IV.H.4 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

The goal is to produce hydrogen economically using photo-electrochemical (PEC) electrolysis of water directly from sunlight with corrosion resistant semiconductor electrodes for catalytic conversion. The specific objectives are:

- Improve (a) photo-conversion efficiency (solar-to-hydrogen ratio) to 10 percent evolving H_2 and O_2 and (b) photo-corrosion resistance of photo-anodes for 5,000 hours of operation generating H_2 from water.
- Synthesize photoanodes maximizing both light absorption and photoactive sites for high solar-to-hydrogen conversion.
- Develop a hybrid semiconducting photoanode, $TiSi_2$, with a corrosion inhibiting TiO_2 protective layer.
- Use heterogeneous, nanostructured, and hybrid semiconductor photoanodes consisting of layered electrodes made of $TiSi_2$ and TiO_2 for electrolyzing water, and perform fundamental studies on surface energetics: (a) control of surface states, (b) minimization of traps that are responsible for recombination of photo-excited charge carriers at the interface, and (c) reduction of photocorrosion of semiconductor electrodes.
- Increase of 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.

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:

Hydrogen Production (3.1.4.2.6)

(AP) Materials Efficiency
(AQ) Materials Durability
(AS) Device Configuration

Hydrogen Storage (3.3.4.2)

(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

Hydrogen Production

Our technical target is to reach the DOE goals:

- Chemical conversion process efficiency: 10% by 2010 and 12% by 2015
- Plant solar-to-hydrogen efficiency: 8% by 2010 and 10% by 2015
- Hydrogen production cost: $3.00/gge (approximately 1 kg of H_2) by 2018

Hydrogen Storage

This project is also conducting studies of complex hydrides (borohydrides and alanates $LiBH_4$, $Ca(BH_4)_2$, $NaAlH_4$) that are considered to have potential for reversibly storing 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

Accomplishments

Hydrogen Production

- Titanium disilicide ($TiSi_2$) thin films as a part of composite multilayer high efficiency photoanodes for hydrogen generation have been synthesized.
- Electrochemical synthesis of patterned TiO_2 nanorods and nanotubes with separations comparable to wavelength of visible light for trapping solar radiation.
- Multi-layered photoanodes for high efficiency photo-conversion and minimization of photocorrosion.
- Plasma treatments of photoanodes for (a) removing charge traps, (b) surface doping with nitrogen, (c) creating oxygen vacancies for achieving high photocurrent density.
- Design of prototype PEC hydrogen generator with a solar radiation concentrator for optimized operation.

Hydrogen Storage

Decomposition studies have been performed on $LiBH_4$, $Ca(BH_4)_2$ and $NaAlH_4$ primarily aimed at species and chemical mechanism identification. A study of the catalytic interactions of transition metal alloys in borohydride thermolysis has been initiated. The potential for novel synthesis methods has been demonstrated for $Ca(BH_4)_2$.

The GLAD technique was utilized for the growth of nanostructured arrays in the shapes of vertical nanoblades and nanorods. Mg nanostructures as a model material system have been studied. Hydrogen storage capacity, adsorption/desorption kinetics, thermal stability, and oxidation properties of Mg nanostructures and conventional thin films have been investigated. Significant increase in low temperature hydrogen storage values (e.g. ~4.8 wt% @ 100°C) has been observed for Mg nanostructures compared to Mg thin films (e.g. ~0.8 wt% @ 100°C). A new quartz crystal microbalance (QCM) system was developed and upgraded for the kinetic investigation of hydrogen storage capacity and adsorption/desorption kinetics properties of nanostructured and thin film coatings. In addition, we have started investigating magnesium borohydride and alanate for GLAD nanofabrication and hydrogen storage studies.

Approach

The experimental studies was organized into two major tasks with several subtasks: (1) Hydrogen Production: Task 1.1, Photo-Electrolysis of Water; Task 1.2, UV/Solar Splitting of Water Using Nanostructured Materials; (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

Our approach has been focused on the design and construction of an integrated laboratory-scale self-standing PEC-based hydrogen generator using heterogeneous, nanostructured hybrid layered electrodes made of $TiSi_2$ and TiO_2 semiconductors.

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 (i.e. GLAD) 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. A homemade QCM system will be used for the investigation of hydrogen storage, thermal stability, and oxidation properties of nanostructures and thin films produced.

