ANL-19/03

“Graphene-Wrapped” Complex Hydrides as High-Capacity, Regenerable Hydrogen Storage Materials

---

Chemical Sciences & Engineering Division

Acknowledgment: This material is based upon work supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Fuel Cell Technologies Office (FCTO) under Agreement #32085-ANL.

About Argonne National Laboratory
Argonne is a U.S. Department of Energy laboratory managed by UChicago Argonne, LLC under contract DE-AC02-06CH11357. The Laboratory's main facility is outside Chicago, at 9700 South Cass Avenue, Argonne, Illinois 60439. For information about Argonne and its pioneering science and technology programs, see www.anl.gov.

DOCUMENT AVAILABILITY

Online Access: U.S. Department of Energy (DOE) reports produced after 1991 and a growing number of pre-1991 documents are available free at OSTI.GOV (http://www.osti.gov/), a service of the US Dept. of Energy's Office of Scientific and Technical Information.

Reports not in digital format may be purchased by the public from the National Technical Information Service (NTIS):
U.S. Department of Commerce
National Technical Information Service
5301 Shawnee Rd
Alexandria, VA 22312
www.ntis.gov
Phone: (800) 553-NTIS (6847) or (703) 605-6000
Fax: (703) 605-6900
Email: **orders@ntis.gov**

Reports not in digital format are available to DOE and DOE contractors from the Office of Scientific and Technical Information (OSTI):
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
www.osti.gov
Phone: (865) 576-8401
Fax: (865) 576-5728
Email: **reports@osti.gov**

Disclaimer
This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor UChicago Argonne, LLC, nor any of their employees or officers, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of document authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, Argonne National Laboratory, or UChicago Argonne, LLC.

ANL-19/03

“Graphene-Wrapped” Complex Hydrides as High-Capacity, Regenerable Hydrogen Storage Materials

---

prepared by
Di-Jia Liu
Chemical Sciences & Engineering Division, Argonne National Laboratory

January 10, 2019

“Graphene-Wrapped” Complex Hydrides as High-Capacity, Regenerable Hydrogen Storage Materials

Di-Jia Liu

Chemical Sciences & Engineering Division
Argonne National Laboratory

DOE Award #:	Agreement # 32085-ANL
Recipient(s):	Argonne National Laboratory (Primary) Southern Illinois University (Subcontractor)
Project Title:	“Graphene-Wrapped” Complex Hydrides as High-Capacity, Regenerable Hydrogen Storage Materials
Principal Investigator:	Di-Jia Liu (Argonne National Laboratory)
Team Member:	Qingfeng Ge (Southern Illinois University)
DOE Manager:	Jesse Adams (U.S. Department of Energy)
Project Start Date:	January 1, 2017
Project End Date:	June 30, 2018

Acknowledgment: This material is based upon work supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Fuel Cell Technologies Office (FCTO) under Agreement #32085-ANL.

TABLE OF CONTENTS

Executive Summary

"Graphene-Wrapped" Complex Hydrides as High-Capacity, Regenerable Hydrogen Storage Materials

This project focused on the development of a new class of hydrogen storage material, hydride@graphene, for the next-generation H_2 powered fuel cell vehicles. The new approach was based on a recent technology breakthrough through the collaboration between Argonne National Laboratory (ANL) and Shanghai Jiao Tong University (SJTU). A "nanoencapsulated" sodium borohydride-graphene composite, *$NaBH_4$@graphene*, was successfully synthesized using a simple solvent-based method. The new composite offers *regenerable* high H_2 storage capacity in multiple dehydrogenation and rehydrogenation cycles.

Under this short project, we successfully synthesized catalyst-doped $NaBH_4$@graphene composite and demonstrated five dehydrogenation (DH) and rehydrogenation (RH) cycles with measured gravimetric capacity > 7.4 wt% at 406 ºC. We also successfully demonstrated the improvement in hydrogen release kinetics by lowering DH temperature of 320 degree over bulk $NaBH_4$ or 138 degree over $NaBH_4$@G as the benchmark at the beginning of the project. We collaborated with members of the Hydrogen Materials – Advanced Research Consortium (HyMARC) team in computational modeling, structural characterization and performance measurement.

Introduction/Background

1.1 Technical Concept/Objectives

Hydrogen storage technology is critical for the next generation transportation technology such as proton exchange membrane fuel cells. To be practical, the storage system should reach gravimetric capacity of 0.055 kg H_2/kg_$_{system}$, volumetric capacity of 0.040 kg H_2/L_$_{system}$ at a cost of \$300/kg_$H_{2\ stored}$ according to the performance targets set by U. S. DOE for 2025. *No current technology meets all of these goals.*

This project aimed at developing a new class of complex hydride@graphene composites as the next generation of on-board hydrogen storage materials. The new approach was based on a recent major advancement achieved through the collaboration between Argonne National Laboratory (ANL) and Shanghai Jiao Tong University (SJTU).[1,2] Using a simple solvent-based method, we successfully synthesized a "nanoencapsulated" sodium borohydride-graphene composite, *$NaBH_4$@graphene*, in which $NaBH_4$ nanocrystallites are wrapped by single layer graphene sheet. The new composite offers ***regenerable*** H_2 storage capacity in multiple dehydrogenation (DH) and rehydrogenation (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 prevents the escape of dehydrogenated phases other than pure H_2, which is the only molecule permeable through the graphene layer. More importantly, the hydride crystallites are encapsulated at the nanometer size, which reduces their formation enthalpy and consequently lowers the DH temperature. The PCT measurement showed a highly reversible DH/RH cycle at lower temperature and pressure than that for the bulk phase hydride. Since the graphene is lightweight, it impacts only nominally on the total storage capacity of the composite. Our $NaBH_4$@graphene has demonstrated a steady and reversible net H_2 capacity of > ***7.0 wt. %*** in a multi-cycle DH/RH test at 460 °C at the beginning of the project.

Under this project, our goal was to expand the method to prepare a broader range of hydride@graphene composites using the complex hydrides of higher intrinsic gravimetric and volumetric densities through collaboration between ANL and Southern Illinois University (SIU). We also planned to explore various morphological and additive approaches to improve the DH-RH kinetics, guided by computational modeling. These tasks required the collaboration with HyMARC team in modeling, characterization and measurement. Our ***Phase I Goal*** was to demonstrate and deliver a hydride@graphene with stable and regenerable gravimetric capacity > 8 wt. % in multiple DH-RH cycles at DH temperature ≤ 400 °C and RH temperature ≤ 350 °C, respectively. Our ***Overall Objective*** was to produce one or more composites with *regenerable* H_2 storage gravimetric density (GD) > 10 wt.% and volumetric density (VD) > 0.055 kg H_2/L. We also planned to develop a scale-up strategy of manufacturing the new composite at the cost < \$333/kg_H_2.

1.2 Accomplishments against Milestones

Three milestones and one go/no-go decision point were assigned for the first 12 month Phase I. A brief summary of the milestones against their status is listed in Table 1 below:

---

[1] $NaBH_4$ in "Graphene Wrapper": Significantly Enhanced Hydrogen Storage Capacity and Regenerability through Nano-encapsulation, L. Chong, X. Zeng, W. Ding, D.-J. Liu and J. Zou, *Advanced Materials*, **2015,** *27*, 5070–5074

[2] "Wrapped by graphene": An efficient way to achieve high capacity, reversible hydrogen storage through nanoencapsulated hydride, J. Zou, L. Chong, D.-J. Liu, et. al. *Science*, **2016**, *351* (6278), 1223. special issue.

