IV.G.2 Fuel Cell and Hydrogen Research – 2006 Annual Report*

Elias K. Stefanakos (Primary Contact),
Yogi Goswami
Clean Energy Research Center
University of South Florida (USF)
4202 E Fowler Ave, ENB118
Tampa, FL 33620
Phone: (813) 974-4413; Fax: (813) 974-5250
E-mail: stefanak@eng.usf.edu

DOE Technology Development Manager:
Grace Ordaz
Phone: (202) 586-8350; Fax: (202) 586-9811
E-mail: Grace.Ordaz@ee.doe.gov

DOE Project Officer: Reg Tyler
Phone: (303) 275-4929; Fax: (303) 275-4753
E-mail: Reginald.Tyler@go.doe.gov

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*Congressionally directed project

Task 1: Hydrogen Production

- **Task 1.1 Thermochemical** (UF) Investigators: D.Y. Goswami, E., Stefanakos, Man Su Lee, S. Dolan, H.S. Ingley
- **Task 1.2 Biomass Gasification** (UF) Investigators: D.Y. Goswami, E. Stefanakos, W. Lear, M. Mahishi, M. Nath
- **Task 1.3 Photoelectrochemical/Photocatalytic** (USF) Investigators: D. Morel, N. Kislov, S. Srinivasan, C.S. Ferekides, E. Stefanakos, S. Bates
- **Task 1.4 Solid State Ionic Conductor** (USF) Investigators: B. Krakow, E. Stefanakos, P. Wiley, L. Ecklund-Mitchell, D. Payne, E. Weaver

Technical Barriers and Targets

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

Task 1.1 (3.1.4.2.7)

(AU) High Temperature Thermochemical Technology

- Process energy efficiency: 40%

Task 1.2 (3.1.4.2.4)

(W) Capital Cost and Efficiency of Biomass Gasification/Pyrolysis Technology

- Efficiency: 50%
- Plant gate cost: $1.75/gge

Task 1.3 (3.1.4.2)

(AP) Material Efficiency
(AQ) Material Quality
(AR) Efficiency
(S) Cost

- Chemical conversion process efficiency (EC): >10%
- Durability: >1,000 hr

Task 1.4 (3.1.4.2.1 and 3.1.4.2.4)

(W) Capital Cost

- Total cost: $2.75/gge H_2

(3.1.4.2.2)

(H) System Efficiency
(I) Grid Electricity Emission
(K) Electricity Costs

- Efficiency: 76%

Accomplishments/Results

Task 1.1 Thermochemical

- A procedure to make the solid reactant was developed and characterized, that employs metal alkoxide chemistry to make the precursors, followed by drying, molding, and sintering processes. Predetermined amounts of corn starch, stearic acid, and graphite powders were added to the slurry as pore forming agents.
- The reactions of selected Ca-pellets were conducted using a laboratory experiment set-up. Degradation and low hydrolysis rate were observed during cyclic operations.
- In order to investigate the mechanism of degradation, the changes of the pore size distributions by bromination and hydrolysis process were measured. This showed that the reduction in pore volume (<5 um) led to degradation.

Task 1.2 Biomass Gasification

- Hydrogen yield and overall gas yield increased by 48% and 62%, respectively at a gasification temperature as low as 600°C in the presence of calcium oxide sorbent.

- Tars and particulates were reduced substantially while using sorbent; calcium oxide was found to play dual role of sorbent and catalyst and helped in improving the overall conversion of solid biomass into gas; improvement in hydrogen yield of any existing process addresses the technical barrier mentioned in section 3.1.4.2.4 of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan.
- Last year's study included theoretical simulations – the current year's work so far has experimentally proved the theory suggested in the last year's simulations and analysis.
- A physics-based model of the system has been developed that represents the reformer of a gasifier.
- The partial differential equation has been discretized into a set of ordinary differential equations. The set of equations are represented with a banded penta-diagonal matrix.
- The set of ordinary differential equations is solved using Matlab/Simulink, that predicts the spatial temperature profile across the reformer.
- Benchmarking the numerical approach with analytical approach is under progress.
- Experiments were conducted by steam gasifying pine mulch with and without calcium oxide sorbent. The temperature, while the pine mulch and catalyst bed kept at thermal equilibrium and steam flow at steady state, was varied from 500°C to 700°C. The sorbent to biomass molar ratio was maintained at one for all the experiments.
- On comparison it was found that at 500°C the total gas yield had more than doubled and at 600°C it has increased by almost 60% as compared to the no sorbent case. The hydrogen yields at 500°C and 600°C in presence of sorbent were comparable to the yield at 700°C for the no sorbent case. Sorbent enhanced biomass gasification had less tars and particulates as compared to the conventional gasification.

