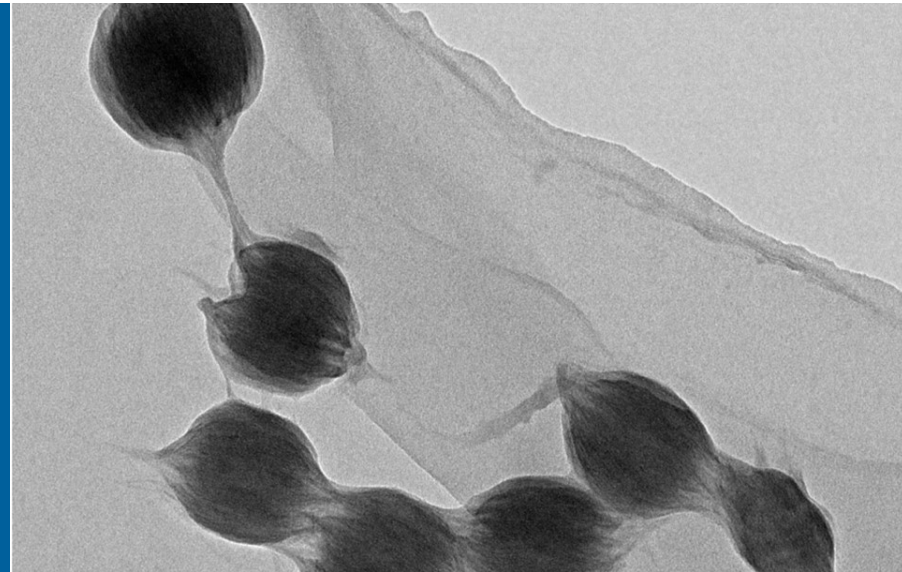


HYMARC SEEDLING: “GRAPHENE-WRAPPED” COMPLEX HYDRIDES AS HIGH-CAPACITY, REGENERABLE HYDROGEN STORAGE MATERIALS



DI-JIA LIU (LEAD) & LINA CHONG, ARGONNE NATIONAL LABORATORY
QINGFENG GE (SUB), SOUTHERN ILLINOIS UNIVERSITY

Project ID: st136

This presentation does not contain any proprietary, confidential, or otherwise restricted information

2018 DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting
June 13-15, 2018, Washington, D.C.

OVERVIEW

Timeline

- Project start: Oct. 2016
- Phase I end: Mar. 2018
- Phase II end: Sept. 2019*

*(If Go decision is made)

Budget

- Total project requested: \$1.114 Million
 - DOE share: \$1 Million
 - Contractor share: \$114 K
- Funding in FY2017 (Phase I)
 - DOE fund received: \$ 250 K
 - DOE Fund Spent: \$ 250 K

Barriers

- Barriers addressed
 - A. System Weight and Volume
 - B. System cost
 - C. Efficiency
 - D. Durability/Operability

Partners

- Interactions/collaborations
 - Argonne National Laboratory (Lead)
 - Southern Illinois University (Subcontractor)
 - HyMARC (SNL, LLNL, LBNL)
 - HySCORE (NREL, PNNL)

RELEVANCE – CURRENT CHALLENGES FOR ONBOARD HYDROGEN STORAGE TECHNOLOGIES

Complex Hydride H₂ Storage Materials

Advantages

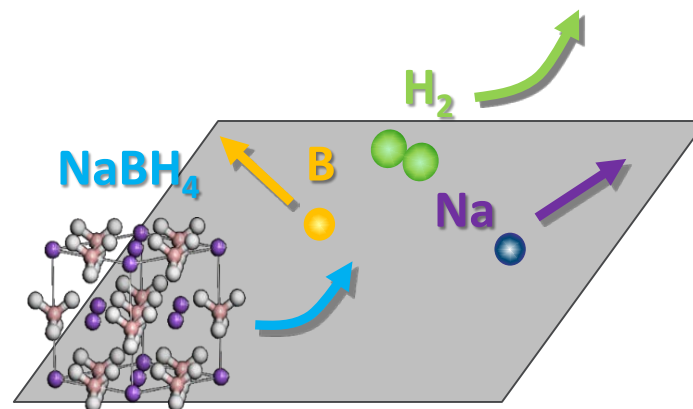
- High gravimetric & volumetric capacities
 - Typically (10 ~14 wt.%) (0.08 ~0.15 kg/L)
- Low on-board storage pressure
 - Normally at ambient

Challenges

- Poor recyclability
 - Typically less than 2 ~ 3 cycles
- Poor H₂ Purity
 - Often contaminated by by-products
- Poor DeH₂/ReH₂ Kinetics
 - High temperature required for DH₂, high pressure required for RH₂
- Lack of confinement media
 - Most hosts have high parasitic weight, causing reduction of overall capacity

DOE H₂ Storage Technology Target

Storage Parameter	Units	2020	Ultimate
System Gravimetric Capacity:	kWh/kg (kg H ₂ /kg system)	1.5 (0.045)	2.2 (0.065)
System Volumetric Capacity:	kWh/L (kg H ₂ /L system)	1.0 (0.030)	1.7 (0.050)
Storage System Cost	\$/kWh net	10	8



