ΣΠΣ Undergraduate Research Award Proposal

Project Proposal Title	**High-Throughput Synthesis and Characterization Studies of Novel Nanoscale Hydrogen Storage Systems**
Name of School	Tuskegee University
SPS Chapter Number	7446
Total Amount Requested	$2,000.00

Abstract

The objective of this *SPS-ΣΠΣ undergraduate research award* proposal is to investigate high throughput synthesis and characterization of novel nanoscale hydrogen storage systems for stationary and mobile applications. In this proposed work, the synthesis procedures will be optimized by combinatorial methods of tailoring the composition, and catalyst doping concentrations.

Proposal Statement

It is proposed to investigate novel nanoscale light weight materials for high capacity reversible hydrogen storage.

Overview of Proposed Project

The main objectives of this proposed investigation is to develop and demonstrate novel nanoscale complex hydrides by high-throughput synthesis and characterization techniques. Hydrogen can be stored in many ways such as (i) gas in high pressure cylinders, (ii) liquid at cryogenic temperatures and (iii) interstitial atoms or molecular hydrogen species in solid state metal hydrides. The long term stability and safety of storing hydrogen in solid state materials such as complex metal hydride nanocomposites, has been undoubtedly surpassed the other two options mentioned above. Recently the faculty mentor (SPS advisor) of the proposed project was granted two US Patents[1,2] on developing the hydrogen storage system based on the combination of light weight compounds such as Lithium Borohydride, Lithium Amide and nano Magnesium Hydride ($LiBH_4$/$LiNH_2$/nMgH_2). This Li-nMg-B-N-H system has demonstrated the hydrogen reversibly at a moderate temperature and meets or exceeds the technical targets in terms of gravimetric and volumetric hydrogen storage densities. Based on the previous research literature, the project participants will design, develop and deliver the state-of-the-art hydrogen storage material or system that can store and release hydrogen at ambient or near ambient temperature and pressure conditions. The proposed hydrogen storage material based on light weight elements or compounds, will not only enhance the current capabilities of the alternative fuel storage technologies, but also will lead to sustainable and long term storage solutions. This proposed project involving underrepresented Physics major students of Tuskegee University will strengthen the research portfolio and program objectives of the Society for Physics Students (SPS) at the university wide and national level as well.

Overall, the proposed study will certainly address both the near and long term goals with a focus of understanding the various phenomena such as, (i) atomic processes associated with hydrogen uptake and release kinetics, (ii) the role of nanocatalysts for the hydrogen-material interactions, (iii) hydrogen-promoted mass transport, (iv) degradation due to cycling, (v) reversibility, (vi) volumetric and gravimetric hydrogen densities, (vii) hydrogen dissociation, transport and recombination within the inter/intra grain boundaries of complex composite hydrides, (viii) surface and interface properties (such as specific surface area, pore size volume of the nanocatalysts), (ix) reaction thermodynamics etc.

PROJECT OBJECTIVES:

The research goals of the proposed investigation are to synthesize and characterize the pristine and nanomaterials doped complex multinary hydride, Li-nMg-B-N-H employing high energy mechanical milling. The nanomaterials doping and compositional modifications on the bulk structure of these hydrides however demand for high-throughput synthesis procedures. Nanomaterials [Multi-Walled Carbon Nanotubes (MWCNT) and transition metal nanoparticles (TMN)], with large intrinsic specific surface area and high chemical reactivity, offer an enhancement of the physico-chemical hydrogen sorption behavior at moderate temperatures. The role of catalytic dopants and their synergistic effects on the dehydrogenation and/or reversible rehydrogenation characteristics of complex hydrides will be studied experimentally. Fundamental mechanistic behavior of hydrogen atom/ion transport within the complex hydride matrix via the surface active nanotubular or nanoparticular species will be investigated with respect to structure-property relations. The project participants will develop rapid test procedures that can enable to obtain answers to the following questions:

1. How do the structural, thermodynamic, physical, chemical and surface properties affect the hydrogen storage characteristics (sorption kinetics, plateau pressure of sorption, cycle life) and atomic hydrogen transport?
2. What dopants and dopant concentrations are needed to achieve reasonable kinetics and long term cyclic reversibility?
3. What is the synergistic effect of mixed dopants such as CNT/transition metal nanoparticle?
4. How do carbon-based additives Carbon Nanotubes (CNT), graphite Nanotubes (GNT) modify surface and structural?
5. How does hydrogen interact with surface, interface, and bulk defects of complex hydrides with respect to their tailoring or destabilization strategies?