Task 1.3 Photoelectrochemical/Photocatalytic

- A SnO_2/n-Si device process has been developed. The special feature of this process is that the SnO_2 was deposited using the same deposition process as that used for deposition on glass to serve as substrates for stand-alone SnO_2/CdSe/ZnSe devices. We have found that device performance, particularly short circuit current density (Jsc) is very sensitive to the SnO_2 deposition conditions. By tuning the process on glass we have attained record Jsc's of 17.4 mA/cm^2. It is important to be able to transfer the same SnO_2 properties when deposited on Si.
- Voltage open circuits (VOCs) up to 500+ mV were demonstrated with SnO_2/n-Si. This represents achievement of one of our key milestones for the first year. While of and by itself this is not a notable accomplishment, the fact that VOCs of this magnitude are realized using a SnO_2 process that is compatible with CdSe is.
- Operable CdSe devices have been deposited on SnO_2/Si substrates. These are the first CdSe devices fabricated and evaluated on a SnO_2/Si substrate. VOCs are 310 mV which is typical of what is seen for glass substrate devices and validates the properties of the SnO_2.
- The first operable tandem devices have been fabricated. Total VOC for the tandem was 420 mV with about equal contributions from the Si and CdSe devices. This accomplishes the primary objective for the first year and demonstrates compatibility of the processes. The process of optimization can now be set into motion.
- Deposition parameters have been identified that allow some control over $ZnTe_xSe_{1-x}$ film stoichiometry. Stoichiometric films for Te composition in the range 3–10% can be attained even with the activated N doping source on.
- Techniques have been developed for depositing superlattice structures that help preserve the Te content in the ternary films by avoiding competition between Se and Te at the growth surface.
- $ZnTe_xSe_{1-x}$:N films have been produced in which the N is electronically active. Conductivities up to 2 x 10^{-8} Ω-cm have been attained.
- Developed sol-gel and co-precipitation/hydrolysis method of TiO_2-$ZnFe_2O_4$ nanocomposite production:
  - Experiments successfully concluded the photoactivity of TiO_2-$ZnFe_2O_4$ catalysts at irradiation wavelengths longer than 400 nm.
  - Optimized the factors influencing the $ZnFe_2O_4$ structure such as effects of PH, calcinations temperature, precursor concentration.
  - Optimized the alloying concentrations of TiO_2-(X)$ZnFe_2O_4$ to achieve the anatase structure.
- Developed reverse micelle process of preparation TiO_2-CdS nanocomposite:
  - The experimental parameters such as water to surfactant ratio, water to alkoxide ratio, precursor concentrations, calcination temperature have been optimized to obtain TiO_2-CdS nanocomposite.
  - The photocatalytic activity of the TiO_2-CdS nanocomposite was performed by degradation of phenol concentration under visible light irradiation.

- Developed radio frequency sputtering method of porous TiO_2 thin film fabrication. It was found that:
  - As-deposited at room temperature films were amorphous.
  - Annealing in air at high temperatures yields polycrystalline TiO_2.
  - Annealed films contain peaks corresponding to both the Anatase (desirable) and Rutile phases. Deposition at temperatures as low as 250°C yield polycrystalline films with a dominant anatase phase.
- Developed mechanochemical technique of synthesis of $TiO_2/ZnFe_2O_4$ alloyed nanocomposite for use as solar light activated photocatalyst.
- Designed an efficient photocatalytic reactor for solar light simulation.
- Developed TiO_2 carbon doped photocatalyst having improved photocatalytic properties. Particularly, the carbon doped TiO_2 photocatalyst is more than 60% efficient in comparison with pure TiO_2 photocatalyst.
- Using mechanochemical technique for TiO_2 doping by carbon, the red shift in optical absorption as high as 0.25 eV in comparison with pure TiO_2 has been observed, which is an indicator of the improvement of light harvesting efficiency of the photocatalyst.
- A multicomponent approach in the analysis of optical spectra of organic aqueous solutions has been proposed, which results in better interpretation of the results of photocatalytic efficiency interpretation.
- Characterization of the photocatalysts have been carried out by analytical procedures, x-ray diffraction (XRD), fourier transform infrared (FTIR), optical measurements and scanning electron microscopy.

Task 1.4 Solid State Ionic Conductor Development

- $CsHSO_4$ was chosen to be the first solid acid electrolyte investigated. Material was prepared by reacting sulfuric acid with Cs_2SO_4 or Cs_2CO_3 and selectively precipitating $CsHSO_4$ with an organic solvent. One half inch and two inch diameter pellets of this material were made for study and its conductivity was measured.
- Pellets that have been run under high temperature methanol exhibit impermeability to methanol and methane compared to Nafion.

Future Directions

Task 1.1 Thermochemical

- To understand the mechanism of degradation to prevent it.
- To speed up the hydrolysis process.
- To evaluate the effects of additives on the strength quantitatively.
- To develop a pelletization process for Fe-pellets.
- To study kinetics of Fe-pellets.
- To do a thermodynamic analysis of the cycle for evaluation.

Task 1.2 Biomass Gasification

- Thermodynamics:
  - This task has demonstrated improved hydrogen yields over conventional technologies.
  - For this method to become viable the sorbent must be recovered and regenerated, which is the next area of investigation in our research.
- Optimization:
  - The numerical model of the biomass reformer provides a tool for developing the controller for a biomass gasifier. Various input parameters can be adjusted to study the behavior of the reformer under different operating conditions.
  - Future work: design an ideal model based controller for a biomass reformer to optimize the hydrogen yield to meet the DOE targets.

Task 1.3 Photoelectrochemical

- Emphasis will continue to be placed on development of the p-contact for the CdSe device. We will follow-through with efforts to develop $ZnTe_xSe_{1-x}$:N to determine the levels of p-doping that can be attained.
- As improvements are made in the p-contacts, the improved contacts will be applied to CdSe to determine the effect on VOC. We hope to establish a correlation between the doping and Fermi levels in the $ZnTe_xSe_{1-x}$:N contact and VOC.
- Alternative p-contacts and deposition processes will be considered. Co-doping has proven effective using molecular bean epitaxy (MBE) and indiffusion, and we intend to explore its efficacy under our deposition conditions.
- Complete experimental transformation from oxidation of organic contaminants to redox water splitting into H_2 and O_2 using visible light photocatalysis.
- Develop new generation visible light activated nanoparticulated photocatalysts via surface modification using coupled semiconductor nanocomposites and TiO_2 carbonization for water splitting experiments.
- Investigate the effect of size of the photocatalytic nanoparticles in relation to the light harvesting efficiency and overall photoreduction yield.

- Provide structural, microstructural, chemical and optical properties of the photocatalysts for understanding and supporting proposed mechanisms.

