

## HyMARC Seedling Projects

Project title	PI	Affiliation	Subs	Status	Abstract
Development of Magnesium Boride Etherates as Hydrogen Storage Materials	Godwin Severa	University of Hawaii at Manoa		Project in Phase 3	Magnesium borohydride, $Mg(BH_4)_2$ , is one of the few materials that has a demonstrated gravimetric hydrogen storage capacity greater than 11 wt % and thus a demonstrated potential to be utilized in a hydrogen storage system meeting US DOE hydrogen storage targets. However, due to very slow kinetics, cycling between $Mg(BH_4)_2$ and $MgB_2$ has been accomplished only at high temperature ( $\sim 400^\circ C$ ) and under high charging pressure (900 bar). Previous work has shown, rapid kinetics at moderate temperatures for the reversible dehydrogenation of $Mg(BH_4)_2(ether)_x$ to $Mg(B_3H_8)_2(ether)_x$ . These type of materials have much lower hydrogen cycling capacities as a consequence of the weight contribution of the coordinated ethers. However, they do show the plausibility of continual improvement in hydrogen cycling kinetics in the $Mg(BH_4)_2$ system. The development of modified $MgB_2$ by either extending the dehydrogenation of magnesium borane etherates to $MgB_2$ or by direct combination of $MgB_2$ with sub-stoichiometric amounts of additives (e.g. ethers, reactive liquids, metals or hydrides) would result in the $H_2$ wt % of the system potentially meeting DOE targets. If successful, the solid-state modified $MgB_2$ would be safer and cheaper than the high pressure compressed $H_2$ (700 bar) or liquid $H_2$ alternative onboard storage systems on the market.
Electrolyte Assisted Hydrogen Storage Reactions	Channing Ahn	Liox Power, Inc.	HRL Laboratories	Project in Phase 2	Liox Power, Inc, together with HRL Laboratories, LLC, propose experimental studies to develop complex hydride and multiple component hydrogen storage materials (hydride destabilization), with vastly improved rates of dehydrogenation and rehydrogenation (greater than 10x state-of-the-art) enabling practical use at near equilibrium conditions while retaining optimized thermodynamic properties and high gravimetric and volumetric capacities (over 11 wt % $H_2$ and 90 g/L $H_2$ on a materials basis). Two novel concepts for hydrogen storage will be explored: (1) formulations that include electrolytes to facilitate atomic rearrangement and diffusion thereby reducing activation barriers and (2) reactions promoted by modest electrochemical potentials to supplement the thermochemical (i.e., temperature and pressure based) free energy driving forces that have hindered consideration and implementation of systems based on these materials. Our concepts originate from analogous multiple component Li battery reactions that have been shown to operate at room or near room temperatures. We propose to apply these concepts to hydrogen storage materials for the first time and

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					anticipate that if successful, will pave the way toward more modest system complexity and cost than presently required for high pressure physical storage approaches.
Optimized Hydrogen Adsorbents via Machine Learning and Crystal Engineering	Don Siegel	University of Michigan	Ford Motor Company	Project in Phase 3	This project aims to overcome volumetric limitations associated with physisorptive hydrogen storage at both the materials and system level. This goal will be achieved using a combination of computational techniques and experimental synthesis and testing. Our efforts will target storage media based on metal-organic frameworks (MOFs), a class of hydrogen adsorbents with highly tunable properties. At the materials level, machine learning methods will be applied to our database of 476,007 real and hypothetical MOFs. This analysis will guide the discovery of new compounds that can break through the so-called Volumetric Ceiling. This performance ceiling was identified in our prior screening studies; it reveals that no known MOFs can surpass a usable volumetric capacity of 40 g H <sub>2</sub> /L (assuming an isothermal pressure swing between 100 and 5 bar at 77 K). In contrast to the conventional approach to MOF discovery, where capacity is predicted from a known crystal structure, this project aims to invert this process and "reverse engineer" optimal MOFs with the aid of machine learning. The most promising compounds will be synthesized and assessed experimentally with respect to their usable hydrogen capacities. At the system level, we will develop crystal growth and processing techniques that result in MOF-based adsorbent beds with low void fractions. Packing inefficiencies have the potential to negate improvements in volumetric performance achieved at the materials level. This project aims to close this performance gap by developing synthetic procedures that optimize particle morphology and size distribution.
ALD (Atomic Layer Deposition) Synthesis of Novel Nanostructured Metal Borohydrides	Steven Christensen	National Renewable Energy Laboratory	H2 Technology Consulting, LLC	Project in Phase 3	The goal of this project is to develop a completely new reversible hydrogen storage materials matrix based on encapsulation via atomic layer deposition (ALD) of nanostructured metal borohydrides. ALD is a vapor phase method to grow thin films layer-by-layer. The metal borohydride-encapsulation architecture will include layers that will protect against loss of the nanostructure hydride and impart chemical additives to enhance kinetics and reversibility. The concept was motivated by a substantial research where ALD coatings provided protective and catalytic properties to heterogeneous catalysts. ALD offers: (1) conformal coatings of materials like aluminum oxide that are inert to hydrogenation/dehydrogenation conditions; (2) a wide variety of chemical additives previously shown to enhance metal borohydride reversibility and kinetics like palladium or cerium oxide; and (3) a

