cobalt in an O_2/Ar atmosphere at 200 and 250°C. The films were found to be very stable with excellent current density but the absorption in the visible spectrum is lower than expected.
- 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 are approximately 80% transparent and show approximately 0.2 mA/cm^2 photocurrent. The films were from 200 to 300 nm.
- Studied the deposition of $InFe_2O_4$ by rf co-sputtering of Fe_2O_3 in an O_2/Ar atmosphere with the best films made at 200°C, but the photocurrents are only at 0.05 mA/cm^2. However, the current density was found to triple by annealing for 4 hours (see Figure 3).
- Studied the deposition of F-doped Sn_2O_3 by rf sputtering of 75% Sn_2O_3 / 25 % Sn_2F_3 target in an O_2/Ar atmosphere. The films are made at 250°C and have demonstrated 200 µA/cm^2 at 1 V (see Figure 4).
- Development of transparent, conductive and corrosion resistant polymer nanocomposite coating
  - Silane-NH_2 and silane-vinyl treatments under the appropriate condition improved the adhesion between polymer nanocomposite and solar cell so that no degradation of polymer nanocomposite coating was observed after the solar coated with polymer nanocomposite Flexbond-ATO had been immersed in 2N KOH for 5 days at room temperature.
  - However, the polymer nanocomposite film was still observed to peel off from the solar cell that was treated with either silane-NH_2 or silane-vinyl first and coated with Flexbond-ATO polymer nanocomposite after the coated solar cell had been immersed in 2N KOH to generate gases under halogen light for about 3 hours. This might be because polymer nanocomposite film has larger thermal expansion coefficient than the solar cell.
  - One approach is to add negative thermal expansion (NTE) nanomaterial into the Flexbond-ATO mixture to fabricate the Flexbond-ATO-NTE composite coating.
  - One approach is to choose the ceramic conducting as coating, such as single nanotube thin films.

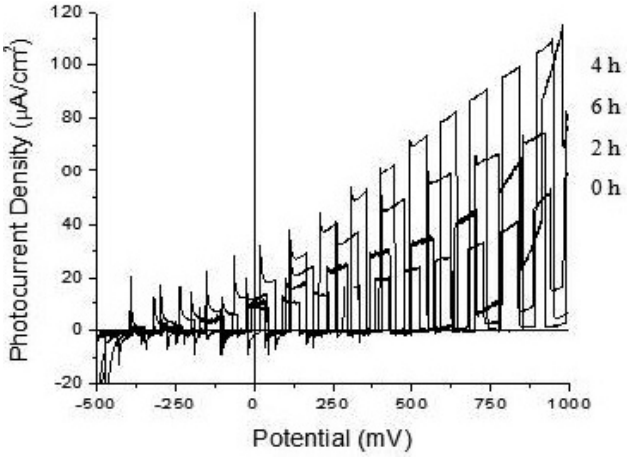

FIGURE 3. Chopped scan of In-Fe_2O_3 thin film using a 100 W xenon arc lamp. Film performance improved with annealing time up to four hours at 550°C, after which any annealing provided no benefit.

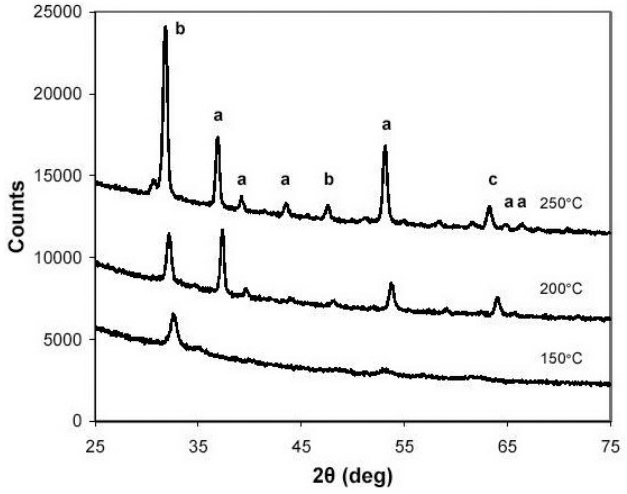

FIGURE 4. X-ray diffraction measurements of In-Fe_2O_3 thin film electrodes deposited at varying substrate temperatures with an indium target deposition power of 10 W. Peak intensities are greater for higher temperatures, indicating greater crystallinity. Film composition includes Fe_2O_3 (a), $InFeO_3$ (b), and $InFe_2O_4$ (c).