Task 1.4: Solid State Ionic Conductor Development

- Impermeability of pellets after high temperature treatment with methanol while maintaining other crucial characteristics (conductivity, strength) supports viability of $CsHSO_4$ as material in combined hydrogen production/separation processes.
- Membrane production techniques will continue to be refined.
- Performance and stability studies of electrolytes and cells will continue.
- Electrolyte, feedstock and scavenger will be matched for compatibility.
- Electrode attachment techniques to minimize contact resistance will be pursued.
- Catalysts and surface treatments will be applied to increase power densities.
- Thin-pellet designs to reduce electricity requirements will be explored.
- during electrolyte fabrication will be investigated.
- New electrolyte materials will be sought and investigated in a search for better electrical and mechanical properties.

Task 2: Advanced Material-Based Technologies for On-Board Vehicular Storage

Investigators: S. Srinivasan, L. McElwee-White, M. Smith, Y. Goswami, E Stefanakos

Objectives

- Synthesis and characterization of advanced material-based technologies with high reversible hydrogen storage capacity that can operate at temperatures less than 100°C.
- New complex borohydrides and alkali amides/hydrides. Catalytic doping and substitution mechanisms to tailor the kinetic and thermodynamic properties.
- Electronic structure calculations to determine thermodynamically stable phases of complex borohydrides.

Technical Barriers

This project addresses the following technical barriers from section 3.3.4.2 of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume
(B) System Cost
(C) Efficiency
(D) Durability/Operability
(J) Thermal Management
(P) Lack of Understanding of Physisorption and Chemisorption
(Q) Reproducibility

Technical Targets

- Volumetric hydrogen density: $> 4.5\%$ (kg H_2/L)
- Gravimetric hydrogen density: > 6.0 wt.%
- Operating temperature: < 150°C
- Cycle life: 1,000 cycles
- Fast rate of H_2 absorption/desorption

Accomplishments

- Identified the candidate hydride zinc borohydride, which exhibits a thermal decomposition temperature of 85°C and a theoretical storage capacity of 8.4 wt% which meets the DOE target.
- Successfully prepared the new complex borohydride $Zn(BH_4)_2$ by an inexpensive mechanochemical process; optimization of milling parameters such as speed and time duration for favorable hydrogenation and thermal properties.
- Characterization of these hydrides has been carried out by XRD, FTIR, Raman spectroscopy and scanning electron microscopy.
- Destabilization of the borohydride materials for reversible storage characteristics; $LiBH_4/MgH_2$ milling with different stoichiometric ratios for optimized storage performances.
- Prepared $LiNH_2/LiH$ and $LiNH_2/LiH/MgH_2$ materials with various compositions by wet chemical synthesis (sonication).
- Pressure composition temperature (PCT) and thermal characterizations of as-developed complex hydrides at different temperatures and pressures.
- Developing density functional theory (DFT) calculations for determining the thermodynamically stable phases of $Zn(BH_4)_2$.

Introduction

Complex chemical hydrides bearing light weight elements such as Li, Na, Mg, B, Al etc. show promising hydrogen storage behavior at moderate temperatures. Some of the complex hydrides have high theoretical capacities of 10.0-18.0 wt% (e.g. $NaBH_4$, $LiBH_4$ etc).

However, the release of hydrogen from sodium borohydride is possible only by hydrolysis (reaction with water) and this process is irreversible. However, upon addition of transition metal complexes, borohydrides derived from $NaBH_4$ ($LiBH_4$) undergo thermal dissociation of molecular hydrogen at low temperatures. A new transition metal assisted complex borohydride, $Zn(BH_4)_2$ with the high theoretical hydrogen storage capacity of 8.4 wt%, has been recently reported to have a thermal decomposition temperature of 85°C. The preparation of $Zn(BH_4)_2$ via wet chemical synthesis route or mechanical milling is being investigated according to the stoichiometric reaction,

$$2NaBH_4 + ZnCl_2 \rightarrow Zn(BH_4)_2 + 2NaCl$$

$Zn(BH_4)_2$ thermally decomposes into the constituent elements and releases hydrogen,

$$Zn(BH_4)_2 \rightarrow Zn + 2B + 4H_2$$

The reversibility of hydrogen dissociation from these hydrides requires the following individual or combined effects (i) catalyst doping, (ii) lattice substitution, and (iii) high temperature and pressure of hydrogen absorption/desorption. Destabilizing the borohydride complexes by reacting them with the alkaline binary compound MgH_2 may yield better reversibility with greater hydrogen storage capacity at moderate temperatures.

The breakthrough discovery of Ti-catalyzed $NaAlH_4$ for the reversible onboard hydrogen storage may not be the ideal system to attain technical targets. This is because for $NaAlH_4$, the usable hydrogen storage capacity achievable is 5.4 wt%. The alternative $LiNH_2$/LiH system has shown promising hydrogen absorption and desorption characteristics. Reactions of $LiNH_2$ and LiH to give Li_2NH have also been shown to have a reversible storage capacity of 6.5 wt%. Partial substitution of lithium by magnesium in the nitride/imide system (Li-Mg-N-H) may destabilize the Li-N-H system.

Keeping these facts in view, the present investigation explores various complex hydrides for efficient hydrogen storage. A new hydrogen storage system based on $Zn(BH_4)_2$ with a theoretical hydrogen capacity of 8.4 wt% has been synthesized by an inexpensive mechanochemical process. The enthalpy of decomposition and the gravimetric capacity of these hydrides are measured using high pressure differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) techniques. The structure-property correlations of the as-prepared material have been analyzed via various metrological tools. A new approach of sonication under tetrahydrofuran (THF) has been adopted to prepare $LiNH_2$/LiH (2:1) and the PCT characteristics were measured. We have also developed the novel light weight complex hydrides and demonstrated their hydrogenation characteristics.

Approach

- Chemical, mechanochemical processes employing wet chemical synthesis (sonication) and high energy ball milling to synthesize new complex hydride systems. Optimizing the milling parameters to achieve required material with high storage efficiency and fast kinetics.
- Thermal and volumetric characterizations, such as heat of formation/decomposition, weight loss, kinetics, PCT and life-cycle analysis of the as-prepared hydrides.
- Electronic structure calculations based on density functional theory to predict thermodynamically stable phases of complex borohydrides.