Results

Hydrogen Production

- Development of titanium disilicide thin films as a part of composite multilayer high efficiency photoanodes for hydrogen generation (Figures 1, 2).
- Deposition of thin layer of $TiSi_2$ (Figure 1).

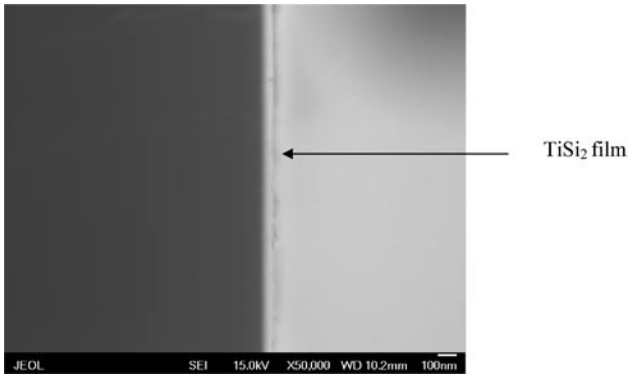

FIGURE 1. Scanning Electron Microscope Image of a Titanium Silicide Film on a Silicon Substrate

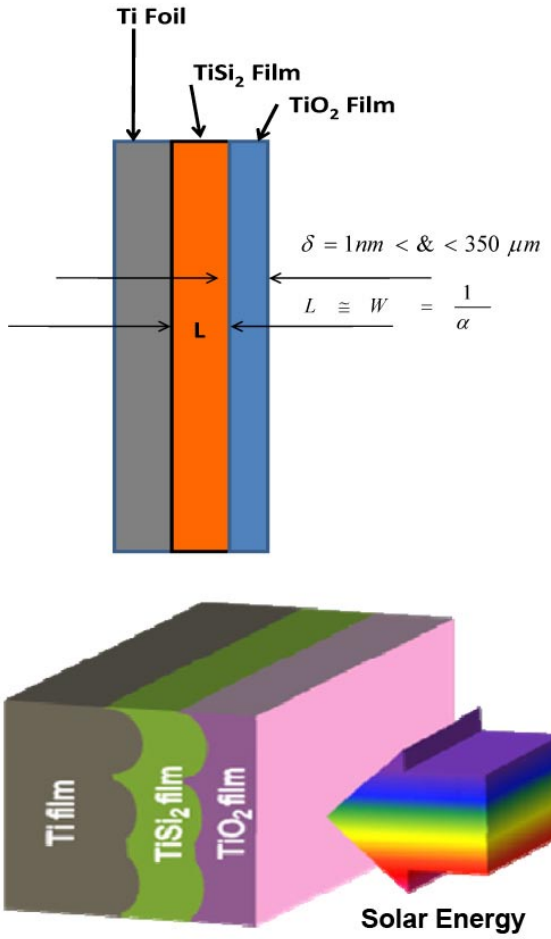

FIGURE 2. Application of layered photoanodes using $TiSi_2$ and TiO_2 semiconductors. Titanium disilicide ($TiSi_2$) electrode with coating of a transparent TiO_2 electrode to be used for studying the PEC activities.

- Development of patterned nanotubular structure by ramping voltage during electrochemical anodization process (Figure 3).

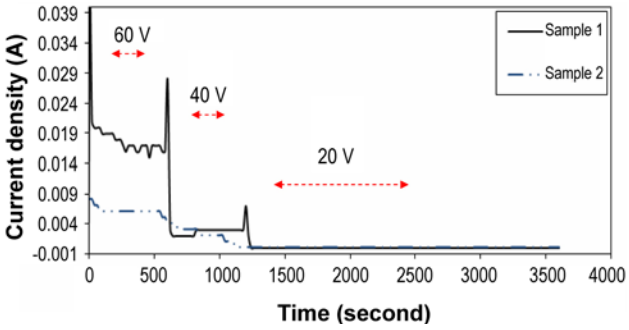

FIGURE 3. Current transient during anodization of Ti while ramping the voltage from 60 V to 20 V.

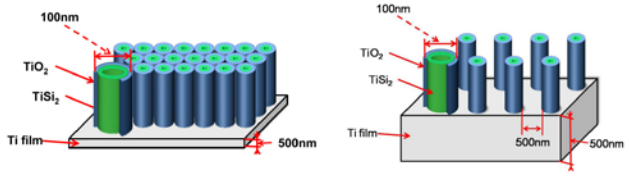

FIGURE 4. Design of two-layered nanotubes in packed form with their outer walls in contact with each other (left) and two-layered nanotubes with their walls separated from each other with spacing equal to the wavelength of incident light (right). The separation between the walls traps incident light for improved absorption.

