IV.F.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

1. Improve (a) photo-conversion efficiency 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 using photoelectrochemical (PEC) cells.

2. Develop surface engineered TiO_2 and $TiSi_2$ nanostructured photoanodes (nanotubes and nanorods) doped with N, C or F to (1) reduce the effective band gap at the surface by introducing surface states that have energies within the band gap of the bulk semiconductor, (2) straddle photoanode band edges with respect to the electrochemical potentials of (H_2/H_2O) and (H_2O/O_2), (3) minimize Fermi level pinning, and (4) reduce charge carrier traps at the interface for improving light absorption and increasing efficiency of photo-electrolysis of water generating hydrogen.

3. Perform fundamental studies on surface energetics such as generation and control of surface states, role of surface states in H_2 generation, minimization of surface states that are responsible for recombination of photo-excited charge carriers at the interface, and on photocorrosion of semiconductor electrode exposed to different wavelength of solar radiation.

4. Optimize surface structure for enhancing scattering cross section for improving light absorption.

5. Design and fabrication of a Sievert-type high-pressure, high-temperature gas titration/chemical reactor setup.

6. Increase of reversible hydrogen storage capacity in complex metal hydrides by developing new systems including hydride phases.

7. Development of catalytic compounds to enhance the formation and decomposition of complex metal hydrides.

8. Investigation of hydrogen storage capacity in metal decorated polymers.

9. Investigation of enhancement of hydrogen storage capacity in metal hydrides dispersed in polymer matrix.

10. Investigation of maximum hydrogen storage capacity, adsorption/desorption kinetics, and catalyst effects in thin films and nanostructures of magnesium alanate and magnesium borohydride for hydrogen storage.

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 (3.1.4.2.6)

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

Storage (3.3.4.2)

(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption.
(D) Durability/Operability
(E) Charging/Discharging Rates

Technical Targets

Hydrogen Production

The primary focus of this project is to achieve high photo-conversion efficiency in generating hydrogen by splitting water. Taking every technical aspect into account, a band gap (Eg) of 2.5 eV is most desirable. However, most stable semiconducting electrodes have large band gaps and hence low efficiency for photo-conversion for the entire spectrum of solar radiation. Reduction of band gap by doping has not been found successful. Small bad gap electrodes suffer from poor stability, inadequate charge transfer properties and a high charge recombination rates. Finding the right material for high efficiency and durability is of highest importance. Our technical target is to reach the DOE goals:

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

Hydrogen Storage

This project is also conducting studies of complex hydrides such as magnesium alanate, magnesium borohydride, and borohydrides (e.g. $Ca(BH_4)_2$) that are considered to have a high potential for reversibly absorbing large amounts of hydrogen. We are studying the possibility of hydrogen storage in metal decorated polymers and metal hydride dispersed polymers. Effect of nanostructured materials fabricated by glancing angle deposition (GLAD) on adsorption/desorption kinetics in elemental magnesium, magnesium alanate, magnesium borohydride, and these materials with catalyst additives 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

- TiO_2 nanorods were synthesized using electrochemical anodization of Ti foil.
- A low-pressure helium, nitrogen, and oxygen plasma was used for modifying surface energetics, surface chemical and physical structures.

- The plasma treated TiO_2 samples were analyzed for their PEC activity.
- The photocurrent density of nitrogen plasma treated samples was 80% higher as compared to untreated samples.
- Plasma treated samples were analyzed for determining the surface chemical structure using X-ray photoelectron spectroscopy (XPS); it shows that N atoms can substitute O atoms in the surface lattice structure.

Hydrogen Storage

- The sievert type gas titration setup has been completed and verified using hydrogen storage grade $NaAlH_4$ sample obtained from Sigma-Aldrich.
- A simple but highly effective mathematical model based on the Ideal gas law has been developed and tested successfully to remove the effect temperature gradient on pressure measurements. This has proven significantly more accurate than empirical correction.
- Initial experiments on hydrogen storage capacity of Ti decorated polyaniline samples have been performed.
- Initial experiments on polymer dispersed complex metal hydride samples have been carried out.