Results

1. New complex hydride, $Zn(BH_4)_2$ - Synthesis and Characterization

Powder x-ray diffraction, of the complex mixture ($2NaBH_4 + ZnCl_2$) mechanically milled under a N_2 ambient for durations of 30 min, 2 hr, 4 hr and 8 hr, was performed. The major peaks correspond to NaCl and $Zn(BH_4)_2$. In this present study, we communicate the x-ray profiles of the complex mixture ($Zn(BH_4)_2 + 2NaCl$) with mixed phases before employing any purification. It is interesting to note that neither starting material $NaBH_4$ nor $ZnCl_2$ is present in the mechano-chemically milled complex mixture. This indicates the formation of a new complex borohydride structure $Zn(BH_4)_2$ with a milling duration of 30 minutes. The FWHM (full width at half maximum) of the NaCl reflection increases with an increase in the milling duration for 30 minutes to 8 hr. Scherrer's equation was used to determine the crystallite sizes in the range 25-40 nm, depending on the ball milling duration.

The B-H bonding environment of $Zn(BH_4)_2$ was examined by FTIR and Raman spectroscopic techniques. The FTIR spectra of the BH_4^- ion in $NaBH_4$ has characteristic bands at 2,283 and 2,217 cm^{-1}, whereas in the $NaBH_4$+$ZnCl_2$ ball milled mixture, the signals appear at 2,084 cm^{-1} (bridging B-H bonds) and 2,453 cm^{-1} (terminal B-H bonds). The Raman spectral shifts at these wavelengths confirm again the formation of $Zn(BH_4)_2$.

The simultaneous differential scanning calorimeter and thermalgravimetric analyzer (SDT) of the complex hydrides mechano-chemically prepared with different milling durations are shown in Figure 1. Degassing of 8.4 wt% at 100°C has been experimentally obtained for $Zn(BH_4)_2$ milled only for 15-30 minutes, that matches with the theoretical hydrogen capacity values. However, this capacity decreases as the milling duration increases. This is apparently due to the partial release of hydrogen during the extended milling process; say from 1 hr to 8 hr. An endothermic reaction due to hydrogen decomposition was observed from the DSC profiles as represented in the inset of Figure 1.

It is known that $NaBH_4$ undergoes a hydrolysis reaction to release hydrogen and hence the thermolysis of $NaBH_4$ shows 0% weight loss even at temperatures > 400°C. On the other hand, 10-12 wt% of H_2 decomposes at above 350°C for the case of the $LiBH_4$ complex hydride as shown in Figure 2. This agrees well with the theoretical prediction based on the reaction,

$$LiBH_4 \rightarrow LiH + B + 3/2\ H_2$$

Parallel experiments were carried out to mix stoichiometric amounts of different transition metal halides such as ZnX_2 (X = Cl, F), $NaBH_4$ and MgH_2 to the $LiBH_4$ complex hydride by the ball milling process. Figure 2 represents the thermal decomposition profiles of these mixtures which occur at temperatures comparatively lower than the decomposition temperature of the pristine $LiBH_4$ material. In addition, a hydrogen storage capacity of ~10 wt% is observed for the metal halide assisted $LiBH_4$. For the case of TiF_3 mixed $LiBH_4$, the low temperature decomposition was not observed.

It is clearly seen from dehydrogenation kinetic studies using temperature programmed desorption analysis that $NaBH_4$ does not release hydrogen at 100°C, a small amount of hydrogen desorption (~0.1 bars H_2) occurs at the higher temperature of 250°C. On the other hand, for the new complex hydride, $Zn(BH_4)_2$, the dehydrogenation rate increases rapidly (~0.8 bars H_2) at 100°C. After the first decomposition run, the material was evacuated and rehydrogenated at high hydrogen pressure of ~60 bars H_2 and a temperature of 100°C for 10-12 hours. In the 3rd dehydrogenation cycle, $Zn(BH_4)_2$ exhibits reversibility of hydrogen desorption. This shows the potential cycling reversibility of the new complex hydrides. Work is underway to explore the long term cycling capacity measurements with an increase in temperature.

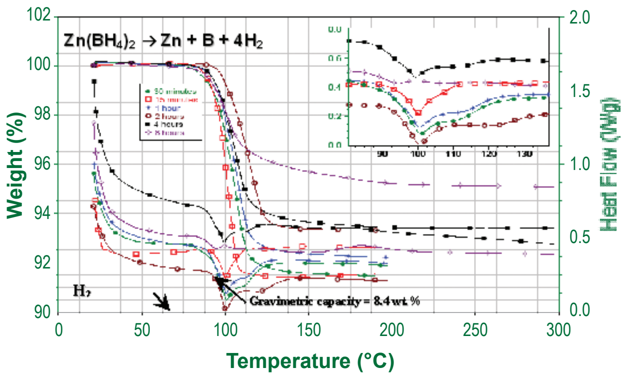

FIGURE 1. SDT of thermal decomposition profiles of $Zn(BH_4)_2$ with different milling durations, 30 minutes, 1h, 2h, 4h, 8h.

Scanning electron micrographs of the $Zn(BH_4)_2$ + NaCl mixture before and after four dehydrogenation and rehydrogenation (DH-RH) cycles at 100°C was performed. The 2 hr ball milled mixture indicates coalescence of grains, whereas after several dehydrogenation and rehydrogenation cycles, a uniform homogeneous surface is observed throughout the material at the same magnification. Moreover, the surface tends to be more porous which explains the effective hydrogen uptake and release from the host material. For the case of the ($2LiBH_4 + ZnCl_2$) mixture ball milled for 30 minutes, the scanning micrograph shows very fine crystallite sizes due to the pulverization effect as clearly seen. However, after TGA decomposition, there is no existence of individual crystallites due to thermal decomposition of hydrogen.