Encapsulating dehydrogenation products is essential for regeneration

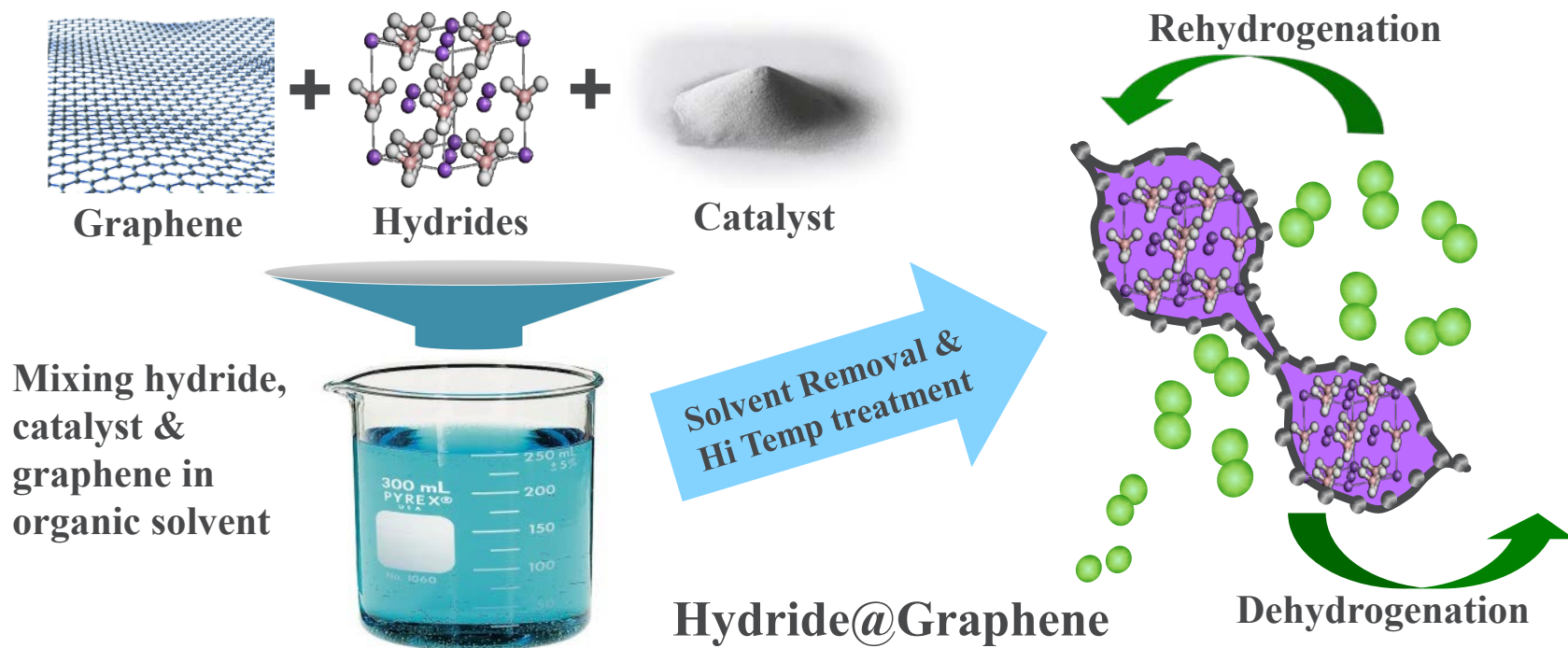
RELEVANCE – OBJECTIVE

- **Phase I** – Deliver at least one “hydride@graphene” material with reversible total gravimetric capacity >8 wt% H₂ and total volumetric capacity >0.03 kg H₂/L at temperatures $<400^{\circ}\text{C}$ over at least five sorption/desorption cycles as validated by a DOE designated lab.
- **Overall** – To produce one or more hydride@graphene composite material with *regenerable / reversible* H₂ storage total gravimetric capacity >10 wt.% and volumetric capacity greater than 0.055 kg H₂/L.

Potential Advantages of Hydride@Graphenes & Their Impact to Technology Barriers

- **System Weight and Volume** – Hydride@Graphenes have potential to reach both gravimetric and volumetric based on theory and preliminary experimental data
- **System Cost** – Hydride@Graphene is synthesized from robust, solution based chemistry, scalable for industrial production.
- **Efficiency** – Hydride@Graphenes has improved dehydrogenation (DH) and rehydrogenation (RH) kinetics and temperatures compared to bulk hydrides.
- **Durability/Operability** – Hydride@Graphenes show promise to improve DH/RH regenerability with cleaner hydrogen.

APPROACH – COMPLEX HYDRIDE ENCAPSULATED BY GRAPHENE “HYDRIDE@GRAPHENE”



- Improved DH/RH recyclability by retaining DH byproducts for hydride recovery
- Improved DH/RH kinetics by encapsulated catalyst in conformable graphene
- Improved gravimetric capacity by using lightweight graphene as encapsulating agent
- Improved hydrogen purity with graphene permeable to H_2 but not byproducts

APPROACH – DEVELOPMENT STRATEGY

Hydride@Graphene & Catalyst Exploration (ANL)

Characterization & Optimization (ANL/HyMARC/HySCORE)

Computational Modeling (SIU/HyMARC)

- Improving existing and exploring new hydride@graphene syntheses through rational design
- Structure characterization
- Post synthesis treatment

- H₂ storage capacity & reversibility measurements
- DeH₂/ReH₂ kinetics measurement
- Surface/structural property characterizations

- Computational guidance on size-dependent DeH₂/ReH₂ activation energy
- Computational guidance on dopant catalytic effect

- Exploring new hydride@graphenes with enhanced H₂ storage capacities
- Reducing graphene usage in hydride@graphene for higher capacities
- Lowering DH/RH temperatures through catalytic additives

Collaboration with HyMARC/HySCORE to accelerate project development!

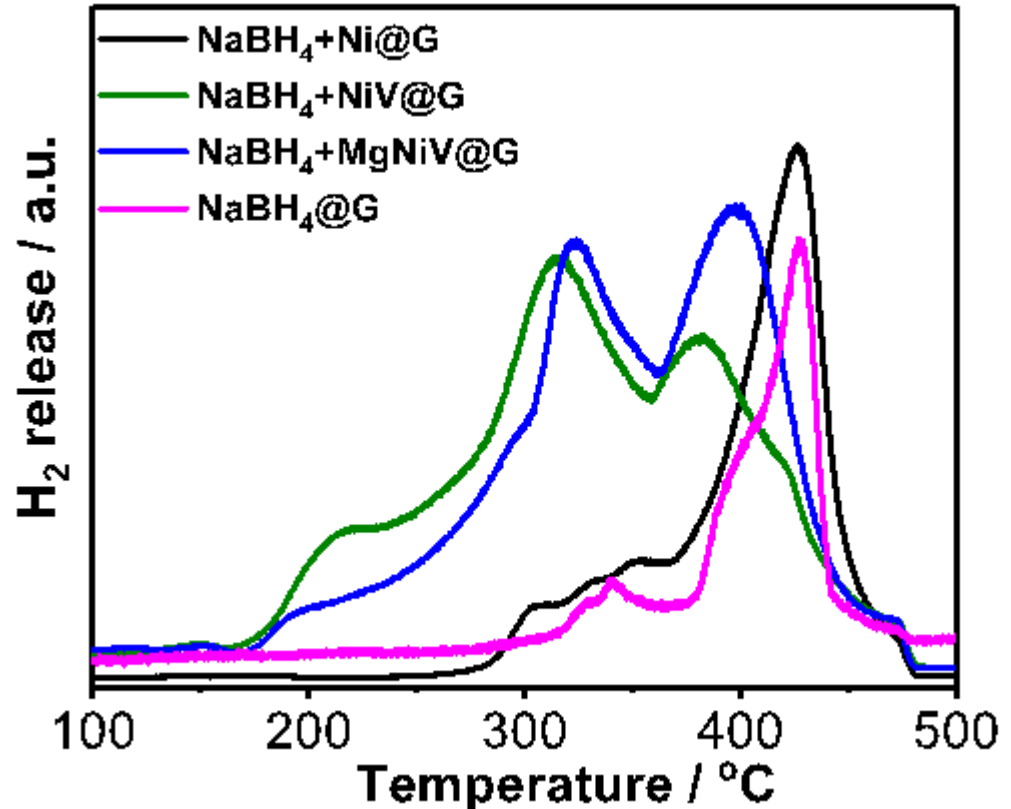
APPROACH – PHASE I MILESTONES

Month/ Year	Milestones/Go-NoGo DP	Milestone Status
June/17	Regenerable $\text{DeH}_2/\text{ReH}_2$ storage capacity of > 8 wt.%	<i>Completed:</i> Storage capacities ranging from 9 wt.% to 7.4 wt.% achieved during six DH/RH cycles over a new batch of NaBH_4 @graphene with 9.1 wt.% theoretical capacity
Sept/17	To produce sufficient quantity MgH_2 @graphene as precursor for binary hydride@graphenes	<i>Completed:</i> New solution based MgH_2 @graphene synthesis was successfully developed and tested in combination of NaBH_4 .
Sept/17	To complete structural & capacity characterization for modified NaBH_4 @graphene	<i>Completed:</i> TPD, TGA, XRD, and FTIR and experiments are completed for the NaBH_4 @graphene and several related systems with catalytic additives
Dec./17	Deliver a “hydride@graphene” with reversible total gr. capacity >8 wt% H_2 and total vol. capacity >0.03 kg H_2 /L at $T < 400^\circ\text{C}$ over 5 sorption/ desorption cycles	<i>70% completed:</i> Over 300 mg of catalyst added NaBH_4 @graphene was shipped and tested at SNL for 5 DH/RH cycles. Gr. capacity ranges from 7 wt.% to 4 wt. % and Vol. capacity ranges from 0.04 kg H_2 /L to 0.022kg H_2 /L, test under temperature between 390°C to 395°C .