In addition, we identified magnesium borohydride and alanate as materials of choice for nanofabrication and hydrogen storage studies. We have continued to work on Mg nanostructures as the model material system. For Mg nanostructures produced by GLAD in our labs, hydrogen storage capacity, adsorption/desorption kinetics, thermal stability, crystal orientation, and oxidation properties have been investigated. The GLAD technique was utilized for the growth of nanostructured arrays in the shapes of vertical nanorods and nanoblades. Furthermore, a new quartz crystal microbalance (QCM) system has been developed for the kinetic investigation of hydrogen storage capacity and adsorption/desorption kinetics properties of nanostructured and thin film coatings.

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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, 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

TiO_2, being the workhorse of photoelectrolysis for the last four decades for its advantages in electrode fabrication, stability, inertness and cost effectiveness, was chosen for our fundamental investigations on interfacial charge carrier generation and transport systems. We will use both TiO_2 photoanodes with n-type dopants and $TiSi_2$ photoanodes to cover the ultraviolet (UV) and visual (VIS) regions of the solar radiation spectrum. Since interfacial generation, recombination and transfer of charge in the PEC system is dominated by the surface states and the surface structures, our research is focused on the control of surface states using TiO_2 photoanodes.

We are using plasma surface treatment (1) to remove surface contaminants and unwanted surface states caused by uncontrolled chemisorption of gases and vapors on the dangling bonds of surface atoms that act as charge carrier traps and (2) for surface doping of TiO_2 photoanodes with n-type dopants (N, C, Si, …) on annealed TiO_2 nanotubes and nanorods. The plasma surface modified TiO_2 anodes are tested for their photocurrent density when illuminated by artificial solar radiation. Results are compared to examine the improvement in photocurrent density with surface modification. We now plan to use $TiSi_2$ photoanodes to examine similar improvements of photocurrent density under visible portion of the solar radiation. We are currently testing the photo-corrosion resistance of TiO_2 and $TiSi_2$ photoanodes using electrochemical impedance spectroscopy under UV and VIS radiation exposures.

Hydrogen Storage

Sieverts apparatus: We have designed and constructed a highly automated instrument for measuring the hydrogen sorption characteristics with a scalable sensitivity, wide range of operating temperature and pressure conditions.

Metal hydrides: Our aim is to decrease reaction temperature, increase reaction rates and decrease reaction pressure of certain metal hydride complexes. We intend to destabilize the complexes by encouraging energetically favorable decomposition byproducts. Additionally, we will to aid decomposition and reformation of these compounds by addition of small amounts of selected catalytic compounds.

Polymer-based materials: We will pursue stable metal decorated polymer using metal nanoparticles for synthesis. We will explore various techniques to reduce the effect of cluster formation caused by nanoparticles.

For the fabrication of magnesium nanostructures, we have utilized a GLAD 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 inch 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, we designed and finished the set-up of a new QCM system that has a nanogram sensitivity in dynamic mass changes. The QCM system will mainly be used for the kinetic investigation of hydrogen storage capacity and adsorption/desorption kinetics properties of nanostructured and thin film coatings.

Results

Hydrogen Production

Surface modification was performed using low-pressure oxygen, nitrogen and helium plasma, operating at 13.56 MHz at a pressure of 150 mtorr. Samples were exposed to plasma for 10 minutes in each test run. Plasma treated samples were tested for photocurrent density, optical absorbance and surface chemical structure. Figures 1 and 2 show the photocurrent density obtained from as-anodized and oxygen annealed photoanode samples, with and without plasma surface treatments, respectively. The current density for the nitrogen plasma treated samples (0.21 mA/cm^2) was higher as compared to the as-anodized sample (0.08 mA/cm^2) at 0.2 V (Figure 2). In case of oxygen annealed samples (annealed at 500ºC for 6 h in oxygen) the nitrogen plasma treated sample again demonstrated higher photocurrent densities (1.2 mA/cm^2 at 0.2 V) as compared to untreated sample (0.8 mA/cm^2 at 0.2 V).