It has recently been reported by Vajo et. al (JPCB 2005) that destabilization of alkali borohydrides by MgH_2 incorporation leads to cycling reversibility with high hydrogen storage capacity (>6.0 wt%). In order to improve the reversible hydrogenation properties of complex borohydrides, we have established an inexpensive mechanochemical approach for synthesizing $LiBH_4$ + ½ MgH_2 with various mol concentrations of $ZnCl_2$ catalyst. The structural and microstructural characteristics are determined by XRD analysis. No apparent formation of MgB_2 was observed for the ball milled samples. It is interesting to note that the LiCl peak intensity increases with increased amount of catalyst concentration ($ZnCl_2$). The optimum concentration of 4 mol% of catalyst seems to have correct phase proportions as observed in the profile treatment.

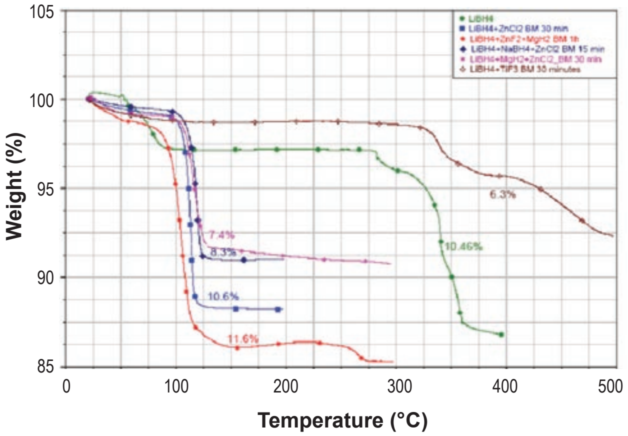

FIGURE 2. SDT of thermal decomposition profiles $LiBH_4$, $LiBH_4+ZnCl_2$ ball milled 30 min, $LiBH_4+ZnF_2+MgH_2$ ball milled 1h, $LiBH_4+NaBH_4+ZnCl_2$ ball milled 15 min, $LiBH_4+MgH_2+ZnCl_2$ ball milled 30 min and $LiBH_4+TiF_3$ ball milled 30 min.

The PCT dehydrogenation behavior of these materials is examined by HY-Energy sorption set-up. A plateau pressure of 4-5 bars at 350°C and a volumetric capacity of 3.0 wt% have been obtained in the 11th cycle. This capacity increases with increase of DH-RH cycling.

The surface morphology and the elemental stoichiometry of the complex mixture $LiBH_4/MgH_2$ with 2 mol% ZnF_2 catalyst doping have been determined using scanning electron microscopy (SEM) in imaging and energy dispersive spectrum (EDS) mapping modes. It is clearly seen from these studies that various elements such as Mg, B, Zn, F are present in their correct atomic ratios. Elemental boron presents in the EDS profiles and it is not clear at this stage whether it is in crystalline or amorphous form.

2. Lithium Amides/Imides for Hydrogen Storage

Lithium amides and imides are now considered to be potential practical hydrogen storage systems with available hydrogen storage capacity of 11.5 wt% at around 200°C according to the reaction:

$$LiNH_2 + LiH \rightarrow Li_2NH + H_2$$

We have prepared lithium amides with different compositions of LiH via wet-chemical routes involving different solvents. The Li-amides/LiH materials with different mole ratios have been prepared by sonicating the mixtures in organic solvents such as THF, diglyme, and diethyl ether. The sonication procedure yields homogeneous mixtures of $LiNH_2/LiH$ when compared to the ball milling technique. Thus obtained powders have been hydrogenated and dehydrogenated at temperatures in the range of 280-375°C.

The family of pressure-composition (P-C) isotherms for $LiNH_2/LiH$ (2:1) material sonicated in THF was analyzed using the PCT. The reversible capacity is found to increase with temperature and cycling. Clear-cut plateau pressures ($P_{absorption} = 3\text{-}5$ bars and $P_{desorption} = 0.2\text{-}2$ bars) have been observed for this system at temperatures of 280-375°C.

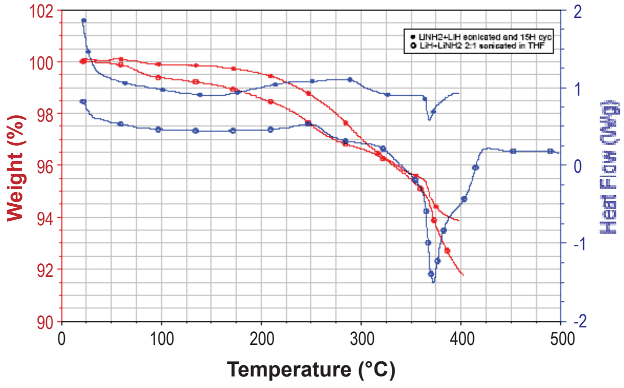

FIGURE 3. TGA and DSC profiles of $LiNH_2/LiH$ before and after 15 H-cycles.

The plateau pressure of the Li-amide/LiH system has been modified by ad-mixing the MgH_2 during the milling process. The $LiNH_2/LiH$ system exhibits a plateau pressure around 0.5-3 bars H_2 and this is not suitable for vehicular applications. In order to increase the plateau pressure, these materials are stoichiometrically mixed with equal amount of MgH_2 and ball milled under N_2 for 4 hr. Thus, we have found that the MgH_2 ad-mixed $LiNH_2/LiH$ shows an increase of desorption plateau pressure to 30-40 bars H_2.

Thermal analysis of $LiNH_2/LiH$ before and after 15 hydrogenation cycles has been carried out by simultaneous DSC and TGA. The TGA profiles exhibit weight loss due to H_2 decomposition of about 8 wt% with an endothermic DSC signal as shown in Figure 3.

Figure 4 represents the thermogravimetric analysis (TGA) weight loss curves for the plain $LiNH_2/LiH$ sample and Ti- doped and MgH_2 ad-mixed $LiNH_2$ prepared by ball milling process.