ACCOMPLISHMENT – CATALYST-ADDED NaBH₄@G's IMPROVED DH KINETICS

- Transition metals (TMs) are known to promote dehydrogenation from NaBH₄@G
- New wet-chemistries were developed in FY18 to add several TMs into NaBH₄@G composites
- Ni, Mg and V were found to significantly improve DH kinetics by reducing H₂ release temperature

TGAs of several TM added NaBH₄@Gs

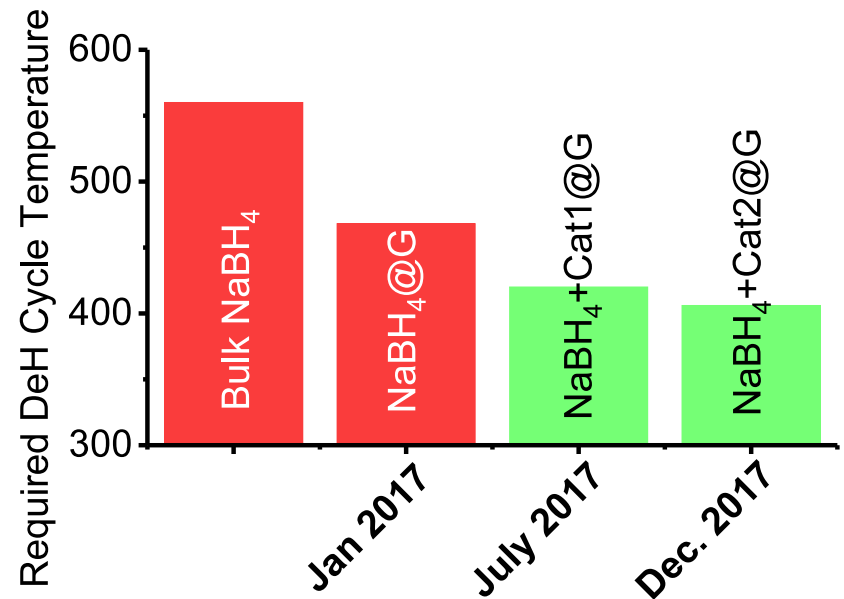
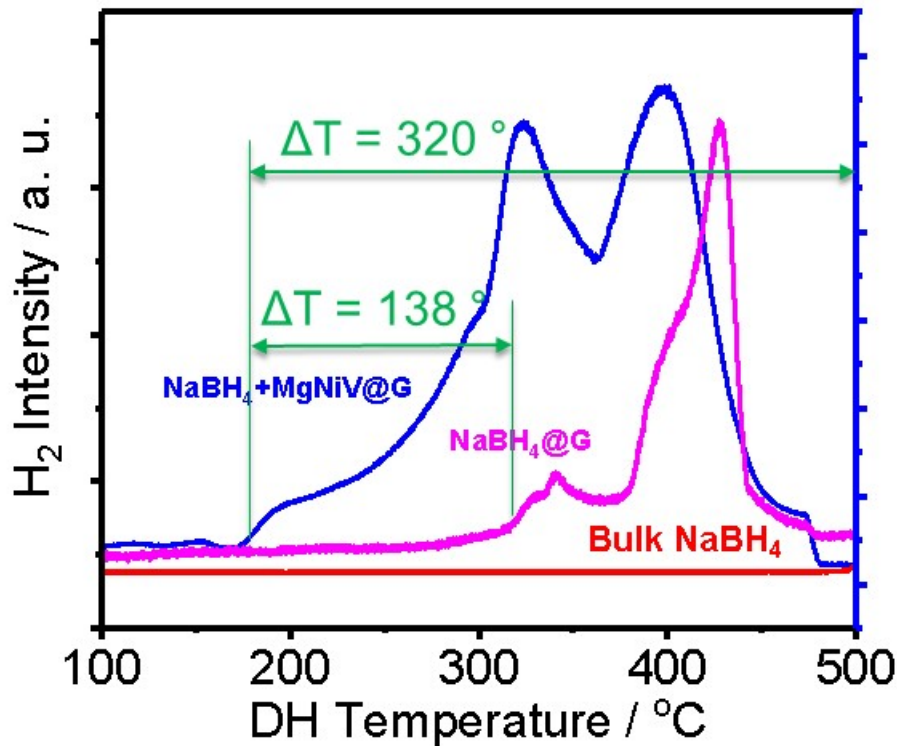


Significant improvements in DH kinetics over undoped NaBH₄@G by catalysts were observed!

ACCOMPLISHMENT – DH TEMPERATURE SIGNIFICANTLY REDUCED BY CATALYST

Improving DH kinetics by catalytic additive...

... led to gradual reduction of DH temperature applied for DH/RH cycling studies in our lab.