Table 1. Progresses against Milestones

Milestones	End Date	Status
Improving $NaBH_4$@graphene system to produce regenerable sorption/desorption storage capacity of > 8 wt.% total.	6/30/2017	*Completed:* Storage capacities ranging from 9 wt.% to 7.4 wt.% achieved during six DeH/ReH cycles over a new batch of $NaBH_4$@graphene with 9.1 wt.% theoretical capacity
Storage capacity measurement & structural characterization for modified $NaBH_4$@graphene	9/30/2017	*Completed:* TPD, TGA, XRD, FTIR and NMR experiments are completed for the $NaBH_4$@graphene and several related systems with catalytic additives
Investigating MgH_2@hydride@graphene by producing sufficient quantity MgH_2@graphene as precursor for binary hydride@graphenes	9/30/2017	*Completed:* New solution based MgH_2@graphene synthesis was successfully developed and tested in combination of $NaBH_4$.
Go/No Decision Point: Deliver at least one "hydride@graphene" material with reversible total gravimetric capacity >8 wt% H_2 and total volumetric capacity >0.03 kg H_2/L at temperatures <400°C over at least five (5) sorption/desorption cycles as validated by a DOE designated lab.	9/30/2017	*Status:* Over 300 mg of catalyst added $NaBH_4$@graphene was shipped and tested at SNL for 5 DH/RH cycles. Gravimetric capacity ranges from 7 wt.% to 4 wt. % and volumetric capacity ranges from 0.04 kg H_2/L to 0.022kg H_2/L, test under temperature between 390 °C to 395 °C.

The project received a "no-go" decision for Phase II due to its failure in meeting the criteria of regenerable storage capacity >8 wt. % H_2 at temperatures <400°C over five sorption/desorption cycles when measured at Sandia National Laboratory.

Project Activities

2.1 Scientific Hypothesis

The project aimed to develop several complex hydride@graphene composites with high, regenerable H_2 storage capacity. The idea is derived from a recent joint study of SJTU and ANL on a new H_2 storage composites prepared by encapsulating nano-dimensional $NaBH_4$ inside a “graphene wrapper”.[1] The new composite is prepared through a simple yet robust wet chemistry method (**Figure 1A**). Briefly, the hydride is first dissolved in an organic solvent such as alkyl-amine, followed by addition of graphene. To promote DH kinetics at lower temperature, soluble catalyst is added during the mixing process. After a brief period of agitation and sonication under solvothermal condition, the solution is dried and evacuated before loading into a reactor where the composite is subjected to a brief heat-treatment for further drying and initial hydrogenation under high pressure H_2. Under such treatment, the hydride particles are wrapped by graphene, most likely due to the change of graphene sheet curvature through surface hydrogenation reaction, combined with van der Waals interaction between hydride and graphene. The new composite contains hydride particles uniformly distributed over the graphene sheets (**Figure 1B**) with a distinct morphology of hydride nanoparticles encapsulated by a single layer of light-weight graphene (**Figure 1C**). We coined it as “hydride@graphene”.

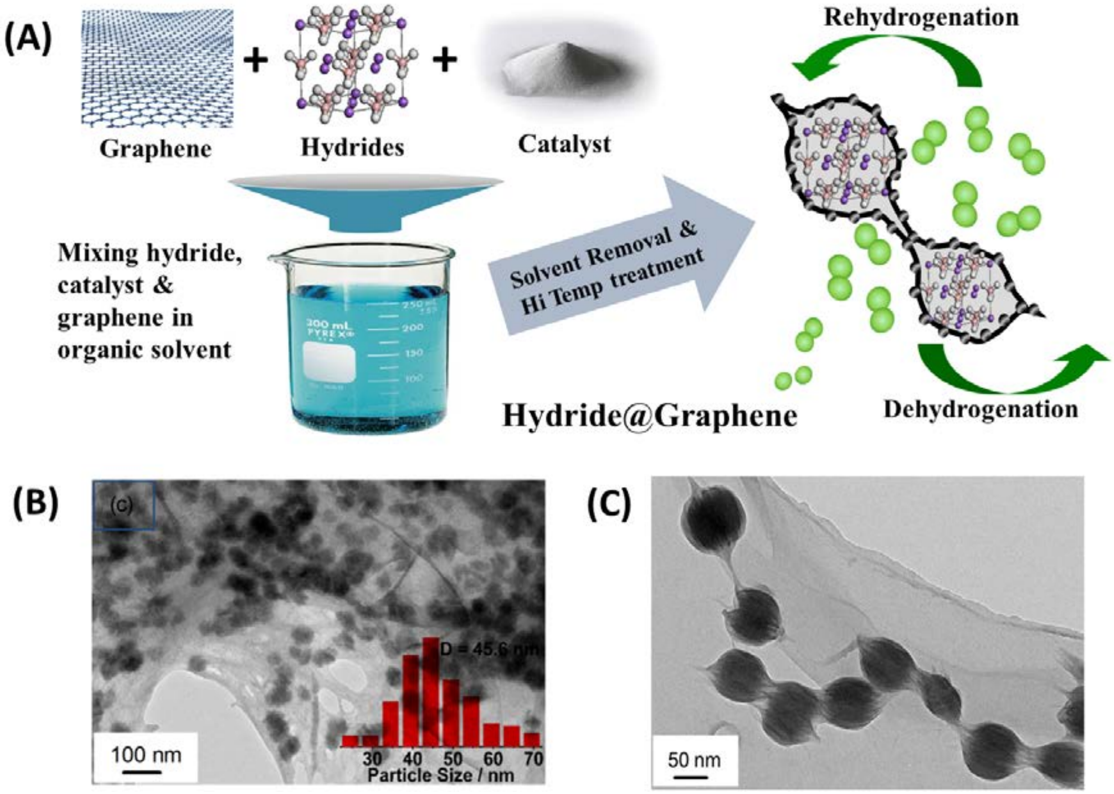

Figure 1. (**A**) Schematics of solution-based synthesis of hydride wrapped by graphene; (**B**) Transmission electron microscope (TEM) image of $NaBH_4$ nanocrystallites uniformly distributed over graphene sheets and (**C**) encapsulated by graphene sheets.

Hydride@graphene offers the following advantages compared to conventional hydride materials for hydrogen storage:

- *Higher regenerability* – Selective permeation of H_2 through single layer graphene has been observed in gas separation, catalysis and hydrogen storage. The graphene serves as a "H_2 sieve" which precludes all elements/molecules other than hydrogen passing through, producing high purity H_2 without degrading fuel cell performance.[3] Such encapsulation traps the dehydrogenated byproducts including the volatile species within the "graphene pocket", increasing their frequencies of encountering and probability to regenerate back to hydride under H_2 during regeneration, as we found in the case of $NaBH_4$@graphene.
- *Higher capacities* – Graphene is a lightweight high surface area material. It contributes minimally to the composite weight and therefore has less effect on the gravimetric capacity compared to other approaches such as porous carbon or polymer matrixes. Our $NaBH_4$@graphene uses only < 25 wt.% graphene in the total composite, which can be further reduced through optimization.
- *Lower operating temperatures* – Graphene encapsulation could improve H_2 release in two ways. Thermodynamically, it can destabilize hydrides by limiting their crystallite sizes at nanoscale and preventing them from agglomeration, therefore reducing ΔH of the overall reaction. Kinetically, graphene has been found to catalyze hydride decomposition for hydrogen release.[4] Wrapping graphene intimately around hydride will increase the interaction between the two, improving catalytic effect and reducing release temperature.

