II.F.1 An Integrated Approach for Hydrogen Production and Storage in Complex Hydrides of Transitional Elements*

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Objectives

- Study methods to obtain gaseous hydrogen from water. These methods will include electrolysis and photoelectrolysis including ultra pure hydrogen for fuel cell applications.
- Increase of reversible hydrogen storage capacity in complex metal hydrides by developing new systems including hydride phases.
- Investigate synergistic coupling of plasma or corona discharge with the electrochemical reactions involved in hydrogen storage in metal alloys.

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

Storage (3.3.4.2)

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

Technical Targets

This project is conducting studies to improve photoelectrochemical cells and improved electrolysis systems to lower the cost of hydrogen produced using these technologies. This portion of the project will work towards achieving the following DOE hydrogen production 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

This project is also conducting studies of Laves Phases metallic alloys that are considered to have a high potential for reversibly absorbing large amounts of hydrogen. 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

Approach

The experimental studies will be 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

This project intends to work on hydrogen production in the areas of photoelectrolysis of water and UV/solar splitting of water using nanostructured materials. Both of these technologies represent renewable sources of hydrogen using water as the substrate and solar power to drive the production process. Investigators will focus on using triple-junction photocells in photoelectolysis and nanostructured materials such as ZrO_2, ZnO, and Pd in the UV/solar splitting area.

Hydrogen Storage

The main goal of this research is to develop new families of alloys that can reversibly absorb large amounts of hydrogen and can be used as active materials in metal-hydride storage systems. Classes of metallic alloys that are considered to have a high potential for reversibly absorbing large amounts of hydrogen are the Laves Phases. These are metallic alloys with the compositions given by the general formula AB_2, where A can be either Zr or Ti, and B can be transitional metals such as V, Ni, Cr, Mn, Co, etc. A further improvement can be accomplished by studying the over-stoichiometric alloys with the general formula AB_3, which are considered to have a more stable behavior during charge-discharge cycles and the fact that most of the volume of absorbed hydrogen can be desorbed. Various compositional substitutions for the A and B atoms will be performed, following the general formula Zr_xTi_{1-x}, $V_yNi_zCr_tMn_uCo_p$, and both the structural and the hydrogen uptake properties of these alloys will be investigated. A starting point will be to reproduce some of the results that were already reported and by performing various compositional changes to further improve the volumetric uptake properties of the alloys. These heavier alloys will only be further pursued if they have the potential of meeting or exceeding DOE's 6 wt% system target and/or will be examined as potential dopant or catalyst materials. Lighter alloys will also be examined if needed to meet DOE's hydrogen storage capacity targets. For this research a large number of analytical tools will be employed such as x-ray diffraction, microscopy, elemental analysis, surface area analysis, etc. The overall process will include measuring the hydrogen uptake values, analyzing the crystallographic structure and the possible formation of secondary phases. Some of the more promising alloys will be thermally treated at different temperatures and time periods, in order to alter their crystallographic structure. The crystallographic structure will be investigated by electron microscopy (transmission electron microscopy, scanning electron microscopy, and x-ray diffraction).

This project will also conduct surface modification for removal of contaminants and reduction of surface oxides using a plasma bed plasma reactor. Plasma is a mixture of highly energetic ionized and partially ionized species which can be utilized to remove contaminants and activate the surface. This can replace conventional methods such as chemical, or mechanical removal of the contaminants. Additionally, plasma treatment would also assist in surface activation of these surfaces. Most of the metallic surfaces once exposed to air are covered by a layer of N, O, C, or H, elements that can reduce the catalytic properties of the surface. In order for the hydrides to be formed, it is required for the surfaces to be activated. This process usually consists of heating at 400^{o}C in vacuum, which allows the reconstruction of an active surface. Many times the activation of the surface is achieved by depositing a noble metal on the surface of the alloy, which will allow the dissociation of the hydrogen molecules. The increased hydrogen concentration chemisorbed on the surface of the metallic systems will result in enhanced thermodynamic driving forces of hydrogenation. Therefore the control of surface properties could potentially play a very important role in the absorption/desorption process.

In addition, characterization of hydrogen absorption capacity as well as the rate of adsorption will be performed for all the metal alloys by volumetric methods (Sievert-type) and Bruner-Emmett-Teller/chemisorption methods.

Accomplishments

- This project is just being initiated and has no progress to report at this time.