- Design of two-layer nanotubes of TiO_2 and $TiSi_2$ (Figure 3).
- Nanotube fabrication with stepped voltage anodization (Figure 4).
- Optimization of nitrogen plasma treatment process for maximizing photocurrent density.

Hydrogen Storage

While our studies of the thermal decomposition of $NaAlH_4$ agree well with published literature, proceding at a repeatable rate through the clearly identifiable inermediate compound Na_3AlH_6, the decomposition of borohydride compounds have proven more difficult to analyze. The decomposition of $LiBH_4$, for instance, has yielded yet unidentified products on numerous occasions (Figure 5). We have observed that the decomposition reaction can be 'catalyzed' by huge range of coumpounds including transition metals (e.g. nickel), alloys ($LaNi_5$), non-metals (SiO_2 [1] and carbon nanotubes [2]) with similar effect. The reason for this and the mechanism is yet unknown.

As regards our nanostructured approach (Figure 6), significant increase in low temperature hydrogen storage values (e.g. ~4.8 wt% @ 100°C) has been observed for Mg nanostructures compared to Mg thin films (e.g. ~0.8 wt% @ 100°C).

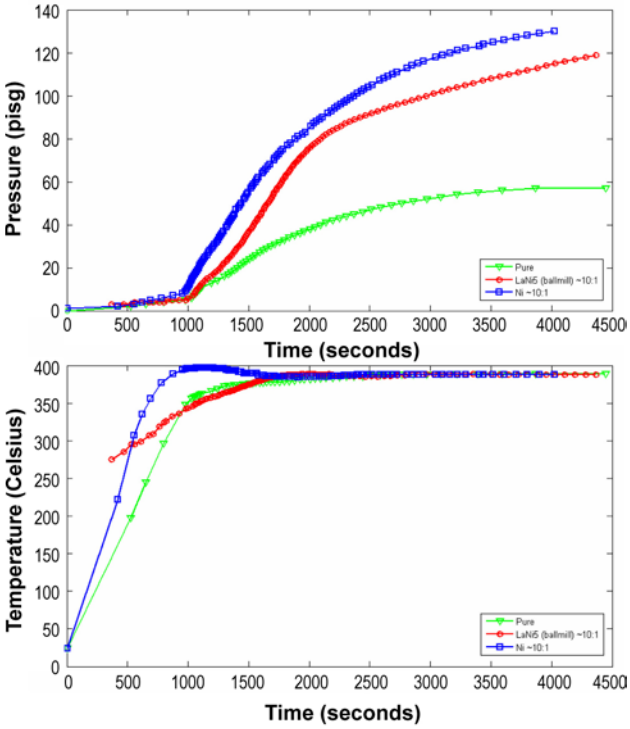

FIGURE 5. Pressure vs. time and temperature vs. time curves for decomposition of $LiBH_4$ in helium atmosphere under a pressure of 15 psi. The top curves in both figures correspond to 400 mg of pure $LiBH_4$ whereas the middle and bottom curves correspond to additives – $LaNi_5$ and elemental Ni – of mass 40 mg each. The behavior is very similar to Fang et al. [2].

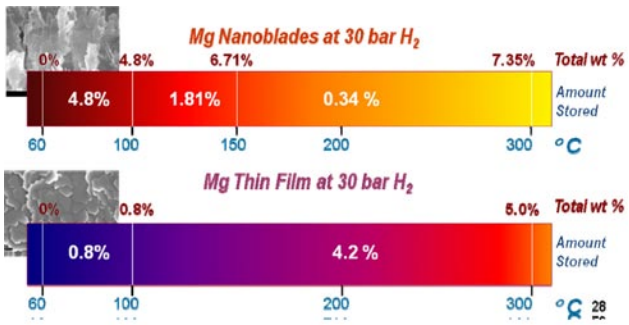

FIGURE 6. Hydrogen storage in Mg thin film and GLAD nanoblades at different temperature intervals.

Conclusions and Future Directions

Hydrogen Production

The present work reports the importance of systematic investigations of (1) the geometric structure of the nanotube arrays, (2) the plasma process for surface doping of TiO_2 nanotubular photoanode with N for decreasing surface bandgaps and (3) annealing process for crystallization for improving photocatalytic generation of hydrogen by splitting water. The test results show promising aspects of tuning several parameters involved in photoelectrochemical processes in improving conversion efficiency.

