IV.G.3 An Integrated Approach for Hydrogen Production and Storage in Complex Hydrides of Transitional Elements and Carbon-Based Nanostructural Materials*

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*Congressionally directed project

Objectives

- Improve photo-conversion efficiency and corrosion resistance of photo-anodes for generating hydrogen from water using photoelectrochemical (PEC) cells to reach DOE goals.
- Develop surface engineered TiO_2 and WO_3 nanostructural anodes doped for the desired band gaps and band edge for improved photo-conversion and light absorption efficiency.
- Increase reversible hydrogen storage capacity in complex metal hydrides by developing new systems including hydride phases.
- Investigate the effects of nanostructures on adsorption/desorption kinetics, and study surface oxidation properties.
- Perform fundamental studies on the cross-cutting areas of surface energetics common to both release and storage of hydrogen.

Technical Barriers

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

Production

(Y) Materials Efficiency
(AC) Device Configuration Designs

Storage

(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption.

Technical Targets

Hydrogen Production

The primary focus of this project is to achieve high photo-conversion efficiency, by first cleaning the surfaces of n-type photo-anodes to remove surface impurities that often modify work function and act as a trap of charge carriers, and second, the application of nanotube-structured TiO_2 with a close control of the surface dopants for the desired Fermi level and Schottky barrier. Application of Pt nanoparticles will be investigated to enhance electromagnetic field enhancement for increasing light absorption efficiency. Since the use of TiO_2 provides a low production cost and a good corrosion resistance, our goals are to reach DOE targets:

- Usable semiconductor bandgap: 2.3 eV by 2010 and 2.0 eV by 2015
- Chemical conversion process efficiency: 10% by 2010 and 12% by 2015
- Plant solar-to-hydrogen efficiency: 8% by 2010 and 10% by 2015

Hydrogen Storage

This project is also conducting studies of complex hydrides (such as alanates, e.g. $NaAlH_4$) that are considered to have a high potential for reversibly absorbing large amounts of hydrogen. Effect of nanostructured materials using glancing angle deposition (GLAD) on kinetics and oxidation is being studied. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials. This portion of the project will work towards achieving, among others, the following key DOE 2010 hydrogen storage system targets:

- System gravimetric energy capacity: 2 kWh/kg
- System volumetric energy capacity: 1.5 kWh/L
- System cost: $4/kWh

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Accomplishments

Hydrogen Production: TiO_2 was chosen as a test material for electrode fabrication due to its stability, chemical inertness and cost effectiveness. An atmospheric pressure fluidized bed He- plasma reactor was designed and developed for cleaning and modifying surface nanostructures of TiO_2 nanoparticles. The plasma treated TiO_2 nanoparticles were analyzed for their surface area increase using the Bruner-Emmett-Teller (BET) method. An electrochemical cell was developed for the deposition of TiO_2 nanoparticles on the Ti surface. A low-pressure plasma reactor has been installed for its use to remove physisorbed impurities and to promote chemisorption of desired species.

Hydrogen Storage: Careful selection of a group of aluminum hydride complexes and acquisition of several preparation methods corresponding to each hydride has been completed. In particular, synthesis of $NaAlH_4$ is underway. The initial design phase of our Sievert type instrument is complete, and construction will now begin. Design of a high temperature furnace is also in progress. Continuum models for simulating the adsorption/desorption kinetics have been identified.

Set-up of a new oblique angle deposition system for the fabrication of nanostructures has been concluded. Preliminary fabrication of Mg nanorods and thin films have been concluded. Investigated the crystal orientation (texture) properties of the Mg nanostructures and thin films produced. Demonstrated that Mg nanorods do not have significant oxidation.

Approach

The experimental studies were organized into two major tasks with several subtasks: (1) Hydrogen Production: Task 1.1, Photo-Electrolysis of Water; Task 1.2, Use of Nanostructured Materials for UV/Solar Splitting of Water; (2) Hydrogen Storage: Task 2.1, Metal Hydride/Storage Materials Screening; Task 2.2, Plasma Reactor Enhanced Hydrogen Storage; Task 2.3, Characterization of Hydrogen Storage Materials.

Hydrogen Production: The goal of this project is to enhance the current technological advancements being made under the sponsorships of the Department of Energy in the multidisciplinary areas of electrophotochemical photo-conversion for the generation of hydrogen. Our approach is to work as a team with other groups working closely in the specific areas of our project.