It is clearly seen from the figure that the Ti-catalyst doping reduces the operating temperature of Li-amide and MgH_2 incorporation increases the overall hydrogen storage capacity. This weight loss due to the hydrogen desorption process is highly endothermic as evidenced from the differential scanning calorimetric measurements.

Conclusions

- Synthesis of new complex borohydride $Zn(BH_4)_2$ by an inexpensive mechanochemical process.
- An optimum milling duration of 15-30 minutes was sufficient to complete the reaction $2NaBH_4 + ZnCl_2 \rightarrow Zn(BH_4)_2 + 2NaCl$.
- Volumetric capacity of 3.0 wt% was achieved in 11 cycles at 350°C and it increases with increased numbers of cycles. The plateau pressure of desorption was found as 4-5 bars.
- PCT characteristics of $LiNH_2/LiH$ exhibit reversible cycling capacity above 300°C.

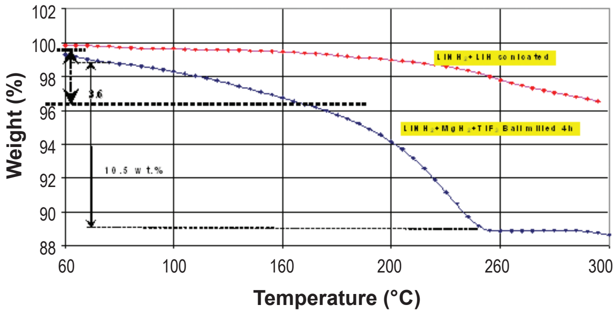

FIGURE 4. Thermogravimetric analysis curves for the plain $LiNH_2/LIH$ and Ti-doped/MgH_2 ad-mixed $LiNH_2$.

- Ti-doped and MgH_2 ad-mixed $LiNH_2$ shows excellent gravimetric capacity of 10.5 wt% below 200°C; the capacity remains the same even after 15 DH-RH cycling.
- The plateau pressure of Li-amide/LiH has been modified to 30-40 bars H_2 by ad-mixing MgH_2 in the ball milling process. The results have been quite promising and encouraging.

Future Directions

- Systematic investigations of the hydrogen storage properties of new complex borohydrides and alkali amides/hydrides.
- Analysis of the residual gas after thermal decomposition of $Zn(BH_4)_2$ by GC/MS.
- Synergistic behavior of catalytic doping and MgH_2 ad-mixing on the kinetics and thermodynamics of $Zn(BH_4)_2$ and related systems.
- Preparation of complex/composite hydrides with mixed hydrogenation properties.
- Structural modification of Li-amides and catalyst doping to enhance the kinetics and reduce the dehydrogenation temperature.
- Long term cycling and hydrogenation behavior of Li-amides and borohydrides.
- Electronic structure calculations of thermodynamically stable phases of complex borohydrides.

Task 3: PEM Fuel Cell Research (USF, UF, UCF)

- **Task 3.1 PEM Fuel Cell Electrode Research** (USF) Investigators: J. Wolan, B. Grayson, E. Stefanakos
- **Task 3.2 PEM Materials and Testing** (UF) Investigators: Y. Goswami, E. Stefanakos, N. Kothurkar
- **Task 3.3 PEM Materials and Performance, Low Cost PEM Electrolytes** (UCF) Investigators: C. Linkous, B. Pearman, N. Mohajeri, K. Speed, D. Slattery, D. Hall

Technical Barriers and Targets

This project addresses the following technical barriers and targets from section 3.4.4.2 of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(B) Cost
(C) Electrode Performance
(D) Thermal, Air and Water Management
(I) Hydrogen Purification/Carbon Monoxide Cleanup

- MEA operating temperature: ≤ 120°C
- Cost: $40/kW
- Total catalyst loading: 1.1 g/kW
- Durability: 2,000 hrs at 80°C

Accomplishments/Results

Task 3.1 PEM Fuel Cell Electrode Research

- Creation of catalyst test station.
- Incorporation of Brust method gold nanoparticles into current Pt/Ru catalyst.
- Initial characterization of titania support and gold nanoparticles complete.
- Development of nanocomposite membrane creation procedure.
- Preliminary characterization of β-zeolites including x-ray photoelectron spectroscopy (XPS).
- Fabrication of nanocomposite/Nafion™ membrane.

Task 3.2 PEM Materials and Testing

- Identified poly(2,5-benzimidazole)-phosphoric acid as a low cost, high temperature, low humidity alternative to Nafion™.
- Synthesized poly(2,5-benzimidazole) (ABPBI) polymer and cast membranes.
- Set up single cell test stand for MEA testing.
- Obtained in-situ baseline data of manufacturer-provided membranes.
- Established freeze/thaw testing regime and characterization techniques.

Task 3.3 Development of High Performance, Low-Cost PEM Electrolytes

- Synthesized SPEEK (sulfonated polyetherether ketone) with equivalent weight 260 g/equivalent, corresponding to a 187% degree of sulfonation (i.e., multiple sulfonic acid groups per monomer unit).
- Developed cross-linking method employing all water-soluble reagents.
- Demonstrated that polymerizing amine groups can be protected from fluorosulfonic acid chemistry by forming the acetamide derivative.

Conclusions and Future Directions

Task 3.1 PEM Fuel Cell Electrode Research

- Brust method gold nanoparticles should prove beneficial for low temperature preferential oxidation of carbon monoxide in a hydrogen PEM fuel cell when combined with a highly reducible support such as titania.

