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 Synthesis

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.

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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...
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$_3$O$_4$ 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$_2$O$_3$ by rf sputtering
  of Fe$_2$O$_3$ 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$_2$O$_4$ by rf co-sputtering
  of Fe$_2$O$_3$ 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$_2$O$_3$ by rf sputtering
  of 75% Sn$_2$O$_3$ / 25% SnF$_2$ 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$_2$O$_4$ 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$_2$O$_3$ 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$_2$O$_3$ (a), InFeO$_3$ (b), and InFe$_2$O$_4$ (c).
Additionally, we can fabricate a free-standing conducting polymer nanocomposite film, which can be directly used to wrap the solar cell, such as polyaniline-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).

**Special Recognitions & Awards/Patents Issued**

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**