Background for Proposed Project

The increase in threats from the global warming due to the consumption of fossil fuels requires our planet to adopt new strategies to harness the inexhaustible sources of energy[3,4,5]. Hydrogen is an energy carrier which holds promise as a new renewable and clean energy option[6]. Hydrogen is a convenient, safe, versatile fuel source that can be easily converted to a desired form of energy without releasing harmful emissions. Hydrogen is the ideal fuel for the future since it reduces significantly the greenhouse gas emissions (GHG), reduces the global dependence on fossil fuels, and increases the efficiency of the energy conversion process for both internal combustion engines and proton exchange membrane fuel cells[7,8]. A fuel cell converts directly the chemical energy of hydrogen into water, electricity and heat[9] as represented by the equation:

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O + \text{Electricity} + \text{Heat.}$$

Hydrogen storage cuts across both hydrogen production and hydrogen applications and thus assumes a critical role in initiating a Hydrogen Economy[10,11,12]. For catering today's Fuel Cell cars and other device applications, the on-board hydrogen storage is inevitable and an integral part of the system to be re-engineered[13,14]. The critical properties of the hydrogen storage materials to be evaluated for automotive and device applications are: (i) light weight, (ii) cost and availability, (iii) high volumetric and gravimetric density of hydrogen, (iv) fast kinetics, (v) ease of activation, (vi) low temperature of dissociation or decomposition, (vii) appropriate thermodynamic properties, (viii) long term cycling stability and (ix) high degree of reversibility. Said properties greatly demand from us to understand the fundamental mechanistic behavior of materials involving destabilization, catalyst doping and their physico-chemical reactions toward hydrogen at an atomic or molecular scale. Among the various hydrogen storage systems, metal hydrides, complex hydrides, chemical hydrides, adsorbents and nanomaterials, clathrate hydrates, polymers, metal organic frameworks etc.[15,16,17,18,19] are explored at present, catalyzed light weight complex hydrides show the greatest potential promise for on-board hydrogen storage due to the following fulfilling criteria: (1) high theoretical hydrogen content [>6.5 wt.%]; (2) favorable or tuning thermodynamics [30-55 kJ/mol H_2]; (3) operable below 100° C for H_2 delivery; (4) catalytic enhancement of kinetics and storage capacity; (5) on-board refueling option for a hydrogen-based infrastructure; (6) cyclic reversibility at moderate temperatures etc.

Recently, the SPS faculty advisor and project participants have developed an inexpensive, simple, efficient and solid state mechano-chemical synthesis method, which allows the hydride compounds ($LiBH_4/LiNH_2/MgH_2$)[20,21] to be mechanically mixed and chemically react in a controlled environment. With this technology, nano-level pulverization, homogenization, and tuning of crystallite sizes are achieved simultaneously under ambient conditions. Multinary complex hydrides (Li-Mg-B-N-H) formed from this process have shown an improvement in hydrogen storage properties such as high hydrogen storage capacity and fast sorption kinetics. However with rigorous literature search, the project participants have found no reports on the mechanistic approach to evaluate the reaction pathways on the complex composite hydrides such as $LiBH_4/MgH_2$, $LiNH_2/LiH/MgH_2$ or $LiBH_4/LiNH_2/MgH_2$ etc. The high throughput and combinatorial metrological characterizations such as in-situ XRD, high pressure RAMAN, FTIR, HRSEM, HRTEM, will be employed to understand the structural, microstructural and physico-chemical characteristics of these systems. The goal of this research program will also to demonstrate *proof of concept of the proposed mechanism and methodology and rapidly screen the hydride material components and dopants.* The reversible high volumetric and gravimetric density of hydrogen will be achieved in these new complex composite hydrides by adopting nanotechnology, tailoring the composition, lattice substitution and selective catalyst doping. Another factor related to system weight including the weight of the stored hydrogen will be optimized by screening light weight components and devising new material processing techniques. Keeping these points in mind, the proposed investigation will be focused on the development of novel hydrogen storage systems bearing light weight elements or compounds for clean energy delivery. *A unique approach in designing these complex composite hydrides will be developed by formulating a nanocatalyst doping procedure and adopting a destabilization mechanistic approach as outlined in the following sections.*