2.2 Synthesis and Evaluation of New $NaBH_4$@Graphene

At the start of the project, we first prepared several batches $NaBH_4$@graphene with calculated total composite gravimetric capacities ranging from 7 wt.% to 9 wt.%. To better understand their DH chemistry and kinetics affected by graphene, we investigated their reactivity and structural variation during hydrogen discharge using temperature programmable desorption (TPD) and thermogravimetric analysis (TGA) tools. For comparison, the kinetics of DH for bulk $NaBH_4$ as the function of temperature was also studied. **Figure 2** shows the TPD results for both $NaBH_4$@graphene and bulk $NaBH_4$. Hydrogen released from the hydride samples were also measured at different temperatures. For bulk $NaBH_4$, no decipherable amount of hydrogen release was found until the temperature exceeded 450 °C. The

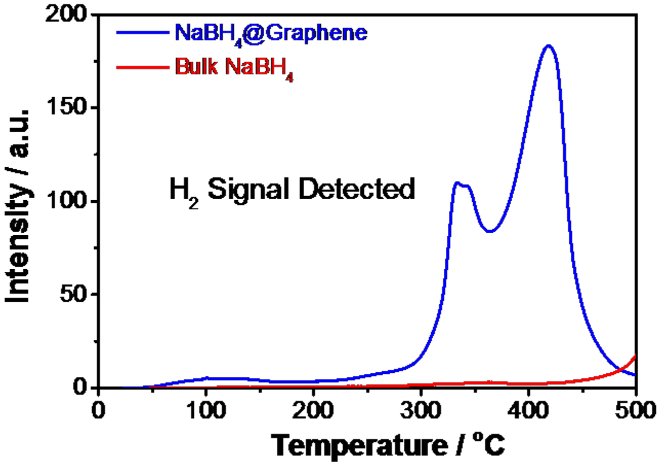

Figure 2. Comparison on TPD studies of $NaBH_4$@Graphene and bulk $NaBH_4$.

---

[3] Q. Ge, *et. al*. in "Energy Efficiency and Renewable Energy Through Nanotechnology, Green Energy and Technology", L. Zang (ed.), Springer-Verlag London Limited **2011**

[4] P. A. Berseth, *et. al*., *Nano Lett.* **2009**, 9, 1501

$NaBH_4$@graphene, on the other hand, started to release a significant amount of hydrogen at the temperature as low as 300 °C. Two peaks near temperatures of 320 °C and 400 °C represent the hydrogen detachment from two different intermediate species during hydride decomposition. A particularly notable observation for $NaBH_4$@graphene is a small amount of hydrogen released at very low temperature of < 100 °C. At this point, we do not know the root cause of the hydrogen release under such low temperature. Better understanding the origin of this hydrogen desorption could be beneficial in improving the DH kinetics through rational design and synthesis of the hydride composites.

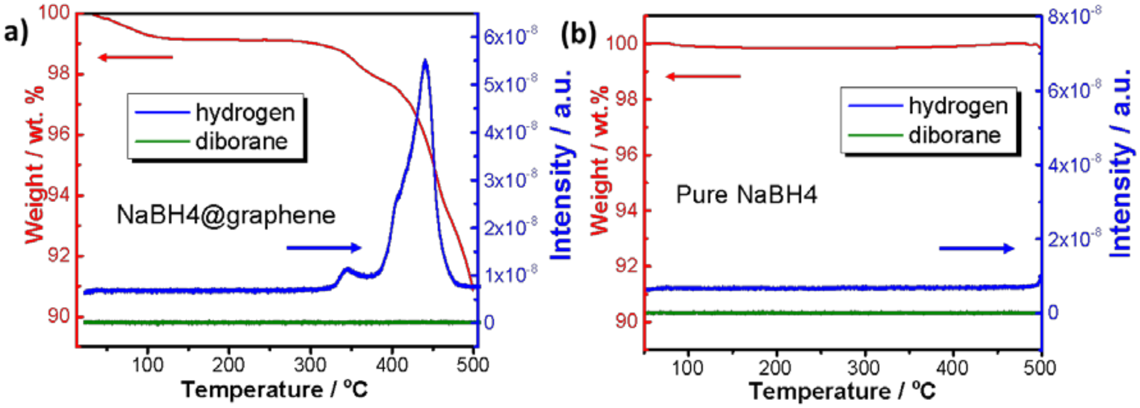

Figure 3. TGA study on dehydrogenation of **(a)** $NaBH_4$@graphene and **(b)** $NaBH_4$ as the function of temperature.

We also corroborated graphene promoted DH activity using the TGA method. **Figure 3a** shows the weight losses as the function of temperature, coupled with the mass spectroscopic analysis for $NaBH_4$@graphene and bulk $NaBH_4$ in **Figure 3b**, respectively. Similar to the TPD analysis, a significant weight loss was observed for $NaBH_4$@graphene starting at the temperature near 300 °C and up, accompanied by two hydrogen peaks detected by mass spectroscopy. No diborane byproduct was observed. On the contrary, no appreciable weight loss was found for bulk $NaBH_4$ until at the temperature approaching 500 °C. The TGA results confirmed the observation in the TPD study.

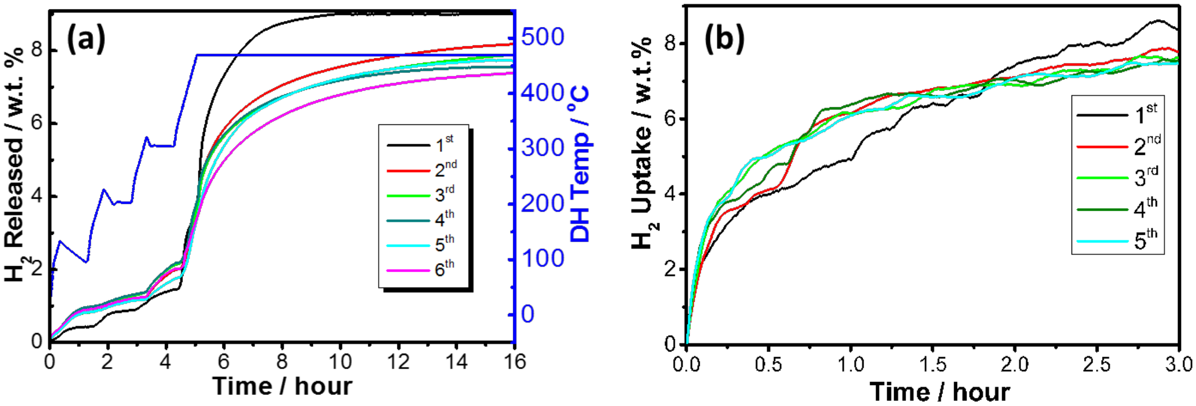

Figure 4. (a) Temperature-programmed hydrogen release from $NaBH_4$@graphene; **(b)** RH adsorption isotherm of dehydrogenation of $NaBH_4$@graphene at 350 °C under 4 MPa. The vacillation of the isotherm plots were due to the temperature fluctuation from the furnace.