Hydrogen Storage

It is unlikely that borohydrides will be a viable reversible storage medium until the decomposition/ dehydrogenation reaction is better understood. More knowledge of the chemical mechanisms involved must be obtained to allow for better control of the reaction, products, reversibility and catalysis. Future studies will be aimed at elucidating the chemical mechanism of decomposition and catalytic mechanisms contributed by additives.

We will study the effect of catalysis addition, nanostructure size, shape and separation on hydrogen storage properties of nanostructured Mg as a model system. In addition, we plan to investigate hydrogen storage properties of thin films and nanostructures of magnesium alanate and borohydride.

FY 2009 Publications/Presentations

1. 2009 DOE Hydrogen Program Review - Washington, D.C. – May, 2009. Presentation # PDP08.

2. Rajesh Sharma, Jacob P. Bock, Alexandru S. Biris, Malay K. Mazumder, Prajna P. Das, Manoranjan Misra, Vishal K. Mahajan, "Evaluation of atmospheric-pressure plasma for improving photo electrochemical response of titania photoanodes," IEEE Transactions on Industry Applications, 2009. [In Press]

3. Hidetaka Ishihara, Jacob P Bock, Rajesh Sharma, Franklin Hardcastle, Alexandru S Biris, and Malay K Mazumder, "Electrochemical synthesis of titania nanotube array for photoelectrochemical hydrogen production," in *Proc. Electrostatic Society of America Annual Meeting*, Boston, MA, June 16–19, 2009.

4. Franklin D. Hardcastle, Hidetaka Ishihara, Rajesh Sharma, and Alexandru S. Biris, "The Structure of Titanium Oxide in Titania (TiO2) Photoactive Water-Splitting Catalysts by Raman Spectroscopy," in *Proc. Electrostatic Society of America Annual Meeting*, Boston, MA, June 16–19, 2009.

5. Jeremy Stark, Hidetaka Ishihara, Rajesh Sharma, and Malay Mazumder, "Role of Optics in Optimizing Photoelectrochemical Activity of Semiconductor Anodes," in *Proc. Electrostatic Society of America Annual Meeting*, Boston, MA, June 16-19, 2009.

6. R. Sharma, P.P. Das, V. Mahajan, J. Bock, S. Trigwell, A.S. Biris, M.K. Mazumder, M. Misra, "Enhancement of Photoelectrochemical Conversion Efficiency of Nanotubular TiO2 Photoanodes using Nitrogen Plasma Assisted Surface Modification," Nanotechnology, Vol. 20, 2009, 075704.

7. M.K. Mazumder, R. Sharma, S. Banerjee, S. Mahapatra, H. Ishihara, A.S. Biris, and M. Misra, " Interfacial Charge Transfer Process in Photoelectrochemical (PEC) Generation of Hydrogen using Layered Semiconductors as Photoanodes," *Materials Research Society Spring Meeting*, San Francisco, CA, April 13–17, 2009.

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10. M.K. Mazumder, R. Sharma, P.P. Das, M. Misra, "Interfacial Charge Transfer in Photo-electrochemical Generation of Hydrogen from Water," *in Proc. Electrostatic Society of America Annual Meeting*, Minneapolis, MN, 2008.

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12. S.U. Bayca, M.F. Cansizoglu, A. Biris, and T. Karabacak, "Thermal Stability and Oxidation Properties of Magnesium Thin Film and Nanorods", submitted to Thin Solid Films.

13. T. Karabacak, "Nanostructures for renewable energy systems", Arkansas NSF EPSCoR Meeting, Little Rock, AR, October 7th, 2008.

14. Q. He, T. Karabacak, and A. Wright, "Re-envisioning energy usage", Arkansas NSF EPSCoR Meeting, Little Rock, AR, October 7th, 2008.

15. Wolverton, M.J., Kannarpady, G.K., Bhattacharyya, A., "Demonstration of sorption measurement principles: Design of a custom Sievert's apparatus and characterization of candidate materials, 64th ACS Southwest Regional Meeting, October 1–4, 2008, Little Rock, AR.

16. Wolverton, M.J., Kannarpady, G.K., Bhattacharyya, A., 2009, A temperature differential model-based Sieverts apparatus (submitted).

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