Expected Results

The expected results of the proposed concept are to device (i) inexpensive and efficient processing schemes, (ii) ease of scalability for industrial production, (iii) repeatable and tunable properties through control of crystallite size and distribution, (iv) one step rapid high yield solid state synthesis involving no solvents, and (v) light weight materials. Competing manufacturing technologies require a multi-step process using solvents, high temperature, high pressure, and long synthesis time leading to higher production costs. Our innovative approach of using finely dispersed absorbent particles (~10-20 nm) enables more efficient system performance compared to existing hydrogen storage materials.

Description of Proposed Research - Methods, Design, and Procedures

The proposed investigation will be focused on the high throughput synthesis and characterization of novel hydrogen storage systems bearing light weight elements or compounds for on board hydrogen storage. The development and demonstration in this proposed study is based on the four tasks given below. A hypothesis driven research to identify effective pathway reactions for the efficient hydrogen storage characteristics is being proposed and are detailed in the following tasks.

Task 1: Develop high capacity nanocomposite multinary complex hydrides by high throughput synthesis

Based on our preliminary experimentation (discussed above) and exciting results, the proposed study aims to develop high capacity nanocomposite multinary hydrides (e.g. $LiBH_4/LiNH_2/LiH/MgH_2$, $LiBH_4/LiNH_2/LiH/$*nano*-MgH_2) by an inexpensive mechano-chemical process. We will study the effects of commercial, microcrystalline and nanocrystalline forms of MgH_2 on the multinary hydride structure formation and overall hydrogen decomposition characteristics. In addition, the synergistic effects of nanocrystallinity and nanocatalytic doping on these hydrides will be investigated with a view to establish structure-property relations. Extensive characterization techniques will be employed to obtain insights into the nanocrystalline and nanocatalytic enhancement of the hydrogenation properties in these solid state multinary hydrides. We will also demonstrate progress in understanding the physico-chemical reaction of hydrogen with the nanocomposite multinary hydride systems.

Task 2: Synergistic effects of nanotube/nanoparticle doping on the reversible hydrogen storage behavior of complex hydrides

Based on an extensive literature search, we found no reports on the synergistic effects of CNT/transition metal nanoparticles on the complex composite hydrides such as $LiBH_4/MgH_2$, $LiNH_2/LiH/MgH_2$ or $LiBH_4/LiNH_2/MgH_2$ etc. Our theoretical formulations will substantiate the experimental predictions of physico-chemical reactivity towards H_2, overall enhancement of kinetics and effective storage capacity of complex hydrides for hydrogen storage. The goal of this program will be to demonstrate ***proof of concept*** of the proposed mechanism and methodology. We propose the following three approaches schematically summarized in Figure 1. In the first approach, the presence of carbon nanotubes (CNT) or graphitic nanofibers (GNF) on the complex hydride families (e.g. $LiBH_4/MgH_2$, $LiBH_4/LiNH_2$, $LiBH_4/LiNH_2/LiH/MgH_2$ or $LiNH_2/LiH/MgH_2$) is expected to enhance the kinetics due to short reaction pathways and also serve as an interconnector between complex hydride particles through which hydrogen absorption/desorption proceeds (Figure 1(a)).

For the case of transition metal nanoparticle dopants such as nano-Fe, nano-Ni and nano-Ti, the surface active species will mediate the molecular hydrogen dissociation and diffusion in the complex hydride structure as shown in Figure 1(b). In the third approach, we propose to investigate the synergistic effects of both CNT (GNF) and (Fe, Ni, or Ti) nanoparticles for the catalytic enhancement of sorption kinetics and hydrogen storage capacity of complex hydrides as shown in Figure 1(c). This will be done by (i) mechanical milling of the CNT/nanocatalyst with the complex hydride or (ii) Fe/Ni/Ti in-situ grown CNT and mechanical milling with the complex hydride. *These approaches closely resemble the transition metals (Pd, V etc.) nanoparticles doped CNT enhance the hydrogen storage behavior by spill-over mechanism and physisorption binding sites of CNTs reported elsewhere.*[22]