Selected $NaBH_4$@graphene samples were investigated under multiple DH and RH cycles. The DH tests were completed through stepwise temperature-programmed discharge with the last temperature step at 465 °C. A RH cycle was inserted in between DH cycle by recharging the composite at H_2 pressure of 4 MPa and temperature of 350 °C. **Figure 4a** and **4b** show the multiple hydrogen release and uptake cycles measured by a Sievert apparatus at Argonne over a $NaBH_4$@graphene composite composed of 86 wt.% of sodium borohydride and 14 wt.% of graphene. The theoretical hydrogen storage capacity for this composite was 9.13 wt.%. For DH, the first cycle reached a gravimetric capacity of 9.01 wt.% at the end of the first discharge. After the regeneration, the gravimetric capacity reached to 8.1 wt.% and was maintained near this value with slightly decrease during the subsequent cycles.

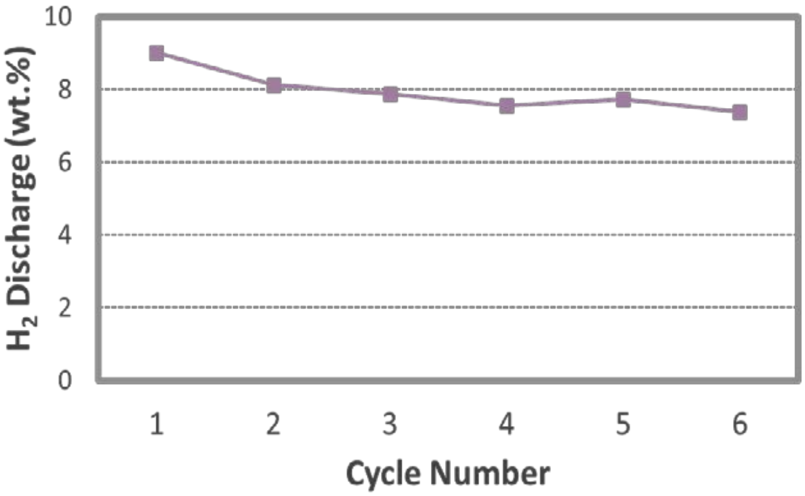

Figure 5. The hydrogen discharge gravimetric capacity as the function of cycle number for new ANL's $NaBH_4$@graphene.

Figure 5 shows the change of hydrogen discharge capacity at different cycles. The gravimetric capacity was maintained from 8.1 wt.% to 7.4 wt.%, representing the retention of 89% to 81% of the theoretical value of the $NaBH_4$@graphene composite. These values are also listed in Table II. Compared to previous literature reports on bulk or nano-confined complex hydrides, the graphene encapsulated hydride from our approach show significant improvements in capacity, cyclability and regenerable condition. Such regenerability was further confirmed by a series of characterization experiments as described below.

Table II. Gravimetric capacities and their percentage against the theoretical value during six DeH_2 cycles

Cycle #	1	2	3	4	5	6
H_2 Discharge (wt.%)	9.01	8.12	7.88	7.55	7.72	7.38
% to Theoretical Value	99%	89%	86%	83%	85%	81%

2.3 Structural Characterizations of $NaBH_4$@graphene

We investigated the structural reversibility of $NaBH_4$@graphene through hydrogen discharging and regeneration using several characterization techniques. For example, powder x-ray diffraction (XRD) method was used to study the phase reversibility of $NaBH_4$@graphene at fresh, dehydrogenated and rehydrogenated stages. As a reference, bulk $NaBH_4$ were also studied side-by-side. The XRD spectra are shown in **Figure 6**. The spectrum of fresh $NaBH_4$@graphene matches well with that of bulk $NaBH_4$, suggesting that sodium borohydride retained it crystal structure after being encapsulated inside of graphene. After DH reaction, the peaks associated with $NaBH_4$ were all disappeared, as was anticipated due to the loss of hydrogen and therefore the crystal structure. No other crystal phase was observed, implying that the dehydrogenated hydride was in amorphous state. The XRD peaks reappeared after the RH reaction, indicating the recovery of hydride crystallites. We also performed the hydride crystallite size estimation using Scherrer equation and found that the average hydride particle size in $NaBH_4$@graphene is about 32 nm for both DH and RH samples, which is about 2/3 of that found in bulk $NaBH_4$ (48 nm).

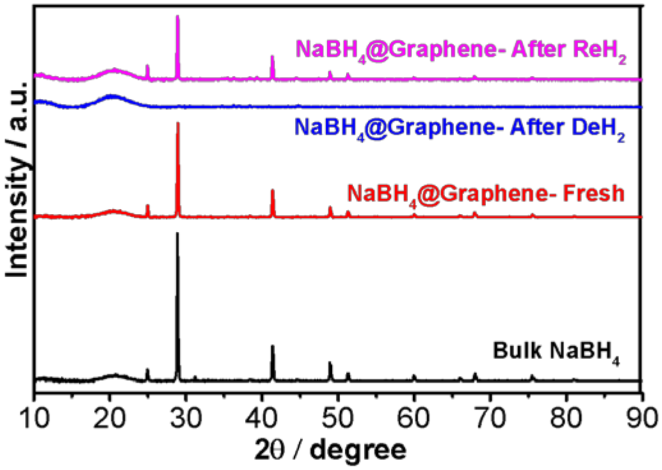

Figure 6. Comparison of XRD pattern and particle size for fresh, dehydrogenated and rehydrogenated $NaBH_4$@graphene samples using bulk $NaBH_4$ as reference.

In addition to XRD, we also investigated ^{11}B NMR spectroscopy of $NaBH_4$@graphene at fresh, DH and RH states, as is shown by **Figure 7**. Similar to that of XRD result, NMR study reaffirmed the regeneration of hydride without producing any other major boron byproduct. This result was later also confirmed by an independent study at PNNL, as will be discussed in the

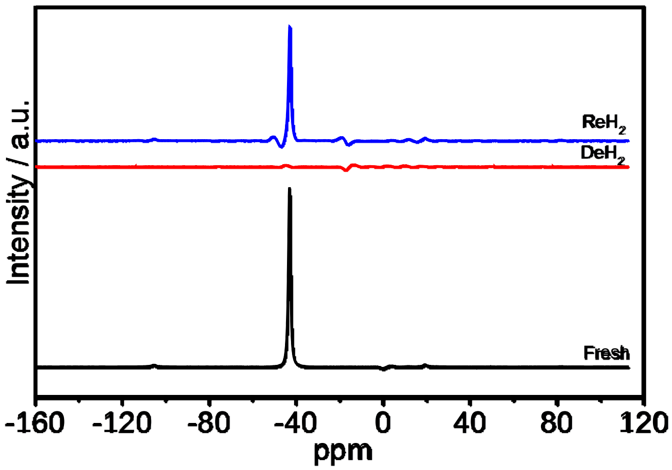

Figure 7. ^{11}B NMR study of fresh, dehydrogenated and rehydrogenated $NaBH_4$@graphene

later section.

2.4 Synthesis and Evaluation of Catalyst-doped NaBH4@Graphene

To reduce DH temperature by improving the hydrogen release kinetics, we explored several transition metal (TM) based catalysts. For catalyst, the loading of these TM-based materials has to be very low (typically < 5%) to avoid adding parasitic weight. Furthermore, they need to be mixed with hydride as uniformly as possible to promote catalytic reaction. This is typically accomplished by dissolving TM organometallic complex in the organic solution followed by adding in the solvated sodium borohydride. The catalyst-doped $NaBH_4$ will be encapsulated by graphene after being blended with graphene followed by drying. Because some of the organometallic complex can only be dissolved in THF, which forms an adduct with the borohydride, the solvent was more difficult to remove from the catalyst doped composite $NaBH_4$+Catalyst@Graphehe compared to $NaBH_4$@Graphene prepared by alkyl amine based solvent. Usually, the solvent can only be completely removed after the first DH cycle at elevated temperature.