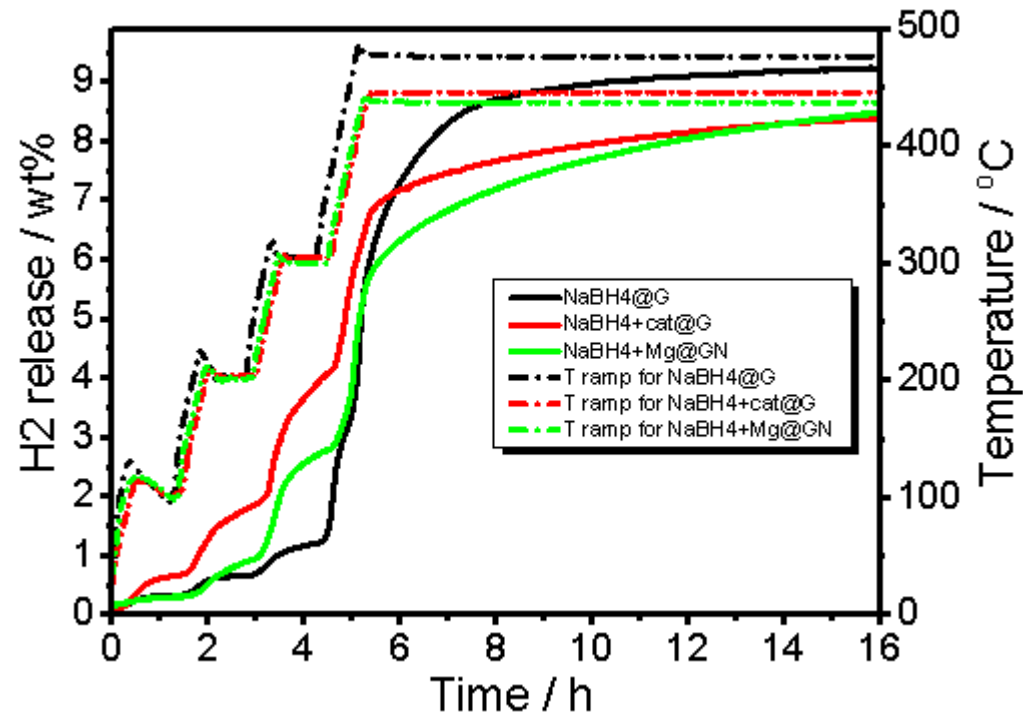


- Catalyst + NaBH₄@G reduced onset H₂ release temperature to as low as 180°, representing 320 degree reduction over bulk NaBH₄ (500°) or 138 degree reduction over NaBH₄@G (318°) at beginning of the project
- The second major H₂ desorption peak still centers at 400 °C.

ACCOMPLISHMENT – KINETICS IMPROVEMENT REFLECTED BY LOWER DH TEMPERATURE ISOTHERM

- Improvement in DH kinetics led to gradual reduction of isotherm temperature for hydrogen desorption
- Mg-based additive is most effective in improving DH kinetics
- Significantly more hydrogen are released at 200 °C and 300 °C plateaus.
- A majority of hydrogen in hydride still desorbs at 400 °C or higher

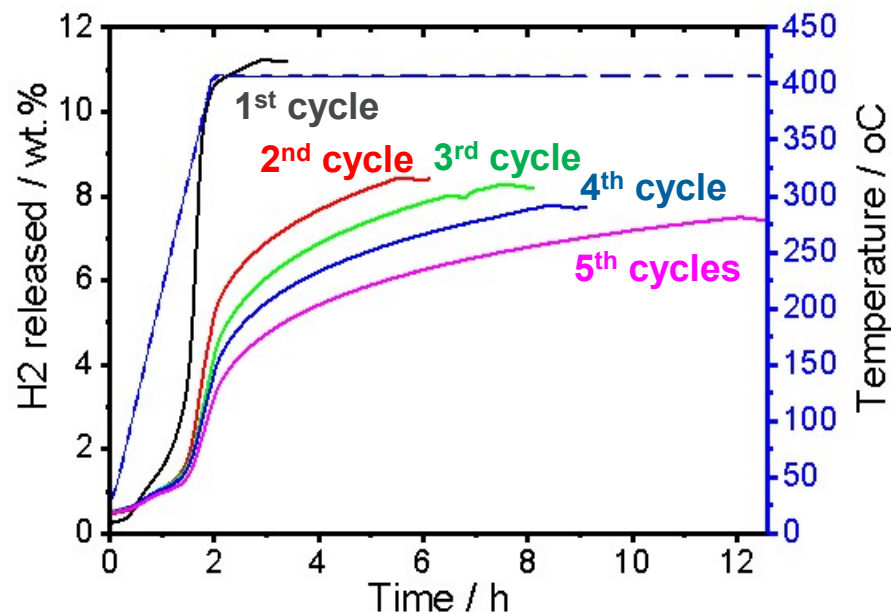
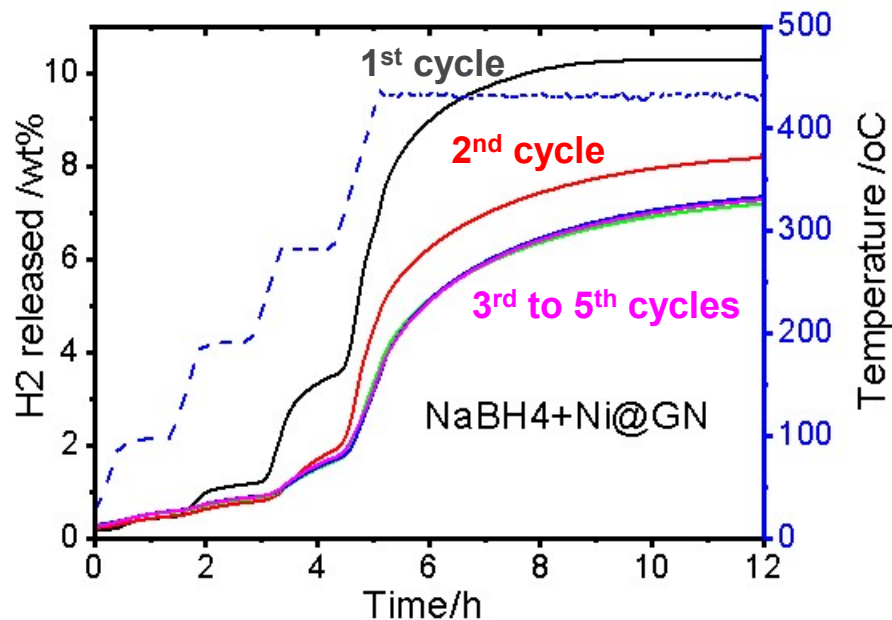
Temperature-programmed desorption



Temperature-programmed desorption showed higher fraction of H₂ released at T ≤ 300 °C after catalyst added. More Improvement is needed to reach 100% release at ≤ 400 °C

ACCOMPLISHMENT – RECENT FIVE DH/RH CYCLE STUDIES AT REDUCED DH TEMPERATURES

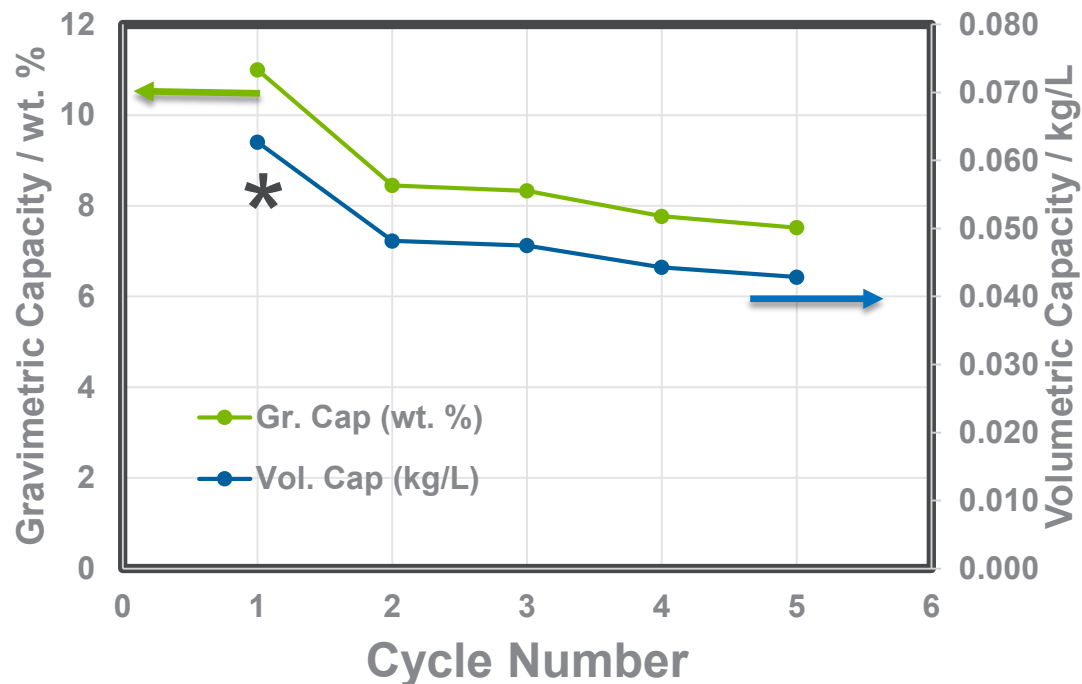
5-cycle DH/RH experiments were successfully carried out through temperature-programmed H₂ discharge at $T_{max} = 430$ °C (left) and one-step discharge at $T = 406$ °C after further catalyst refinement (right), both retained ~ 7 wt.% capacity at the end of the cycle