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					facile means to combine these materials to tailor properties to performance. Recent developments in ALD manufacturing have demonstrated >100 kg per day throughput on powders and other granular materials. Thus, ALD solutions to the challenges with metal borohydrides will bring to front new scientific knowledge with the potential to be scaled.
Methane and Hydrogen Storage with Porous Cage-Based Composite Materials	Eric Bloch	University of Delaware		Project in Phase 1	The objective of the project is to improve the volumetric storage capacities of metal-organic frameworks (MOFs) via a comprehensive, system-level program in which the interparticle void space that is detrimental to capacity is minimized through optimized particle engineering. In addition to this, we will utilize porous molecular materials toward composite MOF/cage adsorbents. Here, the intercrystalline void space of MOF samples will be filled with porous molecular materials with optimized H <sub>2</sub> and/or CH <sub>4</sub> uptake. Importantly, this strategy will not only be applicable across all MOFs, it can be used for all classes of porous solids, as even the best MOFs display capacities that are less than half of target storage values and significant advances in material design and discovery are needed to double their capacities.
Optimal Adsorbents for Low-Cost Storage of Natural Gas: Computational Identification, Experimental Demonstration, and System-Level Projection	Don Siegel	University of Michigan	Savannah River National Laboratory	Project in Phase 1	This research program will develop best-in-class natural gas (NG) and hydrogen adsorbents based on metal-organic frameworks (MOFs). More specifically, high-throughput computational screening coupled to machine learning will be used to identify MOFs that simultaneously achieve high usable gravimetric and volumetric capacities for NG and hydrogen. The most promising materials pinpointed by computation will be synthesized and characterized experimentally. Subsequently, the performance of these materials will be projected to the system level using a modeling framework developed by the Hydrogen Storage Engineering Center of Excellence (HSECoE). As part of this project the developer of these models, Savannah River National Laboratory (SRNL), will extend the hydrogen-based HSECoE models to NG.
Metal-Organic Frameworks Containing Frustrated Lewis Pairs for Hydrogen Storage at Ambient Temperature	Shengqian Ma	University of South Florida	Argonne National Laboratory	Project in Phase 1	The objective of the project is to develop new materials based on metal-organic framework (MOF) incorporated with frustrated Lewis pairs (FLP), FLP@MOF, as the next generation of hydrogen storage sorbent that can meet or exceed DOE's 2025 performance target of hydrogen storage gravimetric density of 5.5 wt % and volumetric density of 0.040 kg H <sub>2</sub> /L. University of South Florida (USF) will team with Argonne National Laboratory (ANL) to develop FLP@MOF systems that exhibit high hydrogen storage capacity at ambient temperature under pressure <100 bar as well as to obtain improved fundamental understanding of hydrogen adsorption mechanism in FLP@MOF system.