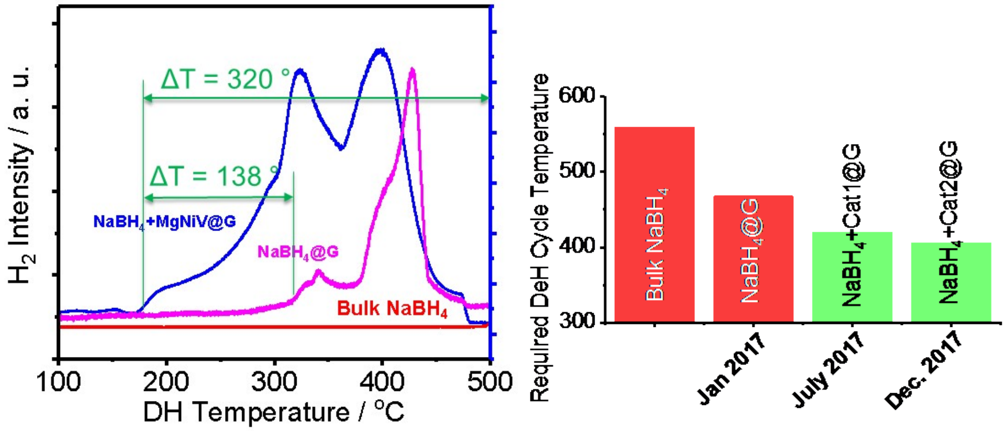

Figure 8. (a) Comparison of hydrogen signal detected from $NaBH_4$+MgNiV@G and benchmark material measured from TGA experiment; **(b)** improvement of minimal DH temperature for stable recycling of sodium borohydride in different composites.

We first investigated traditional catalysts known to be active toward hydrogen bond scission and found out that they did not work in the case of complex hydride. For example, we added low concentration of platinum (<5%) into $NaBH_4$@graphene and found no discernable reduction of DH temperature. However, some TMs prone to form hydride bond were proven to work well. For example, we added some third-row transition metals such as nickel and vanadium into the hydride and achieved some significant improvement in DH kinetics. We also added organometallic Mg during hydride synthesis process and found that it marginally reduced the DH temperature. **Figure 8a** shows the hydrogen release as function of temperature for a catalyst doped sodium borohydride-graphene composites, $NaBH_4$+Cat@G obtained from a TGA study. The catalyst contained low level TM including Ni, V, and Mg. For comparison, the hydrogen releases from $NaBH_4$@graphene and bulk $NaBH_4$ are also included. Clearly, the catalyst improved DH kinetics. The onset hydrogen release temperature was lowered to @ 200 °C, almost 130 degree reduction compared to the benchmark $NaBH_4$@graphene and 320 degree reduction against bulk $NaBH_4$.

Improved DH kinetics through catalyst doping also helped to reduce the cycling temperature. **Figure 8b** shows the progression in DH temperature for multiple discharge-charge cycles from the beginning of the project. While the bulk $NaBH_4$ and $NaBH_4$@graphene require

DH temperature of > 550 °C (non-regenerable) and 460 °C, respectively, the temperature was successfully reduced to 420 °C and 406 °C through the catalyst-doping during the course of the project, very close to the project target of 400 °C.

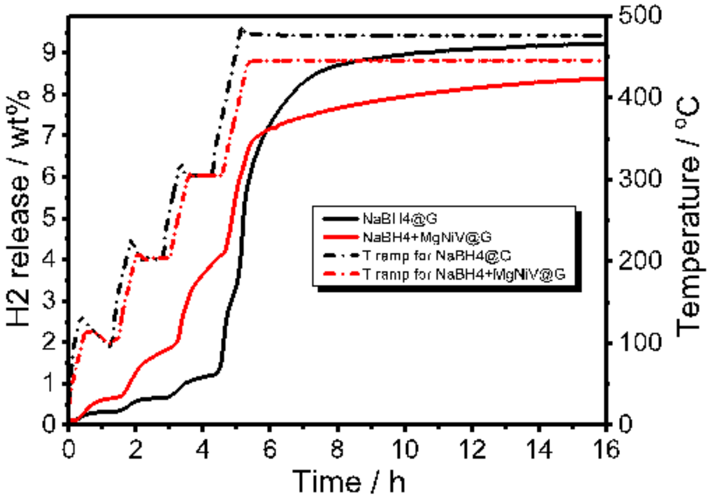

Figure 9. Comparison of hydrogen releases from $NaBH_4$+MgNiV@G and $NaBH_4$@G during step-wise temperature-programmed discharge.

The catalyst promoted DH kinetics was also reflected by the temperature-programmed hydrogen desorption in the discharge capacity measurement. **Figure 9** shows a side-by-side comparison between catalyst-added $NaBH_4$+MgNiV@G and $NaBH_4$@G during step-wise hydrogen release from room temperature to 430 ºC at 100 degree interval. Clearly, with the improved DH kinetics, $NaBH_4$+MgNiV@G composite discharged more $NaBH_4$@G at lower temperature steps. For example, ~ 4 wt.% hydrogen was already discharged at T = 300 ºC for $NaBH_4$+MgNiV@G in comparison of ~ 1 wt.% for $NaBH_4$@G under the same temperature. The total discharged hydrogen reached to 8.2. wt.% at T = 430 ºC for $NaBH_4$+MgNiV@G, compared to $NaBH_4$@G which released a similar amount of hydrogen at the temperature > 475 ºC.

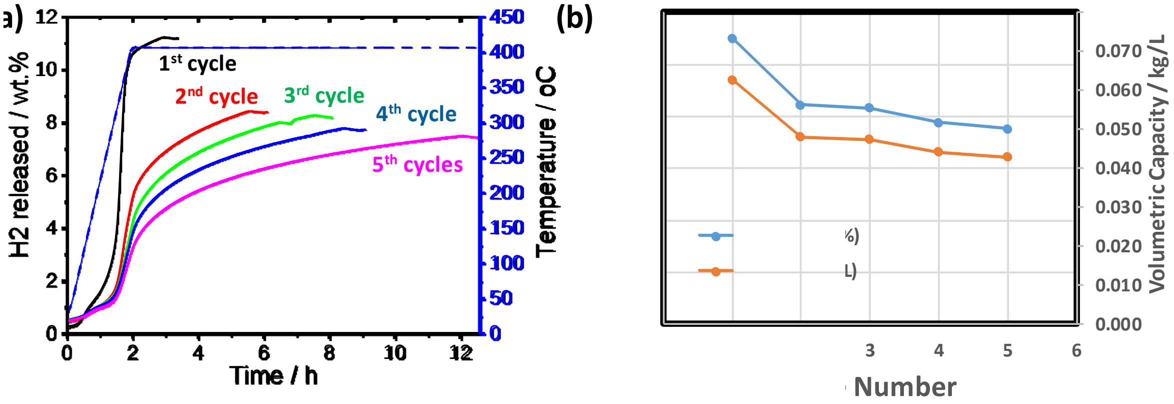

Figure 10 (a) Amount of hydrogen released from five dehydrogenation cycles at one-step temperature ramp to 406 C; **(b)** the gravimetric and volumetric hydrogen storage capacities obtained during the five cycles

We also performed five DH/RH cycles for $NaBH_4$+MgNiV@G composite. The DH temperature was controlled at 406 ºC with background hydrogen pressure less than one bar while the RH temperature was set at 350 ºC under H_2 charging pressure of 40 bars. **Figure 10a** shows the amount of hydrogen released in five DH cycles as the function of time with RH step between each cycle. **Figure 10b** demonstrates the gravimetric and volumetric hydrogen storage capacities obtained during the five cycles. The very high capacity achieved during the first cycle was attributed to the contribution of vapor pressure of the residual organic solvent trapped during the composite synthesis. The capacities of the remaining cycles were all from pure hydrogen released from the composite. The purity of hydrogen released was later proved high from gas analysis. At the end of 5th cycle, the net gravimetric capacity maintained at 7.3 wt. % while the volumetric capacity at 0.042 kg/L, respectively.