Our specific aims are to (1) investigate the effects of physisorption and chemisorption of unwanted species on the metal oxide nanotubes of TiO_2 and WO_3 with respect to the changes in surface Fermi level after modification with nitrogen or carbon, (2) modulate the surface structures of the anodic surface with noble metal nanoparticles, if needed, to enhance the photon induced electromagnetic field for a high absorption, and (3) develop a method for effective photo-absorption measurements since conventional ultraviolet photoelectron spectroscopy measurements (made in a high vacuum) are not easily applicable when the anodic materials are in their real applications.

We will also study the stability of the materials in their application and investigate possible production of an anodic structure containing particles with different band gaps with added protection against corrosion. Most of these studies will be performed with a close cooperation of other PEC centers for synergistic advancements of the technology.

Hydrogen Storage: Our approach will focus on a study of a series of functionally similar hydrides. Hydride complexes that have been more widely characterized by other groups will be tested for verification of our experimental procedures, validation of reproducibility of the hydride and as reference data for model development. Meanwhile, related hydride complexes that are less well documented, or have yet to be investigated for use as storage medium will be investigated for feasibility.

For the fabrication of magnesium nanostructures, we will use a novel oblique angle deposition set-up in the laboratory of Dr. Karabacak. This set-up allows the deposition through direct current/radio frequency sputtering or thermal evaporation of materials on 2" size substrates attached on a special holder which can be tilted to a given angle and can be rotated at a given speed. Because of the limited weight of the nanostructures produced, initial absorption/desorption studies will focus on the kinetics of desorption using a high-temperature X-ray diffraction system, where we will observe the change in the crystal phases during desorption *in situ*.

Results

Hydrogen production: A 5 nm nano-crystalline TiO_2 powders were plasma treated using an atmospheric-pressure He plasma. The plasma treatment caused changes in surface nanosturcture as evidenced by increase in surface area and porosity. Annealing of

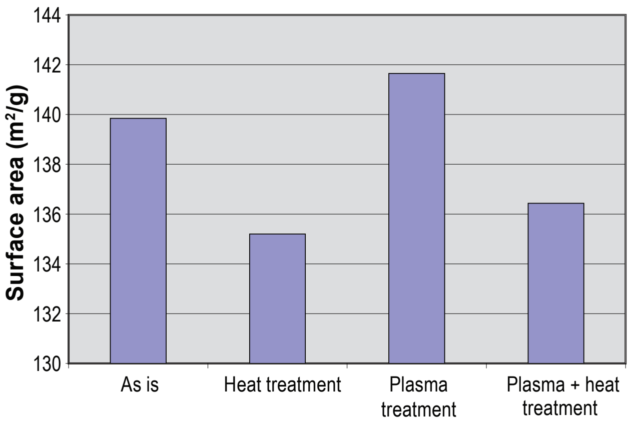

FIGURE 1. BET surface area of nanocrystalline TiO_2 particles. For heat treatment the particles were annealed at 450°C for 2 hrs. Plasma treatment was carried out using atmospheric pressure He plasma for 10 minutes. In the last set of data, plasma treatment was followed by heat treatment.

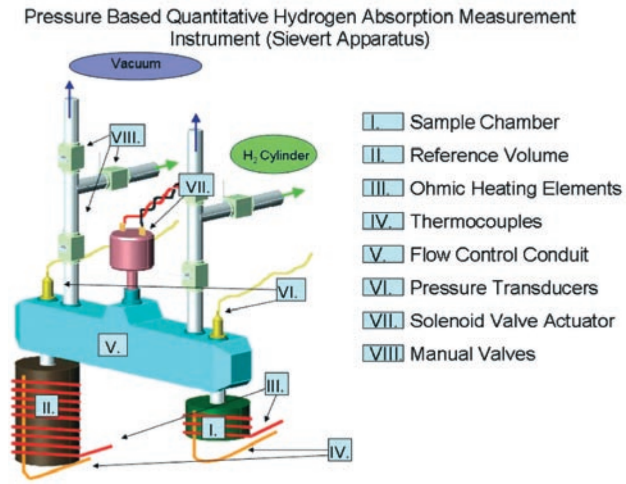

FIGURE 2. Schematic of Sievert-Type Hydrogen Absorption Measurement System

the nanoparticles at 450°C for two hours decreased the surface area. Figure 1 shows the surface area of particles followed by plasma treatment, and then heat treatment and heat treatment followed by annealing.