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Heteroatom-Modified and Compacted Zeolite-Templated Carbons for Gas Storage	Nicholas Stadie	Montana State University		Project in Phase 1	The primary objectives of this project are to synthesize, characterize, densify, and determine the adsorption properties of carbon and heteroatom-modified carbon-based framework materials known as zeolite-templated carbon (ZTC). We specifically focus on the methane storage characteristics per unit volume: the maximum storage capacity as a function of temperature and pressure, the deliverable storage capacity at 273 and 298 K, and the thermodynamic properties of the adsorbed phase. Early objectives are the synthesis and characterization of novel densified monoliths of ZTC; mid-term objectives include the inclusion of heteroatom dopants within the framework; and long-term objectives include the combined effort to synthesize optimal materials for deliverable volumetric methane storage.
Developing a New Natural Gas Super-Adsorbent Polymer (NG-SAP) for a Practical Natural Gas Storage System with Low Pressure, Ambient Temperature, and High Energy Density	Mike Chung	Penn State University		Project in Phase 1	Despite the huge advantages of natural gas (NG) in the United States (i.e., abundant, low price, low carbon and particulate emission, renewable gas), the current NG-powered transportation vehicles are mostly limited to a few compressed natural gas (CNG) powered urban buses due to high storage cost and inefficient NG storage capacity. This research project is to develop a new class of NG adsorbent polymers that can achieve the DOE NG storage goal for heavy- and medium-duty vehicle fleets. We plan to investigate a series of Petrogel materials that can offer a suitable NG binding energy (20–25 kJ/mol) and a swellable interpenetrated polymer network (IPN) morphology with large free volume and high surface area. Our final goal is to achieve the NG storage matrices with volumetric density $>500 \text{ cm}^3/\text{cm}^3$ ( $>360 \text{ g/L}$ ) and energy density $>20 \text{ MJ/L}$ under $<65 \text{ bar}$ pressure at ambient temperature. If successful, we should also significantly close the technical gap for the practical usage of NG fuel in general transportation vehicles. It would also ease several close-related issues relative to storage cost, safety, greenhouse gas, etc.
Uniting Theory and Experiment to Deliver Flexible Metal-Organic Frameworks for Superior Methane (Natural Gas) Storage	Brian Space	University of South Florida		Project in Phase 1	The project aims to design and develop FlexMOF materials having tunable gating pressures (with release cycle around 5.8 bar) and deliverable capacities for methane greater than 300 v/v at 65 bar and 298 K desired to reach 350 v/v storage capacity at standard temperature and pressure. The project will also establish the interaction of methane with the framework and binding sites using modeling, and the FlexMOF will be both internally and external validated.

Hydrogen Release from Concentrated Media with Reusable Catalysts	Travis Williams	University of Southern California	Los Alamos National Laboratory	Project in Phase 1	Project objectives are to (1) demonstrate and scale up H <sub>2</sub> evolution from formic acid or a formic acid fuel blend, (2) demonstrate H <sub>2</sub> flow and purification using a demonstration-scale flow reactor, and (3) use mechanistic studies to understand reaction mechanism; use these data to optimize catalyst and fuel blend.
Theory-Guided Design and Discovery of Materials for Reversible Methane and Hydrogen Storage	Omar Farha	Northwestern University		Project in Phase 1	The objectives of the project are the following: (1) Perform high-throughput computational discovery: a key advantage of MOFs is structural predictability that can be leveraged to rapidly search in silico for optimal materials by expanding current databases of predicted MOFs to include various topologies (i.e., 85 topologies) as well as new building blocks from commercially available sources. (2) Screen database of 100,000 MOFs for hydrogen uptake using machine learning algorithm and GCMC for fast screening and identify materials with total capacity (up to 100 bar) that can reach the storage capacity of hydrogen tank at 700 bar. (3) Synthesize and characterize the top candidate MOFs generated in silico for hydrogen storage while keeping in mind stability (thermal, chemical, and mechanical stability), scalability, and cost. (4) Study catechol and bipyridine/phenanthroline containing MOFs in which open metal sites can be created upon removal of solvent molecules, for storage of molecular hydrogen at and near room temperature.
High Capacity Step-Shaped Hydrogen Adsorption in Robust, Pore-Gating Zeolitic Imidazolate Frameworks	Michael McGuirk	Colorado School of Mines		Project in Phase 1	The objective of this project is the development of a stimulus responsive porous solid hydrogen carrier capable of Type V, or "step-shaped", adsorption and desorption of a high volumetric capacity of hydrogen at pressures relative to transport and delivery. This technological advance would represent a huge step in improving the efficiency of on- and off-loading of hydrogen for target applications, dramatically lowering energy consumption during this process and, therefore, the overall cost of hydrogen. The workplan for this project is divided into three components: (i) programming of hydrogen adsorption in a known pore-gating MOF through the incorporation of modified linkers, (ii) development of an isostructural non-Cd <sup>2+</sup> -based congener with expanded capacity, and (iii) optimization of sorption properties in a non-Cd <sup>2+</sup> -based framework to meet adsorption-desorption target pressures using lessons from components (i) and (ii).
A Reversible Liquid Hydrogen Carrier System Based on Ammonium Formate and Captured CO <sub>2</sub>	Hongfei Lin	Washington State University	8Rivers	Project in Phase 1	The goal of this project is to demonstrate a commercially promising reversible liquid hydrogen carrier system based on ammonium formate and captured CO <sub>2</sub> . This technology enables hydrogen to be stored in the chemical form of ammonium formate in aqueous solutions through the catalytic hydrogenation of ammonia captured CO <sub>2</sub> over the palladium (Pd) on carbon catalyst at near room temperature. The release of H <sub>2</sub> from the catalytic dehydrogenation