2.5 Computational Modeling at Southern Illinois University (SIU)

The SIU team's task is to use computational modeling to support the design and synthesis of hydride@graphene materials. SIU previous modeling works demonstrated the concept that the reaction enthalpy for hydrogen release and uptake could be tuned by controlling the state of the reactants and products.[3] They expanded the computational study to examine the effect of crystallite size and confinement on the reaction enthalpy for a range of hydrides. In Phase I, SIU team worked closely with the experimental team and focused on $NaBH_4$@graphene. In particular, the team carried out DFT calculations to examine relationship between the size/shape of nanosized particles and the strength/nature of hydrogen interactions.

In these studies, the team used Gaussian software package and constructed $NaBH_4$ clusters up to 16 molecular units. They mapped out the elementary hydrogen formation pathways starting from the stoichiometric cluster to the bare NaB cluster. For each elementary step, they isolated the transition state and determined the activation barrier, as is schematically shown in **Figure 11**.

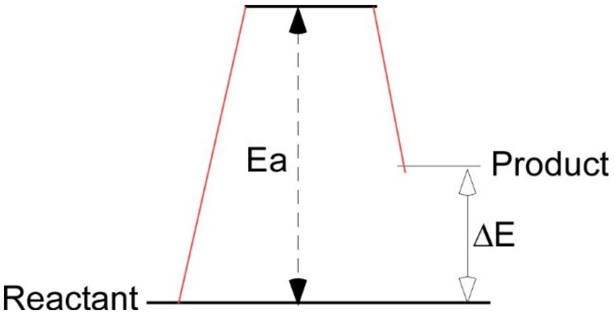

Figure 11. Schematic energy diagram for an elementary reaction involved in hydrogen release from NaBHx based systems.

The team also examined the effect of confinement by placing the cluster in between two graphene sheets. In these calculations, they used the QM/MM approach implemented in Gaussian by treating the atoms in the graphene sheets with the universal force field whereas the atoms of hydride cluster quantum mechanically. They compared the energetic results of the free cluster with those of the encapsulated clusters and summarized the results in the tables. Corresponding the diagram of Figure 11, Ea and ΔE are the activation energy and reaction energy of the elementary step for the corresponding reactant and product states. The highlighted rows in the following table show the encapsulation reduces the activation barrier and overall endothermicity of the reaction. The team performed calculations starting with $(NaBH_4)_2$ and $(NaBH_4)_4$ and followed the pathway leading to complete dehydrogenation in both free and encapsulated form.

Table III. Reactions starting with $(NaBH_4)_2$

Reactant	Product	Free		Encapsulated			
		Ea	ΔE	Ea	ΔE	ΔEa	Δ(ΔE)
(NaBH4)2	**(NaBH3)2+H2**	407.7	185.3	388.7	179.8	-19.0	-5.5

(NaBH3)2	**(NaBH2)2+H2**	233.8	126.8	280.4	142.0	46.6	15.2
(NaBH2)2	**(NaBH)2+H2**	284.4	189.1	275.7	240.8	-8.7	51.7
(NaBH)2	**(NaB)2+H2**	419.2	408.4	362.6	324.5	-56.6	-83.9

Overall Reaction:
$(NaBH_4)_2 = (NaB)_2 + 4 H_2$ Free: 231.3 kJ/mol H_2; Encapsulated: 221.8 kJ/mol H_2.

Table IV. Reaction starting with $(NaBH_4)_4$

Reactant	**Product**	**Free**		**Encapsulated**			
		Ea	**ΔE**	**Ea**	**ΔE**	**ΔEa**	**Δ(ΔE)**
(NaBH4)4	**(NaBH4)2(NaBH3)2+H2**	416.7	152.4	433.8	173.3	17.1	20.9
(NaBH4)2(NaBH3)2	**(NaBH3)2(NaBH3)2+H2**	431.0	187.4	446.8	188.9	15.8	1.5
(NaBH3)2(NaBH3)2	**(NaBH3)2(NaBH2)2+H2**	228.3	129.8	283.5	236.1	55.2	106.3
(NaBH3)2(NaBH2)2	**(NaBH2)2(NaBH2)2+H2**	249.1	158.7	205.9	75.9	-43.2	-82.8
(NaBH2)2(NaBH2)2	**(NaBH2)2(NaBH)2+H2**	270.1	182.9	292.8	270.9	22.7	88.0
(NaBH2)2(NaBH)2	**(NaBH)2(NaBH)2+H2**	324.7	188.2	211.9	85.4	-112.8	-102.8
(NaBH)2(NaBH)2	**(NaBH)2(NaB)2+H2**	424.8	422.5	444.5	423.4	19.7	0.9
(NaBH)2(NaB)2	**(NaB)2(NaB)2+H2**	427.1	423.9	411.6	-164.2	-15.5	-588.1

Overall Reaction:
$(NaBH_4)_4 = (NaB)_4 + 8 H_2$ Free: 228.9 kJ/mol H_2 Encapsulated: 162.2 kJ/mol H_2.

Based on these results, we concluded that encapsulation helps to stabilize the products state and reduces the overall endothermicity of the hydrogen release reaction. We note that this model of simulating confinement effect did not take into consideration of the possible defects and dopants in the graphene that could also affect the reaction, both thermodynamics and kinetics. These effects may be built into future modeling effort as the experimental characterization showing they significantly affect the hydrogen storage performance of the encapsulated $NaBH_4$.

2.6 Collaborations with HyMARC

Collaboration with Sandia National Laboratory (SNL) on DH-RH cycling capacity measurement: The DH-RH capacity of $NaBH_4$+Cat@G was measured at SNL for validation. Three batches of NaBH4+Catalyst@G samples with total weight of 650 mg were prepared and shipped to SNL. A temperature control issue at SNL consumed two batches of samples without producing useful data. The temperature control issue was resolved for the batch #3 after installing ANL-shipped tube furnace and controller. However, the DH temperature was restricted at 392 °C due to the safety regulation at SNL.

Figure 12A shows the 5-cycle hydrogen discharge capacity measurement for Sample #3. It shows that NaBH4@G is regenerable in multiple cycles. The highest capacity was in the first cycle while the remaining cycles have lower but similar capacities among themselves. This observation is consistent with what we found during the measurement at ANL. However, the capacities in the multiple cycles from SNL's measurement were significantly lower than what we found in Figure 10. **Figure 12B** shows that the H_2 released from $NaBH_4$+Cat@G has high purity with only trace amount of residual observed. The hydrogen purity is among the highest over the hydride materials tested by SNL. The mass fragments at m/z between 23 and 27 obtained from residual gas analyzer (RGA) in Figure 12B could be attributed to CO, C_2H_4, B_2H_6 from decomposed THF or $NaBH_4$. As previously mentioned, THF forms adduct with $NaBH_4$, which affects its decomposition chemistry.