The catalyst improvement lowered H₂ release temperature to 406 °C and ~7 wt.% capacity retention. However, the dehydrogenation profile changes as cycle number increases, indicating that the kinetic limitation still exists.

ACCOMPLISHMENT – GRAVIMETRIC & VOLUMETRIC CAPACITIES OF CATALYST-ADDED NaBH₄@G

H₂ DH/RH measurement using one-step isotherm release



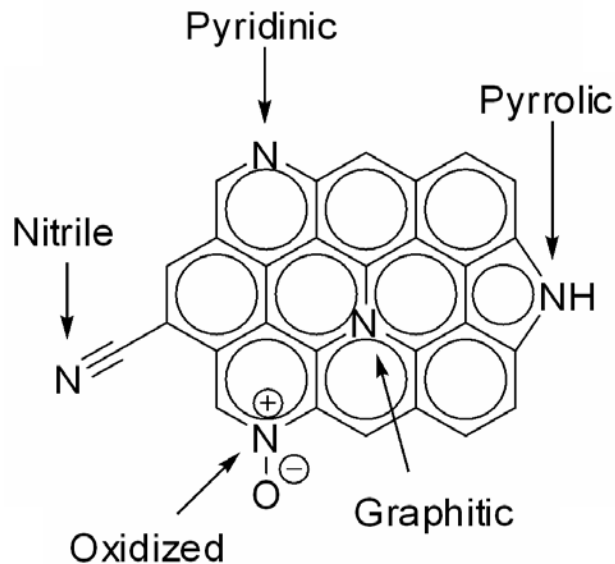
* High values found in the 1st cycle was due to trapped solvent which was not completely removed during pretreatment

Condition: DH $T = 406$ °C one-step process; RH $T = 350$ C, $P = 90$ bars, duration = 10 – 15 hours, packing density 0.57 g/cm³

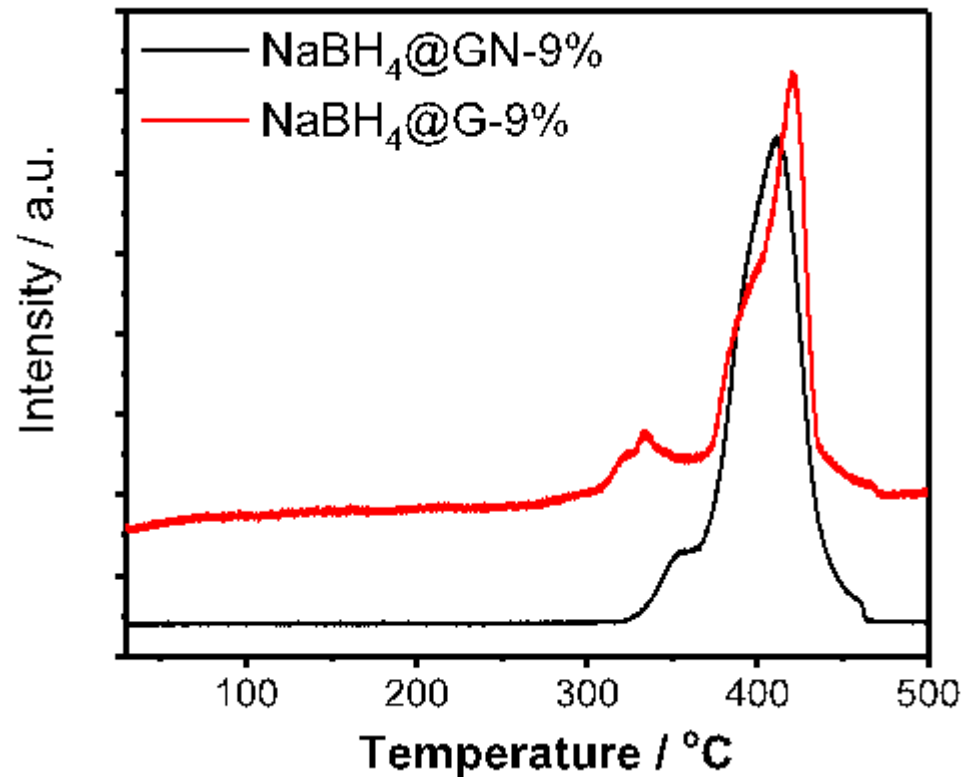
Our in-house measurement showed excellent gravimetric and volumetric capacities measured during five DH/RH cycles

ACCOMPLISHMENT – IMPROVING DH KINETICS THROUGH N-DOPED GRAPHENE

- N-C catalytic sites and defects in graphene may promote dehydrogenation kinetics
- N-doped graphene was prepared through NH_3 treatment under high temperature over pure graphene