					of ammonium formate solutions can be carried out over the same carbon-supported Pd catalyst under the mild temperatures (<100 °C). The project objectives are to build a prototype ammonium formate-based hydrogen uptake and release system and evaluate its techno-economic potential for commercialization. By the end of the project, it is anticipated that the levelized cost of hydrogen distributed to stations using the formate hydrogen carrier will be competitive with the conventional compressed H <sub>2</sub> gas delivery scenario at the scale of 50,000 kg-H <sub>2</sub> per day.
Development of Magnesium Borane Containing Solutions of Furans and Pyrroles as Reversible Liquid Hydrogen Carriers	Craig Jensen	University of Hawaii at Manoa		Project in Phase 1	This project targets the generation of two-way liquid organic hydrogen carriers (LOHCs) by charging selected furans and pyrroles with Mg(BH <sub>4</sub> ) <sub>2</sub> . The resulting LOHC solutions will have adequate hydrogen storage densities to enable practically viable bulk storage and transport of hydrogen. Specifically, these carriers will potentially possess volumetric available hydrogen densities of 80 to 100 g available hydrogen per liter. This is more than twice the volumetric available hydrogen density of methylcyclohexane, which enables low transport costs such that the overall transport and delivery cost of this two-way LOHC could be below those of other hydrogen carriers and compressed gas systems. It will be determined if these pincer catalyst containing solutions show the same (or even further enhanced) hydrogen cycling kinetics observed separately for the catalyzed LOHCs and tightly solvated Mg(BH <sub>4</sub> ) <sub>2</sub> . Our studies will identify the best heterocycle / Mg(BH <sub>4</sub> ) <sub>2</sub> / pincer combination in terms of rate, cycling capacity, and product selectivity with a goal of maximizing energy efficiency of hydrogen storage and delivery. We also plan to explore the further enhancement of the heterocyclic LOHC system by developing higher activity, AsCAs pincer catalysts and developing non-precious-metal based pincer catalysts, which would remove the cost imposed restraint of low catalyst loadings.
Developing a Novel Hydrogen Sponge with Ideal Binding Energy and High Surface Area for Practical Hydrogen Storage	Mike Chung	Penn State University		Project complete	The project objective is to develop a new class of boron-containing polymers (B-polymer) with a network structure and an open “free volume” morphology, which can simultaneously exhibit three essential H <sub>2</sub> adsorbent characteristics, including an ideal H <sub>2</sub> binding energy range of 15–25 kJ/mol, a high specific surface area SSA>4,000 m <sup>2</sup> /g, and a mass density >0.65 g/cm <sup>3</sup> . The resulting hydrogenphilic sorbents (H <sub>2</sub> sponges) shall have the potential to meet the DOE storage targets with material a gravimetric capacity of 1.8 kWh/kg (5.5 wt % H <sub>2</sub> ) and volumetric capacity of 1.3 kWh/L (40 g H <sub>2</sub> /L) under mild (temperature and pressure) storage conditions.