- Typical calcination temperatures for activation of platinum-based fuel cell catalyst may be harmful to the gold species. Further experiments are necessary to optimize the gold nanoparticle oxidation process in order to fully activate the catalyst system.
- Further characterization of the β-zeolite/Nafion™ nanocomposite membranes using SEM, impedance spectroscopy, and XRD are necessary to determine crystal structure modifications and changes in proton conductivity during preparation

Task 3.2 PEM Materials and Testing

- Synthesized ABPBI using a single-step low temperature process.
- Membranes cast by immersion precipitation.
- Designed and built a single cell test stand in-house to test single cells under broad temperature and relative humidity (RH) conditions.
- Control of RH has been improved in the test station from the values that were originally obtained.
- Preliminary operation of test stand commenced using manufacturer-provided membrane.
- Improve ABPBI molecular weight and fabricate MEA.
- Test MEAs at high temperatures and sub freezing conditions.
- Improve catalyst bonding, reducing catalyst content and increasing catalyst efficiency by making a nanoparticulate sol.
- Control membrane microstructure to reduce phosphoric acid leaching.

Task 3.3 Development of High-Performance, Low-Cost PEM Electrolytes

- Work will continue toward fabrication of partially fluorinated, cross-linked membranes and subsequent characterization, especially against oxidative resistance.
- Polyaryletherketones offer a possible compromise between cost and oxidative stability for PEM membranes.
- Ex-situ liquid permeability and conductivity of surrounding peroxide soaking solution were found to be effective means of monitoring membrane degradation.
- The sulfonic acid moiety itself may constitute an attack site for hydroxyl radicals.

Task 4: Hydrogen Delivery (USF)

- **Task 4.1 Geologic Hydrogen Storage** (USF) Investigators: M. Ross, K. Clayback, E. Stefanakos, G. Moore
- **Task 4.2 Advanced Thermal Hydrogen Compressor** (USF) Investigators: B. Krakow, E. Stefanakos, P. Wiley, S. Srinivasan, D. Escobar

Technical Barriers

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

Task 4.1

- Examine economic and technical feasibility of storing bulk hydrogen gas in geologic structures.

Task 4.2 (3.2.4.1, Table 3.2.2)

- Reliability: 90%
- Efficiency: 95%
- Cost: \$0.40/gge of H_2 at 1,500 psi

(3.2.4.2, B)

- 5,000-10,000 psi pressure with no lubricant contamination

(3.3.4.1, Table 3.3.2, note g)

- 10,000 psi near-term and 50 to 150 atm long-term

Accomplishments/Results

Task 4.1 Geologic Hydrogen Storage

- Performed literature study of caverns, aquifers, and depleted reservoirs.
- Determined various parameters (depth, pressure, capacity, and porosity) for modeling.

Task 4.2 Advanced Thermal Hydrogen Compressor

- $ZrMn_2$ was chosen as the working alloy.
- A sample of $ZrMn_2$ powder was prepared by ball milling and sintering the powdered elements.
- Unavailable material properties needed for the compressor design were measured.
- A mothballed DC power supply that had previously been used for lightning research has been reactivated and modified for use on this project.

- The reactivated power supply was tested by producing an arc discharge through air.
- A preliminary design of the compression cell has been prepared.

Conclusions and Future Directions

Task 4.1 Geologic Hydrogen Storage

- Various cavern types have contamination problems specific to each and salt caverns will usually yield the cleanest hydrogen gas.
- Salt caverns show promise for charging and discharging hydrogen due to cushion gas and structural stability.
- Proposed operational ranges and parameters for multiple storage options have been identified.
- Depleted hydrocarbon reservoirs will generally have well known geologic characteristics with a transportation infrastructure in place.
- No appropriate numerical model is available therefore one will have to be developed in the 3rd and 4th quarter.
- The numerical model for reservoir performance will be tested in the 3rd and 4th quarter.
- Initial results for costs of reservoir charging and discharging will be presented in the 4th quarter.

Task 4.2 Advanced Thermal Hydrogen Compressor

- Ball milling and sintering a mixture of Zr and Mn powders appears to be a suitable process for synthesizing $ZrMn_2$ alloy. Optimum milling and sintering times have not yet been established.
- A reactivated high voltage DC power supply is operable and suitable for use as the power source for initial compressor experiments. AC experiments will be conducted later.
- Improvements in measured material parameters will be sought in conjunction with improvements in material synthesis techniques.
- Final design and sizing of the compression cell will be completed. The cell will then be fabricated.
- Electric discharges through hydrogen and hydride will be conducted.

FY 2006 Publications/Presentations

Task 1.1 Thermochemical

1. M.S. Lee, Y. Goswami, B. Hettinger, S. Vijayaraghavan, “Preparation and Characteristics of Calcium Oxide Pellets for UT-3 Thermochemical Cycle, Draft paper submitted for 2006 ASME International Mechanical Engineering Congress and Exposition.

Task 1.2 Biomass

1. Mahishi M.R., Vijayaraghavan S., Deshpande D. A., Goswami D. Y., “A thermodynamic analysis of hydrogen production by gasification of biomass”, *Proceedings of the 2005 ISES Solar World Congress, Orlando, FL, August 6-12, 2005.*

2. Mahishi M.R., Sadrameli, M. S., Vijayaraghavan S., Goswami D. Y., “Hydrogen Production from Ethanol: A Thermodynamic Analysis of a Novel Sorbent Enhanced Gasification Process” *ASME Advanced Energy Systems (publication)* AES, **45**, pp 455-463, 2005.

3. Mahishi M.R., Sadrameli S. M., Vijayaraghavan S., Goswami D.Y. “A novel approach to enhance the hydrogen yield of biomass gasification using CO_2 sorbent” *under review with ASME Journal of Engineering for Gas Turbines and Power.*

4. Mahishi M. R., Goswami D. Y., “An experimental study of hydrogen production by gasification of biomass in the presence of a CO_2 sorbent” *under review with International Journal of Hydrogen Energy*, *(Elsevier publications).*

Task 1.3 Photoelectrochemical

1. P. Mahawala, S. Vakkalanka, S. Jeedigunta, C. S. Ferekides and D. L. Morel, “Transparent Contact Development for CdSe Top Cells in High Efficiency Tandem Structures”, *Proceedings of the 31st IEEE PVSC*, Orlando, 2005.