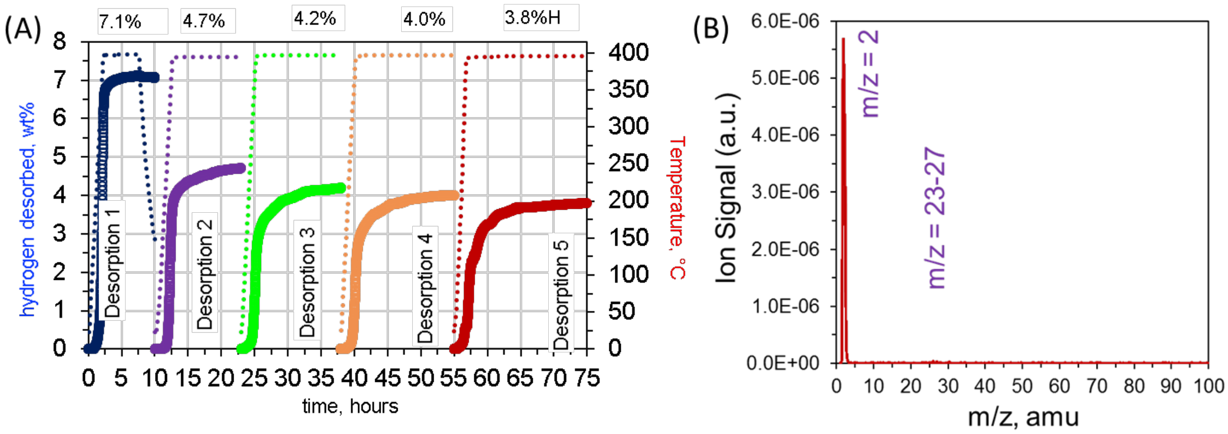

Figure 12. (A) H_2 desorption measured during 5 DH/RH cycle in SNL, **(B)** RGA measurement of the desorbed gas at the end of 5th cycle.

We compared the SNL data with the one measured in our lab and conducted additional post-experimental analysis. We identified the differences in *DH temperature* and *DH/RH cycling condition* as two potential root causes for the discrepancy. Among them, DH temperature was the main factor. Our TGA data in Figure 8a shows a second major DH peak situates at 400 °C even the lowering of the DH temperature by catalyst. This renders the completeness of DH process sensitive to temperature around 400 °C, as we found in our lab. A few degree adjustment can alter the time required to complete DH process. Longer DH period will be needed to completely release H_2 at temperature < 400 °C. We analyzed the XRD for the Sample #2, which presumably completed the 5th DH cycle at SNL. **Figure 13A** shows, however, the sample has a considerably amount of undecomposed $NaBH_4$, together with several identified and unidentified features. This XRD was in stark contrast with the XRD of the same $NaBH_4$@G sample we obtained after 5th DH at 406 °C at ANL. In ANL's measurement, no peaks other than those associated with the catalyst were found after 5th dehydrogenation (**Figure13B**, top trace). We concluded that the samples measured at SNL did not complete the dehydrogenation process, therefore produced a lower capacity.

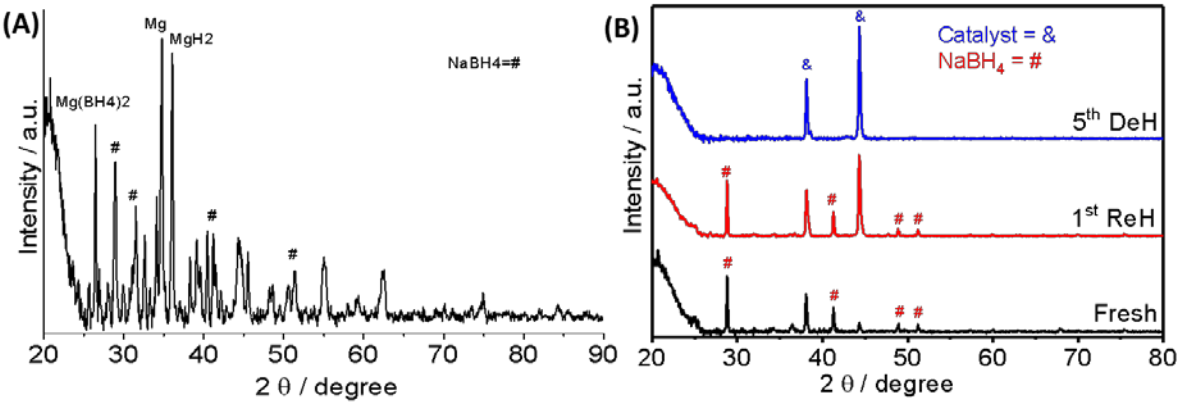

Figure 13. (A) XRD of Sample 2 after 5 DH cycle at 392 °C at SNL. A substantial amount of unreacted $NaBH_4$, together with other unidentified peaks. **(B)** XRD of the same sample after 1st RH and 5th DH measured at ANL.

Collaboration with Pacific Northwest National Lab (PNNL) on NMR study: Three borohydride samples were sent to PNNL, including fresh $NaBH_4$@G, $NaBH_4$@G after DH and $NaBH_4$@G after RH. PNNL investigated ^{11}B and ^{1}H direct polarizations. **Figure 14** shows a sharp resonance at -42 ppm, which is consistent with $NaBH_4$. The peak disappeared after DH and fully reappeared after RH, indicating complete hydride regeneration. This result is consistent with ANL's NMR study shown in Figure 7.

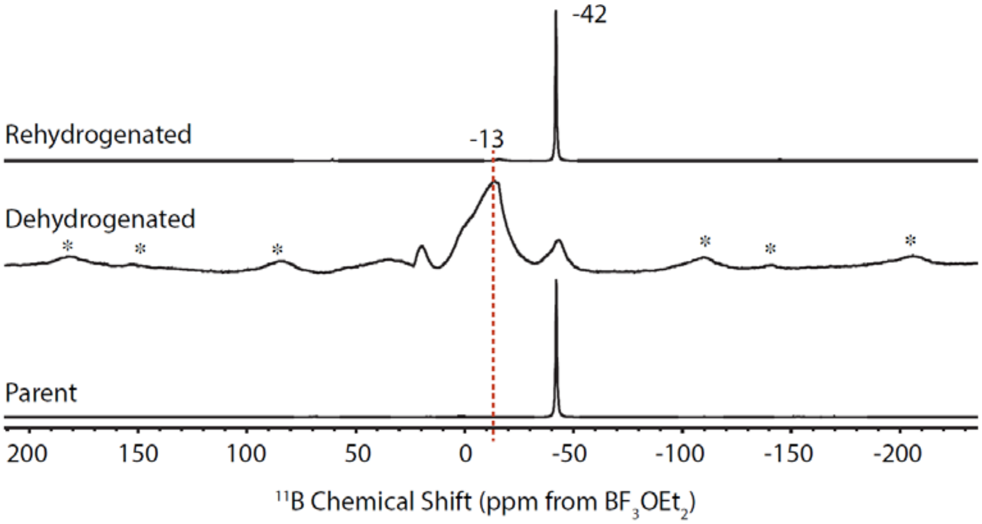

Figure 14. ^{11}B direct polarization from NMR measurement of ANL's $NaBH_4$@G sample at fresh, DH and RH stages.