  - Additionally, we can fabricate a free-standing conducting polymer nanocomposite film, which can be directly used to wrap the solar cell, such as polyimide-single carbon nanotube composites of very low loading.
- Used real time Mueller matrix spectro-ellipsometry (MM-SE) 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

- Development of the stable, active, inexpensive catalyst for aqueous phase reforming (APR) of fermentation broth.
- Understanding of the catalyst deactivation mechanism for APR.
- Study the effects of different reaction parameters on the hydrogen productivity.
  - Temperature, pressure, pH, ionic strength, concentration, residence time.
- Catalyst Pt/S2 is not stable for APR of fermentation broth.
  - Catalyst deactivation in case of the fermentation broth is suspected due to fermentation impurities.
  - ~ 10 ppm of both S and P was observed in the fermentation broth.
  - Effect of S and P will be studied using amino acids (containing S) and ATP as model compounds.

Task 5: Cost and performance analysis of integrated hydrogen systems

- The start of Task 5 was delayed due to the delayed development of PEC systems and manufacturing process at collaborating organization (caused by delayed funding).

Conclusions and Future Directions

Future work has been planned under this project. This includes:

- Task 1: Integration of fuel cell vehicle to solar array power supply.
- Task 2: Production of final module design with electroplated nickel on back of stainless steel with triple junction a-Si on front.
- Task 3: Continued study into optimization of present oxide materials.
- Task 3: Deposition of oxides under higher power and with metallic targets to improve stability and oxide structure.
- Task 4: Understand the catalyst deactivation mechanisms.
  - Use nano- and ultra-filtration to separate the fermentation impurities.
  - Study the effect of S and P on APR of ethanol.
- Task 4: Study the kinetics of aqueous phase reforming of ethanol.
- Task 5: Begin economic analysis in the next quarter.

Special Recognitions & Awards/Patents Issued

1. March 9, 2006; Japan Domestic Announcement; Title of Patent: Integrated Photoelectrochemical Cell and System having a Liquid Electrolyte; Inventors: Xunming Deng and Liwei Xu; Ser. No. PCT2004/557269 filed November 24, 2003; Japan Patent Application. No. 2004-557269; Japan Domestic Announcement [Kohyo] No: 2006-508253; Japan Domestic Announcement Date: March 9, 2006.

2. April 10, 2006; PCT Patent Application; Title of Patent: Integrated Photovoltaic-electrolysis cell; Inventors: Malabala Adiga, Xunming Deng, Aarohi Vijh, and Liwei Xu; Filing No: PCT/2006/013222; Corresp. to Ser. No. 60/670,177 filed April 11, 2005.

3. May 16, 2006; The following PCT patent application has entered into National Phase; Country selected: US; Title of Patent: Interconnected Photoelectrochemical Cells; PCT No. US2005/005121; Priority based on US Ser. No. 60/545,892; Inventors: X. Deng and L. Xu.

FY 2007 Publications/Presentations

1. Sadashiv M. Swami and Martin A. Abraham, "An Integrated Catalytic Process for Conversion of Biomass to Hydrogen" Energy and Fuels Vol 20(6) (2006), 2616.

2. Ingler Jr., W.B.; Sporar, D.; Deng, X. "Sputter Deposition of In-Fe2O3 Films for Photoelectrochemical Hydrogen Production" *ECS Trans.* Vol. 3 (State-of-the-Art Program on Compound Semiconductors 45 (SOTAPOCS 45) -and-Wide Bandgap Semiconductor Materials and Devices 7), 2006, 253.

3. Ingler Jr., W.B.; Attygalle, D.; Deng, X. "Properties of Rf Magnetron Sputter Deposited Cobalt Oxide Thin Films as Anode for Hydrogen Generation by Electrochemical Water Splitting" *ECS Trans.* Vol. 3 (State-of-the-Art Program on Compound Semiconductors 45 (SOTAPOCS 45) -and-Wide Bandgap Semiconductor Materials and Devices 7), 2006, 261.

4. Ingler Jr., W.B., Attygalle, D., Deng, X. "Properties of Rf Magnetron Sputter Deposited Cobalt Oxide Thin Films as Anode for Hydrogen Generation by Electrochemical Water Splitting" Abstracts of Papers, *210th Meeting of the Electrochemical Society*, *Inc.*, Cancun, Mexico, October 29 – November 3, 2006. (Poster)

5. Ingler Jr., W.B., Sporar, D., Deng, X. "Sputter Deposition of In-Fe2O3 Films for Photoelectrochemical Hydrogen Production" Abstracts of Papers, *210th Meeting of the Electrochemical Society*, *Inc.*, Cancun, Mexico, October 29 – November 3, 2006. (Poster)