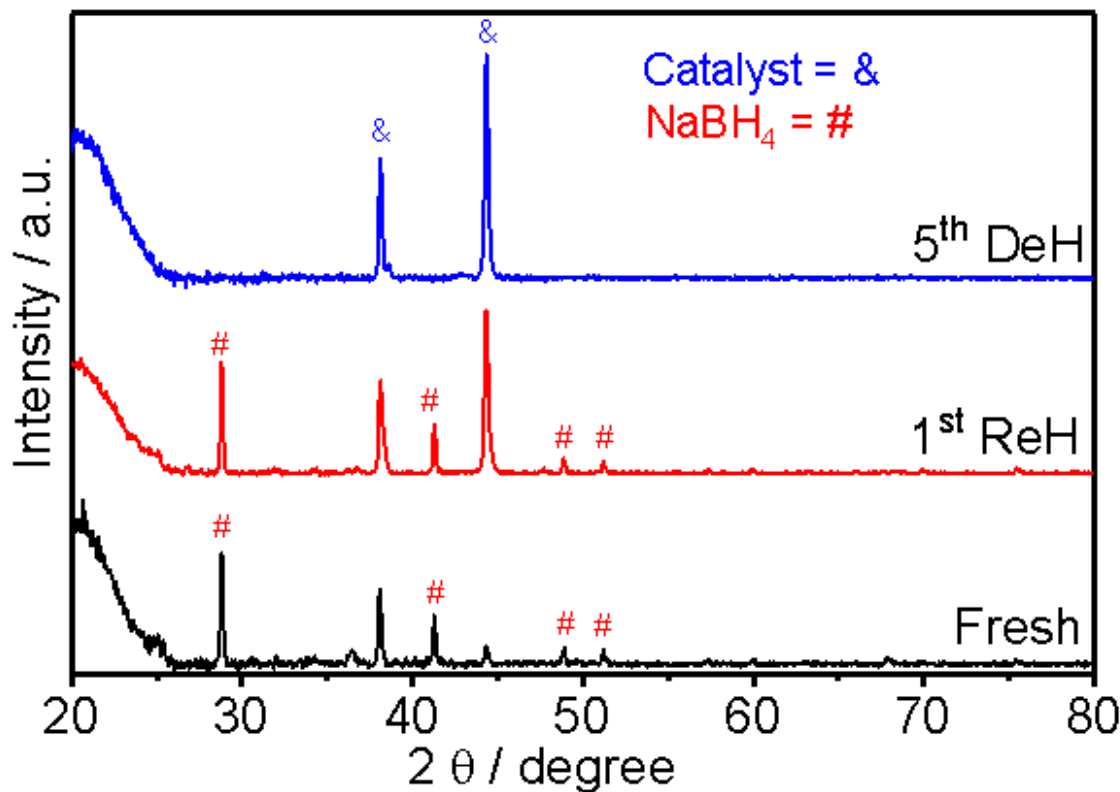
TGA Study of DH_2 from NaBH_4 @GN



N-doped graphene offers only marginal improvement in DH_2 temperature improvement

ACCOMPLISHMENT – UNDERSTANDING OF HYDRIDE STRUCTURE DURING DH/RH

XRD study on fresh, RH and DH sample after 5th cycle

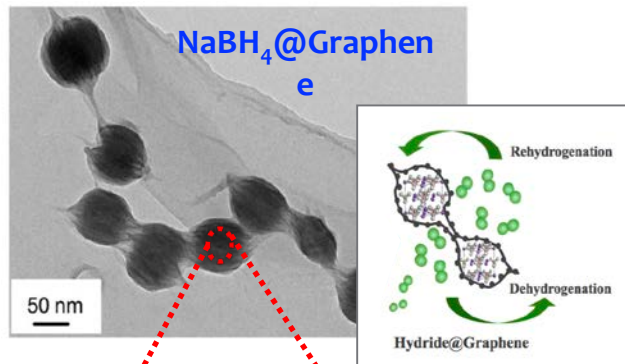
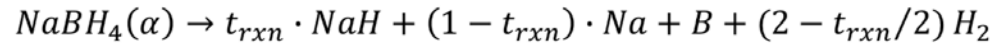
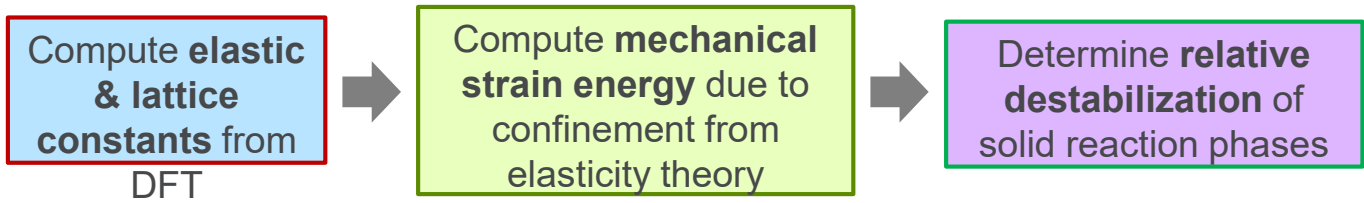


- XRD shows loss of NaBH₄ crystallites during first (not shown) and last DH cycle; and recovery of crystallite structure after RH
- Alloy peaks from catalyst are identified with their intensities increased through multiple cycling

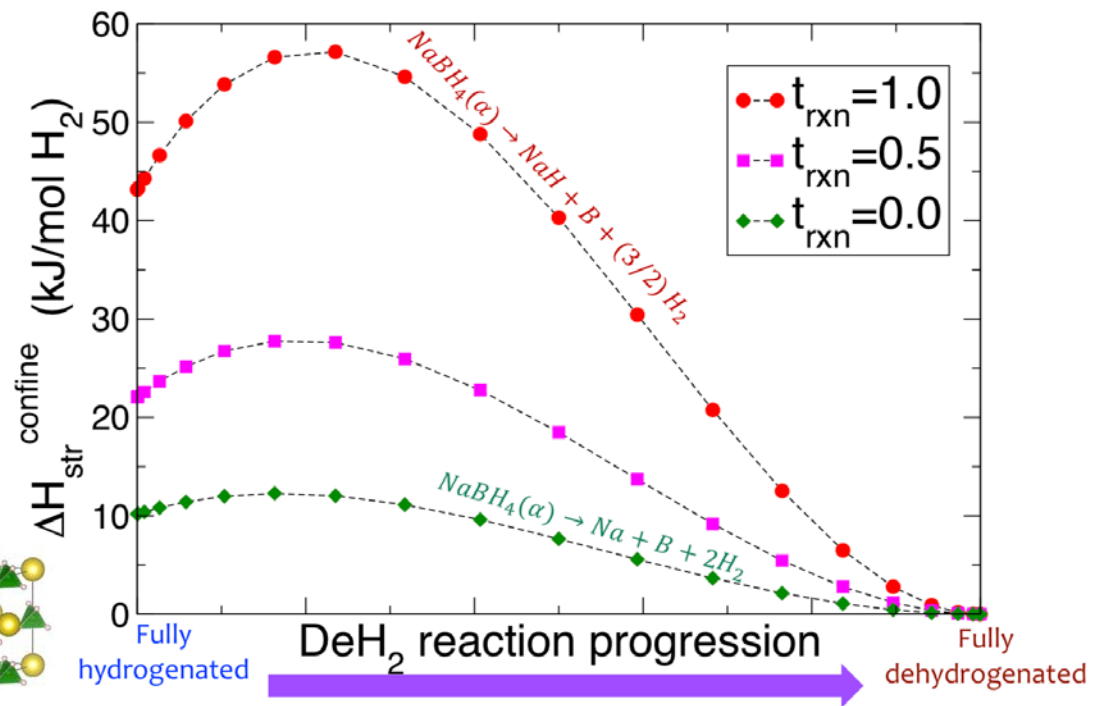
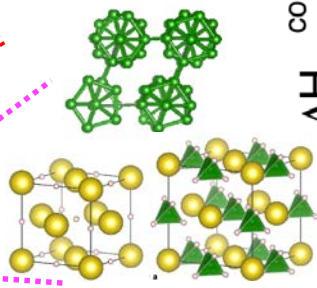
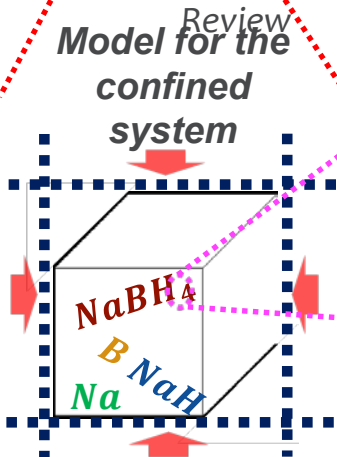
COLLABORATIONS