Collaboration with National Renewable Energy Lab (NREL) on TPD study: Three samples, $NaBH_4$@G, $NaBH_4$+catalyst@G and bulk $NaBH_4$, were sent to NREL for TPD measurement. All the samples were freshly prepared with solvent removed except for $NaBH_4$+catalyst@G, which contained ~60% solvent (THF). The THF binds strongly with $NaBH_4$ in the form of $NaBH_4$-adduct, rendering it difficult to be removed at $T < 100$ °C. **Figure 15** shows the H_2 TPD signals from all three samples during the temperature ramps at a ramping rate = 1 °C/min (method 1). Both $NaBH_4$@G and $NaBH_4$+Cat@G showed significant reduction of DH temperature over the bulk $NaBH_4$. The first H_2 release peaks from $NaBH_4$+Cat@G and $NaBH_4$@G are at 120 °C and 260 °C, respectively, both are significantly lower than that of bulk $NaBH_4$ of > 500 °C. This TPD result is also consistent with our aforementioned TGA study (Figure 7). The intent of this study is to search if diborane can be detected by TPD. The escape of diborane would affect the hydride regenerability. The study did not find detectable diborane. It did detect some vaporized sodium metal, which was consistent with ANL's previous observations. We need to point out that sodium level was very low since we have been able to regenerate > 80% capacity of the storage capacity during multiple RH steps. NREL report estimated the hydrogen capacity from $NaBH_4$+Cat@G is about 4%. Given that their estimation did not account for ~50 wt.% of solvent in the sample, the actual hydrogen released should be ~8% based on the solvent-free calculation, consistent with our aforementioned DH-RH cycling result.

Computational Modeling at LLNL: Drs. T. W. Heo and B. Wood at LLNL recently made some advancement in understanding the improved DH kinetics by graphene wrapping through computational modeling. They demonstrated, depending on the dehydrogenation pathway, the elastic strain energy in $NaBH_4$@G by the confinement effect can destabilize the hydride therefore significantly reduce the DH temperature. To further validate this model, additional experimental verification is needed including controlled dehydrogenation and hydride structural analysis at different stages of DH process.

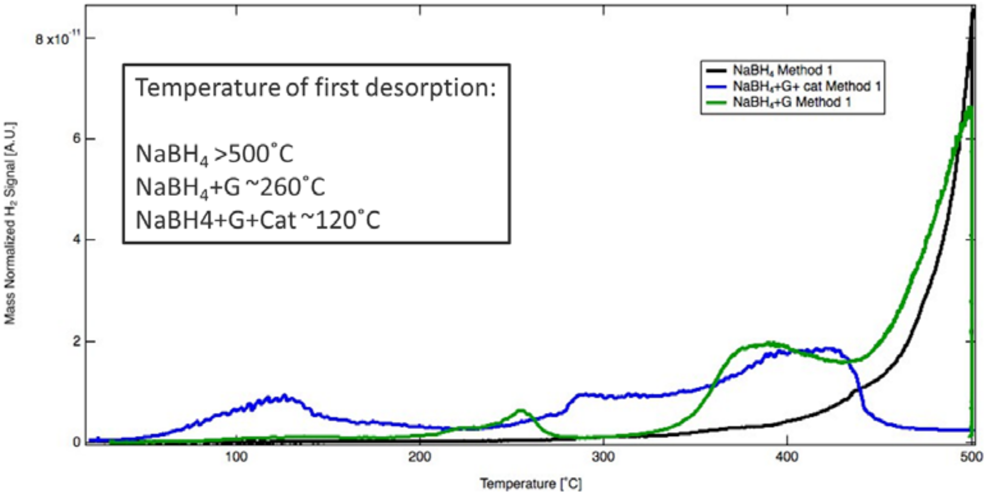

Figure 15. Hydrogen signal detected as the function of desorption temperature during TPD experiment over three ANL sodium borohydride samples.

2.7 Summary

ANL team has developed a new catalyst doped sodium borohydride wrapped by graphene, $NaBH_4$+Catalyst@G through Phase I of this project. The new composite significant improved DH kinetics by lowering initial H_2 discharge temperature from >500 °C in bulk $NaBH_4$ to 180 °C, representing a 320 degree reduction in DH temperature. Compared to $NaBH_4$@G as the benchmark at the project start, the new composite also reduced DH onset temperature by about 138 degree. Regenerable hydrogen release under a simple, one-step temperature process was achieved for the new hydride composite in a five-cycle discharge-charge experiment under the DH temperature of 406 °C and RH temperature of 350 °C, respectively. The gravimetric capacity was retained at 7.5 wt.% at the end of the 5th cycle. The catalyst promoted DH was also confirmed by the experiment at NREL.

Characterization of hydride composite by XRD and NMR at ANL and PNNL reached the same conclusion and verified the regeneration of hydride@graphene after multiple DH-RH cycles. ANL team collaborated with multiple DOE labs under HyMARC consortium in material characterization, computation modeling and hydride performance certification.

Publications/Presentations/Recognitions

3.1 Publications

1. "An International Laboratory Comparison Study of Volumetric and Gravimetric Hydrogen Adsorption Measurements", K. E. Hurst, *et. al.* Submitted
2. "An assessment of strategies for the development of solid-state adsorbents for vehicular hydrogen storage" M. D. Allendorf, Z. Hulvey, T. Gennett, A. Ahmed, T. Autrey, J. Camp, E. S. Cho, H. Furukawa, M. Haranczyk, M. Head-Gordon, S. Jeong, A. Karkamkar, Di-Jia Liu, J. R. Long, K. R. Meihaus, I. H. Nayyar, R. Nazarov, D. J. Siegel, V. Stavila, J. J. Urban, S. P. Veccham and B. C. Wood, *Energy Environ. Sci.* **2018**, 11, 2784--2812
3. "Hydrogen storage and fuel cells", Di-Jia Liu, *AIP Conference Proceedings*, 1924, 020008 (**2018**)

3.2 Presentations

1. HyMARC Seedling: "Graphene-Wrapped" Complex Hydrides as High-Capacity, Regenerable Hydrogen Storage Materials, Di-Jia Liu, Lina Chong, Qingfeng Ge, 2018 DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting June 13-15, 2018, Washington, D.C.
2. HyMARC Seedling: "Graphene-Wrapped" Complex Hydrides as High-Capacity, Regenerable Hydrogen Storage Materials, Di-Jia Liu, Lina Chong, Qingfeng Ge, 2017 DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting June 5-9, 2017, Washington, D.C.
3. HyMARC Seedling: "Graphene-Wrapped" Complex Hydrides as High-Capacity, Regenerable Hydrogen Storage Materials, Di-Jia Liu, Lina Chong, Qingfeng Ge, Hydrogen Storage Tech Team (H_2ST^2), Southfield, MI, August 17, 2017
4. Hydride@graphene composites for hydrogen storage with improved kinetics and cyclability, Lina Chong & Di-Jia Liu, Oral Presentation at 255th ACS National Meeting, New Orleans, LA, March 18-22, 2018
5. Research on Novel Reversible Hydride-based Hydrogen Storage Materials, Lina Chong, Gordon Research Conference, Stonehill College, MA, July 15 – July 21, 2017.

3.3 Recognition

1. The Maria Goeppert Mayer Fellowship, Awarded to Lina Chong, October 1, 2017

Chemical Sciences & Engineering Division
Argonne National Laboratory
9700 South Cass Avenue, Bldg. 241
Argonne, IL 60439

www.anl.gov