Fundamental Studies of Surface-Functionalized Mesoporous Carbons for Thermodynamic Stabilization and Reversibility of Metal Hydrides	Eric Majzoub	University of Missouri-St. Louis	Washington University in Saint Louis; Saint Louis University	Project complete	Metal hydrides used for applications today have a low hydrogen weight percent (e.g., 1.1 wt % H <sub>2</sub> for LaNi <sub>5</sub> H <sub>6</sub> ) due to the much heavier transition metal elements. The light metal hydrides, including sodium alanate (NaAlH <sub>4</sub> ), have a much larger weight percentage of hydrogen but suffer from poor kinetics and reversibility because of phase separation of the components—aluminum metal in the case of sodium alanate. Although many light metal hydrides such as pure alane (AlH <sub>3</sub> ) and many complex light metal hydrides are known, most are either too stable, requiring high temperatures to drive the hydrogen off, or too unstable and difficult to rehydride under safe hydrogen pressures at reasonable temperatures. In order to reach the DOE volumetric and gravimetric targets the light metals must be utilized and these problems must be overcome. The goal of this project is to render light metal hydrides like AlH <sub>3</sub> reversible under moderate conditions. Our approach is to perform fundamental studies on functionalized porous carbons doped with nitrogen heteroatoms to understand the mechanisms of thermodynamically stabilized high-capacity metal hydrides. Ultimately, our goal will be to stabilize AlH <sub>3</sub> in a nanoporous carbon framework through Lewis-acid/base interactions provided by pyridinic nitrogen on the interior wall of the carbon framework. This capping layer should provide the kinetic stabilization analogous to that of the oxide layer on bulk alane that allows it to be stable in air for many years despite the relative instability of the compound. More importantly, in very small pores this interaction is expected to solvate and increase the enthalpy change of alane dehydriding.
"Graphene-Wrapped" Complex Hydrides as High-Capacity, Regenerable Hydrogen Storage Materials	D.J. Liu	Argonne National Laboratory	Southern Illinois University	Project complete	This project focuses on developing a new class of hydrogen storage material, hydride@graphene or hydride@G, for next-generation hydrogen-powered fuel cell vehicles. The approach is based on a recent collaboration between Shanghai Jiao Tong University and Argonne National Laboratory. Using a simple solvent-based method, we successfully synthesized a "nanoencapsulated" sodium borohydride-graphene composite, NaBH <sub>4</sub> @G, in which NaBH <sub>4</sub> nanocrystallites are individually wrapped by single layer graphenes. The new composite demonstrates regenerable and high hydrogen storage capacity in multiple DH and RH cycles. The graphene sheet tightly envelops the hydride nanoparticles like a candy wrapper and restricts the solid hydride phase from segregation and agglomeration. It also prevents the leakage of any harmful byproduct other than hydrogen, which is the only molecule permeable through the graphene layer. The hydride crystallites are encapsulated at nanometer size by graphene and can release/recharge hydrogen more readily than the bulk phase hydride. Under this project, we

					planned to prepare a broader range of hydride@G composites using the complex hydrides of higher intrinsic gravimetric and volumetric densities. We also planned to explore various morphological and chemical approaches to improve the DH–RH kinetics, guided by computational modeling and collaboration with Hydrogen Materials Advanced Research Consortium (HyMARC).
Super Metallated Frameworks as Hydrogen Sponges	Omar Yaghi	University of California, Berkeley		Project complete	Metal-organic frameworks (MOFs) are crystalline porous materials composed of metal cluster nodes linked by organic struts where each component can be altered or functionalized systematically. This tunability coupled with the highly porous nature of MOFs make them ideal for gas storage applications. The state-of-the-art MOF based absorbent (MOF-74 analogue) utilizes coordinatively unsaturated metal sites (open metal sites) which exhibit strong interaction with H <sub>2</sub> (13 KJ/mol) producing the record figure of merit (12 g/L and 0.9 wt % at 25°C 100 bar). However, these values remain below the DOE 2025 target. To address this issue, we propose to utilize molecular chemistry to integrate a highly reactive network (open metal sites linked with metal binding motifs) into a highly robust and porous framework (MOF) with open metal sites and achieve unprecedented high capacity for H <sub>2</sub> storage.
Fluorinated Covalent Organic Frameworks: A Novel Pathway to Enhance Hydrogen Sorption and Control Isothermic Heats of Adsorption	Justin Johnson	National Renewable Energy Laboratory	Colorado School of Mines	Project complete	Organic framework materials, as a unique sub-class of carbon-based sorbents, have gained increasing attention for promising attributes toward gas storage. Calculations of the hydrogen capacity of optimized frameworks show potential to achieve greater than 60 g/L storage of hydrogen, placing metal-organic frameworks and COFs near the top of the class of porous materials. However, at the ensemble level, poor stacking creates a quasi-amorphous material with low structural integrity and low effective surface area. The chemical versatility of COFs allows for additional methods for producing long-range order that specifically target the inter-layer interactions in COFs but that leave key pore-accessible linker sites open. These modifications (either during synthesis or post-synthetic) enable a host of strategies to both improve crystalline order for better stability and higher surface area, as well as add metals with open coordination sites for enhanced H <sub>2</sub> binding enthalpy.