Partner	Project Role
HyMARC – LLNL & LBNL	Computational modeling and simulation on encapsulated hydrides (result included)
HyMARC – SNL	Hydride hydrogen storage capacity validation (first validation experiment result included)
HySCORE – PNNL	Solid state NMR investigation on $\text{NaBH}_4@G$ at different DH/RH stage (sample submitted, study underway)
HySCORE – NREL	Temperature-programmed desorption study on different NaBH_4 composites. (sample sent, study underway)
Southern Illinois University	Project subcontractor on the computational modeling (investigation on confinement effect completed and reported in last AMR)

COLLABORATIONS – MULTISCALE MODELING APPROACH FOR COMPUTING STRAIN ENERGY @ LLNL



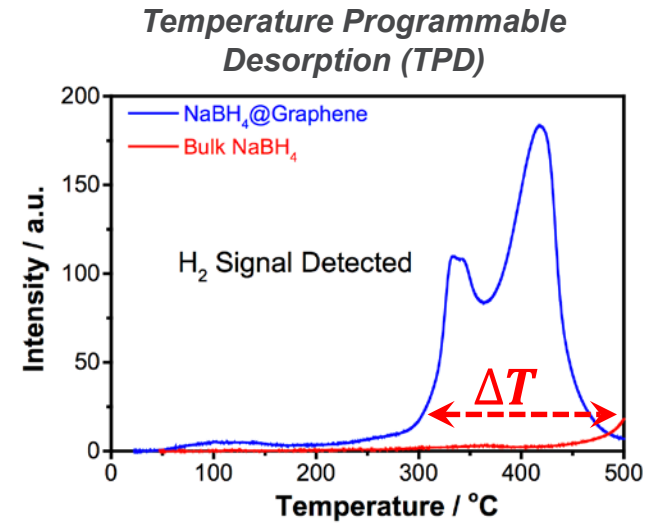
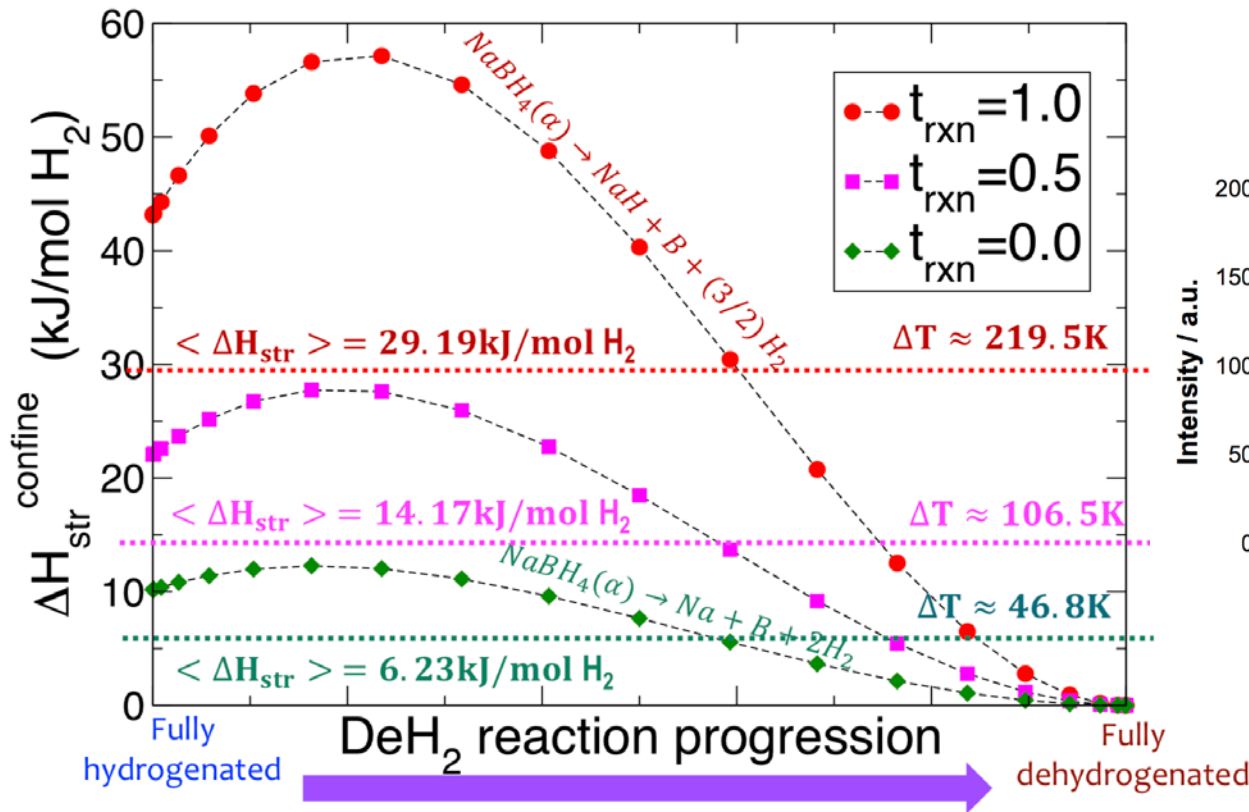
D.J. Liu et al., 2017 Annual Merit Review



HyMARC's multiscale strain energy calculation method has been applied to $NaBH_4@Graphene$ system to compute the confinement strain/stress energy.

COLLABORATION – IMPACT OF CONFINEMENT STRAIN ENERGY ON THERMODYNAMICS

HyMARC's multiscale modeling approach quantifies the destabilizing effect of confinement stress on reaction enthalpy due to volume expansion upon hydrogenation



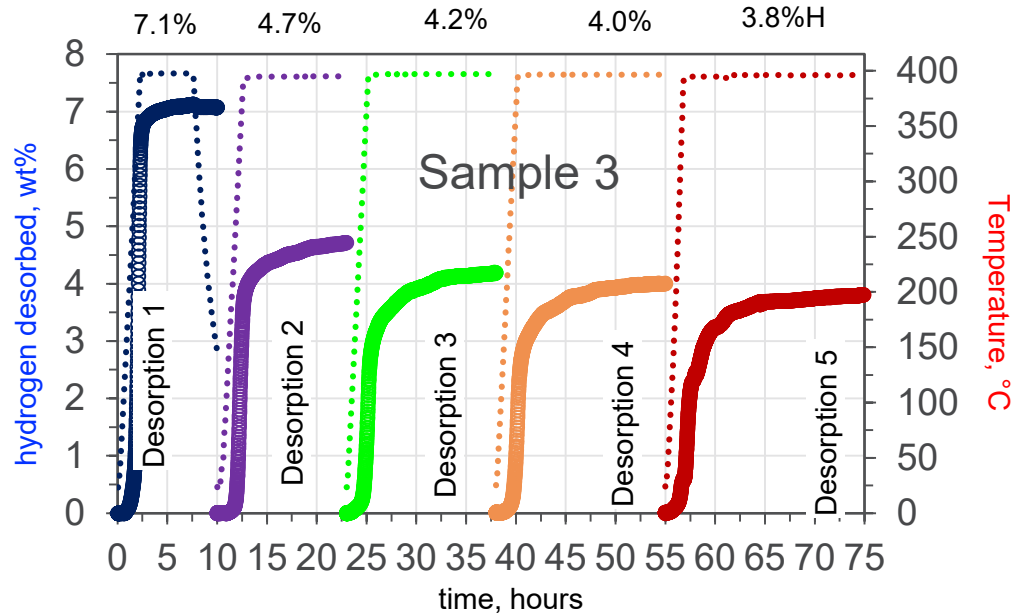
D.J. Liu et al., 2017 Annual Merit Review

Elastic strain energy may explain the confinement effect on ΔT exhibited in TPD measurement.