Table 1 summarizes the open circuit potentials (OCPs) and photocurrent density values for the oxygen annealed plasma treated samples. The OCP values under the dark condition ranged from -0.3 to -0.4 V. The OCP decreased from -0.85 V to -0.97 for N_2 plasma treated sample. This negative shift in OCP values after
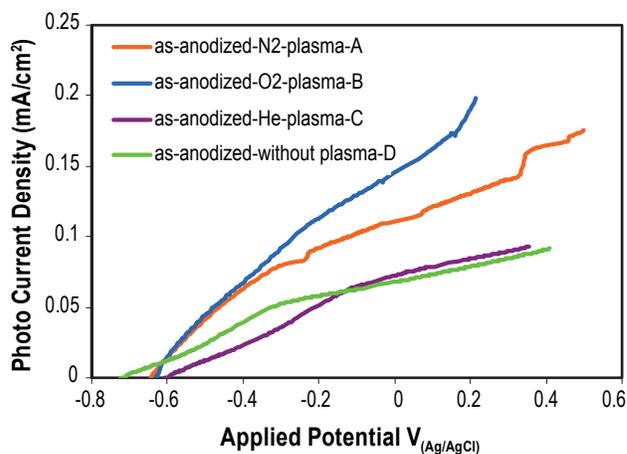
FIGURE 1. Photocurrent Density Data for As-Anodized And Plasma Surface Treated Samples Prepared in Acidic Solution

Oxygen Annealed Plasma Treated Samples
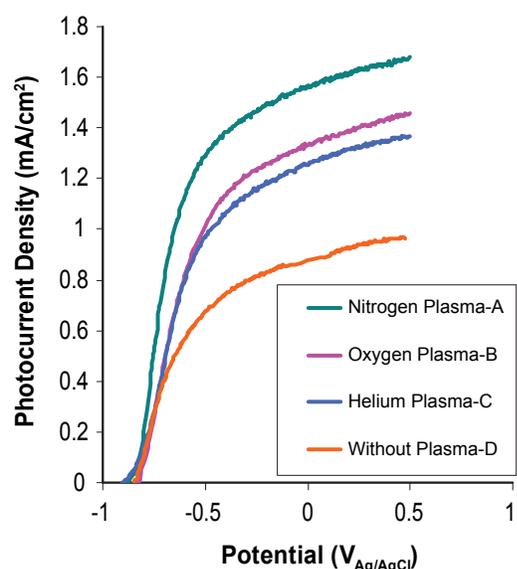
FIGURE 2. Photocurrent Density Data for Oxygen Annealed and Plasma Surface Treated Samples Prepared in Acidic Solution

illumination indicates increase in bend bending after plasma treatment. Since the OCP values reflect the difference between the Fermi level of semiconductor and redox potential of electrolyte, a more negative value of OCP is preferred.

TABLE 1. Summary of Photocurrent Density and the OCP Values of Oxygen Annealed Control and Nitrogen Plasma Treated Samples

Sample Description	OCP (Light), $V_{Ag/AgCl}$	Current at -0.2 V (mA/cm^2)	Current at 0.2 V (mA/cm^2)
Control	-0.85	0.83	0.93
N$_2$ plasma treated	-0.97	0.94	1.68

The experimental results show that the nitrogen plasma treatment of oxygen-annealed samples increased photocurrent density and band bending which manifests into increasing photopotential and thus increasing photocurrent. The increase in photocurrent density after plasma treatment could be ascribed to combination of several factors including removal of surface contaminants, change in surface physical structure and modification of surface chemical structure causing change in surface energetics.