Task 3: Multi-level in-situ and combinatorial metrological measurements for advanced hydrogen storage systems

In this task, a multi-level in-situ approach to synthesize the complex hydride materials using mechano-chemical process and further characterize using sub-multi level in-situ characterization as elucidated in Figure 8. The combinatorial synthesis will be carried out by varying the stoicheometries of parent compounds and also the concentration of the additives. *Once prepared the complex hydrides with multiple stoicheometriess will be simultaneously subjected to in-situ metrological studies ranging from XRD, SEM, TEM, Raman, IR Emissivity and PGAA to rapidly screen the structural and chemical properties.* The optimized material is finally employed to estimate the hydrogen storage performance such as sorption kinetics, cycle life and pressure composition isotherms.

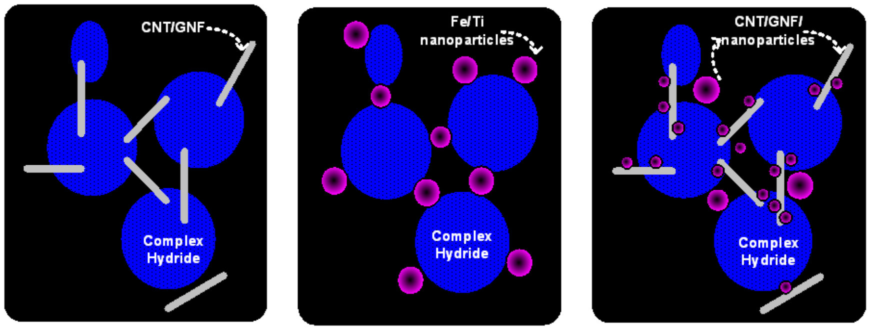


Figure 1: (a) CNT/GNF doped complex hydrides; (b) Fe/Ti nanoparticles doped complex hydrides; (c) Nanocomposite (CNT/nanocatalyst) complex hydrides.

Plan for Carrying Out Proposed Project

- **Personnel** – All the project participants are SPS members and will contribute equally to the project developmental activities such as (i) synthesis of complex hydrides and catalytic doping, (ii) characterization using sophisticated tools such X-ray, electron microscopy and thermal tools, (iii) hydrogen storage property measurement at high pressure and high temperature Sievert's type apparatus
- **Expertise** – Faculty mentors Dr. Sesha Srinivasan, SPS member having expertise on the proposed project and currently established a research laboratory at Tuskegee University funded by the National Science Foundation, Office of Naval Research and US Department of Energy. Research space – The proposed research project can be very well implemented in Physics Department research laboratories (1000 square ft.) which housed many state-of-the-art equipment relevant to the proposed project development.
- **Contributions of faculty advisors or the department (equipment, space, etc.):** Faculty mentor Dr. P.C. Sharma, Head of Physics Department and SPS member will monitor constantly the success of the project by facilitating the necessary support and also organize various SPS research/educational activities. The faculty mentors also organize Alabama Academy of Science Annual meeting, the research outcome from the proposed work will be presented at the Physics section of the AAS meeting.

Project Timeline

Keep in view the goals of SPS-ΣΠΣ proposed study stated earlier, our research plan and tasks will be focused to develop and demonstrate long term storage of hydrogen for device applications. The tentative proposed timeline of 1 year (with the defined tasks are outlined in the table below.

TASK NAME	Jan-May14					June-Dec'14						
	1	2	3	4	5	6	7	8	9	10	11	12
Tasks 1 & 3: Combinatorial Hydrides Synthesis and Characterization												
Tasks 2 & 3: Catalytic and Carbon Nanotube Doping and Characterization												
Deliverables (Interim Report and Final Report), Journal Publications (JURP)												

Budget Justification

Budget for Chemicals, Hydrides, Solvents, Acids and other Lab Supplies: Chemicals such as Lithium Borohydrides, Lithium Amides, Magnesium Hydrides, Calcium Hydrides; catalysts such as titanium, nickel, cobalt, iron, single wall/Multi-Wall carbon nanotube etc. will be purchased to synthesize novel nanscale complex materials for reversible hydrogen storage. Solvents and acids such as acetone, 1-propanol, pentane, HCl, HNO_3 will be procured from Sigma Aldrich for the purification and chemical treatment of hydrides.