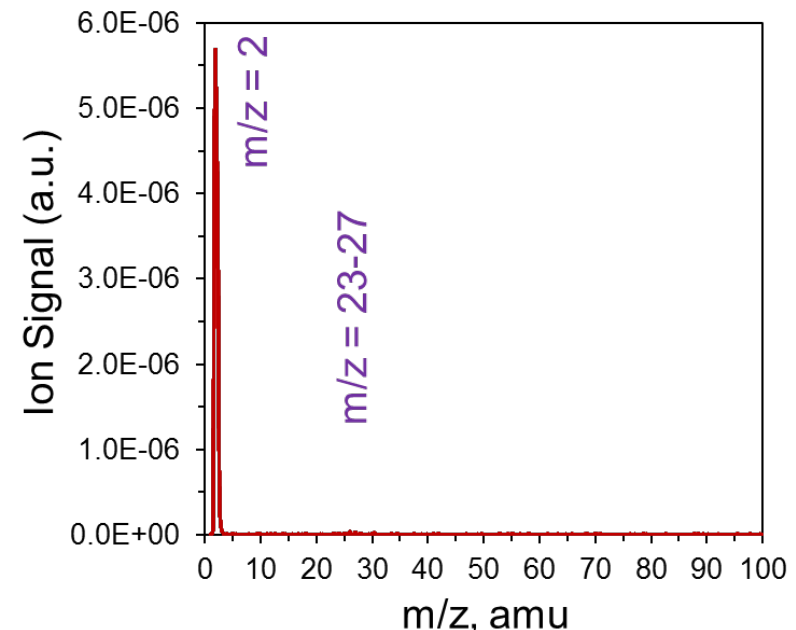
COLLABORATIONS – VALIDATION MEASUREMENT @ SNL

- Three batches of NaBH₄@G samples (total 650 mg or ~ 300 mg solvent-free) were sent to SNL, three separate tests were conducted
- 5 DH/RH cycles were performed. DH capacity was measured at 392 ~ 395 °C, H₂ purity and volumetric packing density were also measured.

5-cycle isotherm measurement



RGA at the end of 5th desorption



- Validation at SNL confirmed the cycloability of NaBH₄@G sample in five DH/RH cycles. However, the capacity was lower than the value by ANL measured at 406 °C.
- RGA measurement showed high purity of H₂ in the dehydrogenation stream with only trace amount to residuals possibly due to fragmented hydrocarbon (solvent) or boranes.

PROPOSED FUTURE WORK

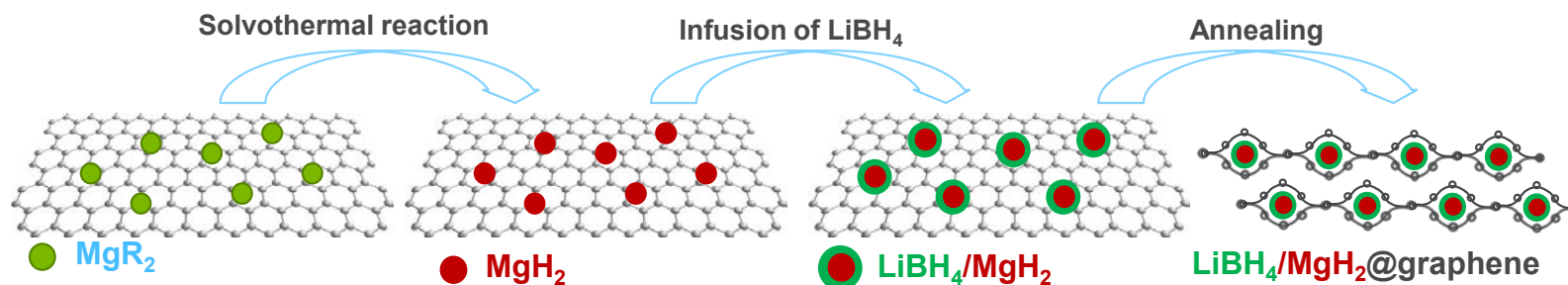
Any proposed future work is subject to change based on funding level

Remaining Phase I Activities

- Continue to explore new catalyst/additive and application method for $\text{NaBH}_4@\text{G}$ to further reduce dehydrogenation temperature and to improve DH/RH kinetics. This approach was originally planned for Phase II, but moved forward to address Phase I DH temperature requirement
- Continue to collaborate with HyMARC on DH and RH mechanisms through computational modeling and structure characterizations (NMR, imaging, etc.)

Planned Phase II Activities

- Initiate synthesis of new binary hydrides with higher theoretical capacities including $\text{LiBH}_4/\text{MgH}_2$ and $\text{LiBH}_4/\text{LiNH}_2$ “wrapped” by graphene, using a sequential synthesis technique (shown by an example below)
- Investigating DH and RH mechanisms through advanced characterization & modeling to guide the design and improvement of hydride@graphene
- Engineering/shaping downselected hydride@graphene for transportation application



SUMMARY

- New catalyst additives significantly improved dehydrogenation kinetics and lowered initial H₂ discharge temperature from >500 °C in bulk NaBH₄ to 180 °C in NaBH₄+Cat@G, a 320 degree of reduction.
- Hydrogen release under one-temperature DH cycle was achieved for NaBH₄+Cat@G and demonstrated through a 5-cycle DH/RH test at 406 °C. The gravimetric capacity was maintained at 7.5 wt.% at the end of 5th cycle.
- Computational modeling from HyMARC-LLNL team revealed an importance of lattice strain to DH kinetics. Their calculation predicts the reduction of DH temperature of graphene encapsulated NaBH₄ from 47 K to 220 K depending on the reaction path.
- Validation experiment at HyMARC-SNL repeated five DH/RH cycle for ANL's NaBH₄+Cat@G at 392 °C with high purity H₂ detected by RGA. However, the gravimetric capacity was lower than that obtained at ANL.

ACKNOWLEDGEMENT

- This work is supported by US DOE, Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Office
- Project Manager: Jesse Adams/Zeric Hulvey
- Hydrogen Storage Program Manager: Ned Stetson