XPS analysis showed that O/Ti ratio decreased from 3.32 in control to 2.80 eV after nitrogen plasma treatment. This suggests removal of oxygen atoms from the surface, which could be due to desorption of water and physisorbed oxygen from the surface or from the lattice or both XPS analysis also showed that the
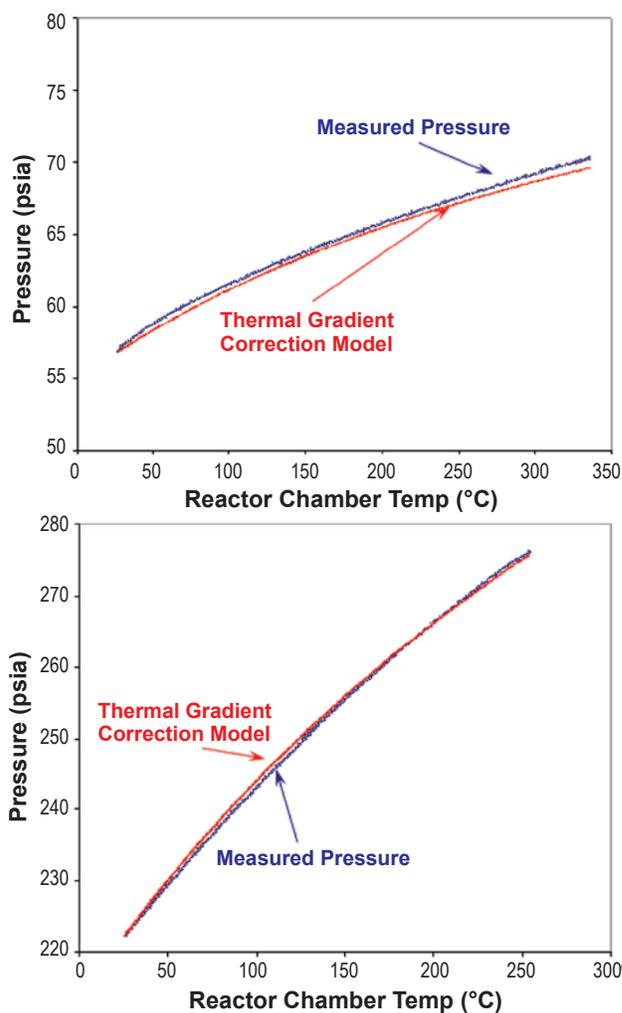
FIGURE 3. Pressure predicted by the thermal gradient correction model compared against measured pressure for static gas quantities in reactor. Our model is in good agreement with the actual pressure changes.

N-concentration increased from 0.24 to 1.21 atomic% after plasma treatment. The significant increase in N concentration after plasma treatment suggests the introduction of N in lattice structure either as substitutional dopant for O, or as interstitial dopant. This hypothesis is supported by several recent studies where N doping has shown a reduction in bandgap of TiO$_2$.

Hydrogen Storage

We completed construction of our Sievert's apparatus. We have written custom control software including an intuitive graphical user interface and flexible measurement routine controls. A simple but effective thermal gradient correction model was developed to account for the temperature differences created by heating of the sample chamber and simultaneous cooling of attached conduits. A comparison of measured and calculated pressure vs.
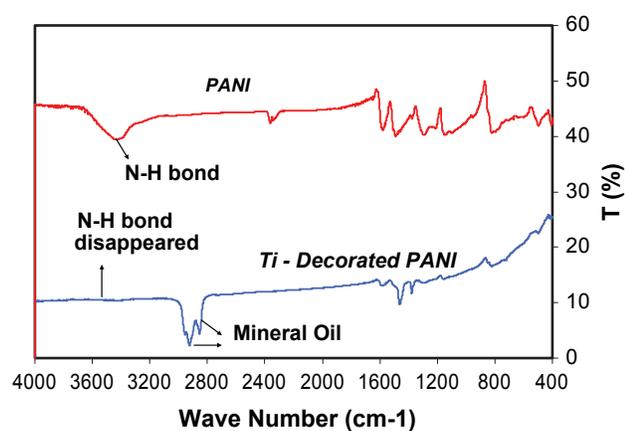
FIGURE 4. IR Spectra of Ti-Decorated Polyaniline (PANI)

temperature plot is shown in Figure 3. Validation testing of hydrogen evolution was carried out using commercially obtained batch certified $NaAlH_4$ with a very small error of 0.87%.

Initial experiments on Ti decoration in commercially obtained polyaniline samples have been carried out. Ti nanoparticles (~100 nm) were used in decorating polyaniline. Figure 4 shows the indication of disappearance of N-H bond in polyaniline suggesting theoretically predicted structure was achieved.

We have continued to work on Mg nanostructures as model material system. For Mg nanostructures produced by GLAD in our labs, hydrogen storage capacity, adsorption/desorption kinetics, thermal stability, crystal orientation, and oxidation properties have been investigated. It has been shown that nanostructures produced by GLAD posses a single crystal structure providing a reduced surface oxidation property. GLAD technique was utilized for the growth of nanostructured arrays of Mg in the shapes of vertical nanorods and nanoblades. In addition, a new QCM system has been developed for the kinetic investigation of hydrogen storage capacity and adsorption/desorption kinetics properties of nanostructured and thin film coatings and some preliminary measurements on Mg nanorods have been performed. These studies are still underway.