Hydrogen Storage: Based on extensive literature survey, we have completed the design of a modified Sievert instrument (Figure 2) capable of measuring hydrogen stored at various temperatures and pressures. Synthesis of $NaAlH_4$ is also underway. Regarding nanostructural fabrication, BET measurements indicate that the nanostructured Mg sample has about 90 times larger effective surface as compared to the smooth Mg thin film (Figure 3).

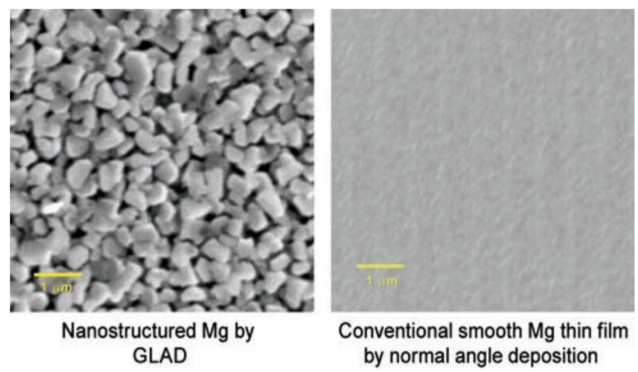

FIGURE 3. Top View Scanning Electron Microscopy Images of Mg Nanorods and Conventional Mg Thin Film Samples (The scale bars are 1 μm.)

Conclusions and Future Directions

Hydrogen Production: Our initial studies with plasma surface modification of TiO_2 nanoparticles have shown increase in surface area and porosity. Low pressure plasma may provide a means to remove unwanted species from the surface and to incorporate gases or nanoparticles of carbon on the surface with a high density such that the effective surface band gap and band edge can be fine tuned. Optimization of surface properties with composite micro- and nanostructured surface could enhance both light absorption and photo-conversion.

We will modify and characterize TiO_2 electrodes for photoelectrolysis. A PEC cell will be fabricated and tested for conversion efficiency analysis using these electrodes. We will optimize the effective bandgap by ion implantation or plasma doping and measure the photoelectron emission efficiency as a function of incident radiation wavelength.

Hydrogen Storage: Development of a generalized direct formation technique for complex hydrides would make viable a few promising materials that are presently infeasible because of the irreversibility of their thermal decomposition. As well, we have successfully finished the installation of the GLAD system for nano material fabrication. The proof-of-concept Mg nanorods have been produced. The dramatic increase in the surface area along with reduction in oxidation of Mg nanorods has been observed. Future experimentation will focus on:

- Characterization of various preparations of $NaAlH_4$.
- Fabrication of $Mn(AlH_4)_2$, $Ga(AlH_4)_3$, and $Mg(AlH_4)_2$ chemically.
- Verification of thermally induced desorption of $Mn(AlH_4)_2$, $Ga(AlH_4)_3$ and $Mg(AlH_4)_2$.
- Development of an intermediate product or catalytic method to enable direct formation of $Mn(AlH_4)_2$, $Ga(AlH_4)_3$ and $Mg(AlH_4)_2$.
- Fabrication of nanostructures of Mg in various shapes of vertical nanorods, tilted nanorods, and

helical geometry, and studying the effect of size and shape of the structures on the kinetics of hydrogen absorption and desorption properties.

- Improvement of the absorption/desorption kinetics by incorporating catalyst impurities in the Mg nanostructures.
- Investigation of the dynamic surface oxidation properties of nanostructures produced.

FY 2007 Publications and Presentations

1. R. Sharma, J. J.Diaz, V. Saini, A. S. Biris, and M. K. Mazumder, "Structural Properties of Atmospheric-Plasma treated Nanocrystalline TiO_2 for Photovoltaic Applications" presented at the Electrostatic Society of America Annual meeting, June 13, 2007.

References

1. O. Khaselev and J. A. Turner, "A Monolithic Photovoltaic-Photoelectrochemical Device for Hydrogen Production via Water Splitting," Science, Vol. 280, 17 April 1998.

2. Mackay, K. M. Hydrogen Compounds of the Metallic Elements. London: E.& F. N. Spon LTD. 1966.