Budget for Gases: Ultra high purity (99.999%) gases such as UHP Hydrogen, helium, compressed nitrogen, argon and liquid nitrogen will be purchased form Dennis Welding, Montgomery for the synthesis, manipulation and characterization of complex hydrides and catalytically doped materials.

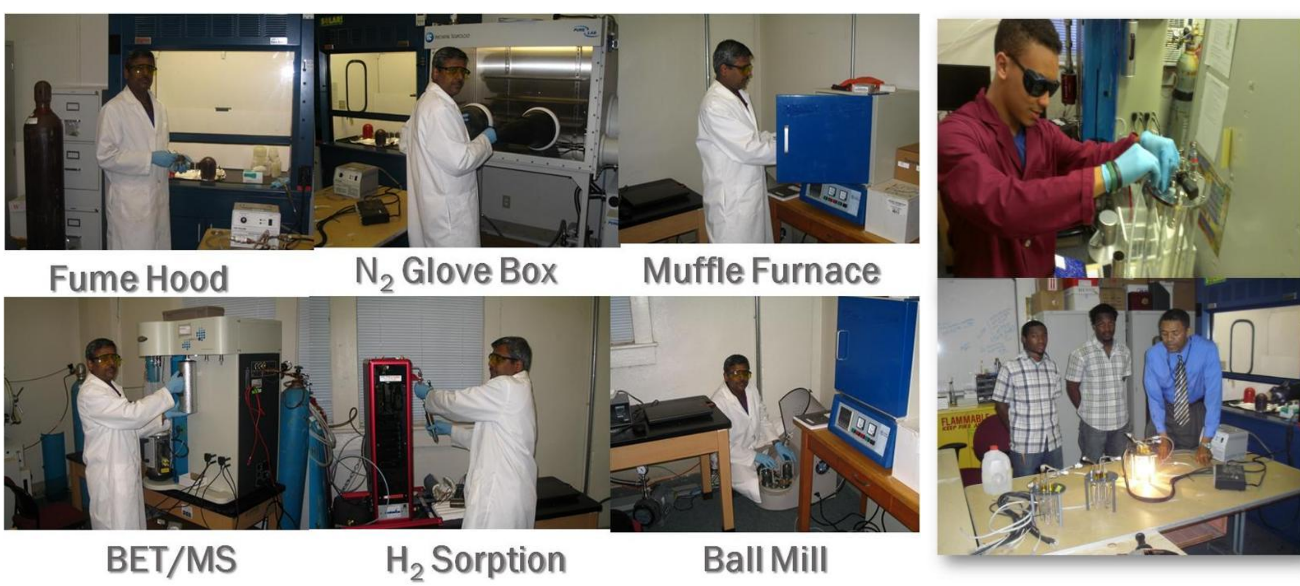
Budget for Glove Box Lid: The lid made of aluminum with screw top is very much needed to protect the glove box if any leaks or rupture occurs due to operation. The lid will temporarily contain the nitrogen atmosphere inside the glove box and will protect the chemicals not exposed to oxygen or moisture.

Budget for Swagelok Gaskets: The gaskets (unfritted and fritted 2micron) made of copper need to be procured since every batch of samples loading in to reactor need to be under the high pressure hydrogen system. So, the gaskets prevent the leak and enable for data collection.

Budget for Hydrogen Loading Sample Cell: Hydrogen treatment sample cells with H_2 permeating filter will be procured for the hydrogen sorption experiments at various experimental conditions. These sample holders are of unique design and hold high pressure about 200 bars.

Budget for Hardware Accessories: Lab supplies and accessories such as ferules, copper tubing, coupling, reducers, and lab tools often needed for the experimental study which is proposed. So, we will use the budgeted amount for this item.

In-Kind Funding Support: The equipment obtained from Department of Energy's Laboratory Equipment Donation Program will be leveraged to accomplish the proposed tasks. Faculty advisors will provide additional support from their other federal projects to foster the proposed SPS-ΣΠΣ research activity. The students will be provided with all infrastructural resources (both department wide and college wide) to accomplish the project goals set forth by the project participants. The laboratory facility available for this SPS project is shown in Figure below.



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