Conclusions and Future Directions

Hydrogen Production

Our experiments with plasma treated TiO_2 photoanodes have shown encouraging results. We will optimize the effective bandgap by plasma doping and measure the photocurrent generation efficiency as a function of incident radiation wavelength. We will determine the optimum plasma treatment methods for surface modification of TiO_2 photoanodes. Optimization

of surface properties with composite micro- and nanostructured surface could enhance both light absorption and photo-conversion.

The surface states of TiO_2 photoanodes will be characterized by determining density of states, surface bandgaps and work function, optical absorption spectrum, photoconductivity, and durability. We will perform comprehensive studies on the improvement of photo-conversion efficiency by modifying surface states and surface structures with the addition of nanoparticles of Au, Pt, and other materials for improved photo-catalytic activity of TiO_2. A multi-dimensional analysis will be performed which will include cost, durability, efficiency and environmental factors. Partnerships with private enterprise are being explored.

Hydrogen Storage

Conclusions

- A highly automated Sievert type gas titration setup to measure the hydrogen sorption has been developed and fabricated in-house. The cost was just $18,000 (as opposed to a commercial system which costs about $100,000).

- Titanium nanoparticle decorated polymer shows promising preliminary results for validating the theoretically predicted hydrogen storage capacity.

Future Directions

- Sorption characteristic studies will be carried out on borohydride compounds such as $Ca(BH_4)_2$ and $Mg(BH_4)_2$. The catalytic effect of a sterically hindered organo-metallic Ni complex on these compounds will be studied.

- To study the decomposition mechanism of $Ca(BH_4)_2$, in situ neutron diffraction technique will be used (at Lujan Neutron Center, Los Alamos National Laboratory, New Mexico) during thermal decomposition.

- Clustering of Ti nanoparticles is one of the biggest problem that is potentially inhibiting the theoretically possible hydrogen storage capacity in polymers. We will try to increase the cross-linking in polymer that might reduce Ti clustering.

- Decoration of Li nanoparticles in polymers is another choice. Theoretical studies have shown that clustering of Li nanoparticles is less in comparison with that of Ti. In addition, Li nanoparticles can store more hydrogen in polymers than Ti nanoparticles.

- We will fabricate thin films and nanostructures of magnesium (as model system), magnesium alanate and borohydride with/without catalyst additives (e.g. Pt, Ti, Ni, Pd, and V) using GLAD and

investigate the hydrogen storage and adsorption/desorption kinetics in these materials using our new QCM set-up. We will also investigate the effect of nanostructure size, shape and separation on such properties.

FY 2008 Publications/Presentations

1. M. F. Cansizoglu and T. Karabacak, "Evolution of Crystal Orientation in Obliquely Deposited Mg Nanorod Arrays for Hydrogen Storage Applications" presented in Materials Research Society Fall-2007 Meeting, November 27, 2007, and is under print to be published in the MRS Proceedings.

2. S. U. Bayca, M. F. Cansizoglu, A. Biris, and T. Karabacak, "Thermal Stability and Oxidation Properties of Mg Nanorods and Thin Film", in preparation.

3. 2008 DOE Hydrogen Program Review - Washington, D.C. - June, 2008. Presentation # PDP21.

4. R. Sharma, M. Misra, V. Mahajan, P. Das, J. Bock, A.S.Biris, M. K. Mazumder, "Application of atmospheric-pressure plasma for enhancing photoelectrochemical properties of TiO$_2$ electrodes," *IEEE Industry Applications Society 43rd Annual Meeting*, Edmonton, Canada, 2008.

5. 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.

6. M. K. Mazumder, R. Sharma, P. Das, A. S. Biris, and M. Misra, "Photo-electrochemical Generation of Hydrogen using Plasma Assisted Self-assembled Titania Nanotubes," CTSI Clean Technology and Sustainable Industries Conference and Trade Show, Boston, MA, June 2-4, 2008.

7. R. Sharma, P.P. Das, M. Misra, V. Mahajan, J. Bock, S. Trigwell, A.S.Biris, and M. K. Mazumder, "Photo electrochemical performance of Plasma treated Titanium-di-oxide nanostructures," Materials Research Society Fall Meeting, 2008.

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2. Y. Chiba, K. Kashiwagi, H. Kokai, "Plasma surface treatment effect of TiO$_2$ thin film," Vacuum, 2004, 74, 643-646.