2. P. Mahawela, S. Jeedigunta, S. Vakkalanka, C.S. Ferekides and D.L. Morel, “Transparent high-performance CDSE thin-film solar cells”, *Thin Solid Films, Volumes 480-481, 1 June 2005, Pages 466-470.*

3. S. Srinivasan, J. Wade and E. Stefanakos, “Synthesis and Caracterization of Photocatalytic TiO_2-$ZnFe_2O_4$ Nanoparticles”, *Materials Research Society Proceedings*, Vol. 876E, 2005.

4. Sesha S. Srinivasan, Jeremy Wade, Elias K. Stefanakos, Yogi Goswami, Synergistic effects of sulfation and co-doping on the visible light photocatalysis of TiO_2, *J. Alloys and Compounds,* 2005, Article in Press.

5. S. Srinivasan, J. Wade and E. Stefanakos, “Synthesis and Caracterization of Photocatalytic TiO_2-$ZnFe_2O_4$ Nanoparticles”, *J. Nanomaterials,* (Accepted).

6. S. Srinivasan, J. Wade; N. Kislov, M. Smith, E. Stefanakos, Y. Goswami, “Mechanochemical synthesis, structural characterization and visible light photocatalysis of $TiO_2/ZnFe_2O_4$ nanocomposites”, Materials Research Society Proceedings, Vol. 900E, 2006.

7. P. Mahawala, G. Silvaraman, S. Jeedigunta, J. Gadupiti, M. Ramalingam, S. Submaranian, S. Vakkalanka, C. S. Ferekides and D. L. Morel, “II-VI Compounds as the top Absorbers in Tandem Solar Cell Structures”, *Materials Science and Engineering B,* 116 (2005) 283–291.

8. P. Mahawela, S. Jeedigunta, S. Vakkalanka, C.S. Ferekides and D.L. Morel, "Transparent high-performance CdSe thin-film solar cells" *Thin Solid Films, Volumes 480-481, 1 June 2005, Pages 466-470.*

9. P. Mahawala, S. Vakkalanka, S. Jeedigunta, C. S. Ferekides and D. L. Morel, "Transparent Contact Development for CdSe Top Cells in High Efficiency Tandem Structures", Proceedings of the 31st IEEE PVSC, Orlando, 2005.

Task 1.4 Solid State Ionic Conductor

1. Krakow, E. Weaver, L. Ecklund-Mitchell, E. Stefanakos, G. Moore, and M. Smith, presented at the Twenty second Annual International Coal Conference, Pittsburgh, PA, September 12-15, 2005.

2. Burton Krakow, Eric P. Weaver, George Moore, Elias K. Stefanakos, American Chemical Society National Mtg, Atlanta, GA, March 2006.

Task 2.1 Advanced materials-based technologies for on-board vehicular storage

1. Synthesis and characterization of nanoscale transition metal complex for hydrogen storage, S. S. Srinivasan, M. T. Smith, D. Deshpande, E.K. Stefanakos, Y. Goswami, M. Jurczyk, A. Kumar, A. Kumar, Materials Research Society Symposium Proceedings, Vol. 884E, Warandale, PA, 2005, GG 3.7.

2. Thermal and volumetric studies of complex chemical hydrides: Li-modified/Ti- doped Mg_2FeH_6, Sonicated $LiNH_2$/LiH and Zn- doped $NaBH_4$, S. S. Srinivasan, S. Dumbris, L. McElwee-White, E. Stefanakos, Y. Goswami, Materials Research Society Symposium Proceedings. Vol. 885E, Warandale, PA, 2005, A07-03.1.

3. Synthesis and characterization of new complex borohydrides for hydrogen storage, S.S. Srinivasan, E. K. Stefanakos, Proceedings of the TMS Annual Meeting and Exhibition, Advanced Materials for Energy Conversion III, March 12-16, 2006, San Antonio, Texas.

4. Novel light weight complex hydrides for hydrogen storage, Sesha Srinivasan, E. Stefanakos, Proceedings of the AIChE spring national meeting, Hydrogen storage scenarios for transport applications, April 23-27, 2006, Orlando, FL (*Published in the AIChE-NED website*).

5. Mechanochemical synthesis and characterization of new complex hydrides for hydrogen storage, S. Srinivasan, E. Stefanakos, MRS Spring Proceedings, April 17-20, 2006 (*Accepted for publication*).

6. Transition metal assisted new complex hydrides for hydrogen storage, S. S. Srinivasan, E.K. Stefanakos, Y. Goswami, 16th World Hydrogen Energy Conference, Lyon, France, June 14, 2006.

7. New complex borohydrides and their hydrogenation characteristics for on-board storage applications, S. S. Srinivasan, E.K. Stefanakos, Y. Goswami, J. Phys. Chem. B, Manuscript Submitted, 2006.

Task 2.2 Nanostructured Materials

1. MRS Fall 2005 Oral Presentation: "Study of Effect of Temperature and Pressure on the Hydrogen Sorption Capabilities of a Polyaniline-CNT Nanocomposite Material"

Task 3.1.1 PEM Fuel Cell Research

1. Black, A., Gannon, A., Wolan, J.T., Nanocomposite β -Type Zeolite Applications for Polymer Electrolyte Membrane Fuel Cells, Florida Chapter of the AVS Science and Technology Society, University of Central Florida, Orlando, FL (2006).

2. Grayson, B. A., Wolan, J. T., Chaparro, D., Gupta, V. K., Initial characterization of Brust method nano-Au/TiO2 catalysts for the preferential oxidation of CO. (Pending Submission).

Task 3.1.3 Development of High Performance, Low Cost PEM Electrolytes

1. C.A. Linkous, B. Pearman, and D. Hall, "Development of High Performance, Low Cost, PEM Electrolytes," proceedings of the 16th World Hydrogen Energy Conference, Lyon, France, June 12-16, 2006.