IV.C.9 HyMARC Seedling: "Graphene-Wrapped" Complex Hydrides as High-Capacity, Regenerable Hydrogen Storage Materials

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Project Start Date: October 1, 2016
Project End Date: September 30, 2019

Overall Objectives

- Produce one or more hydride@graphene composites with regenerable hydrogen storage gravimetric density >10 wt% and volumetric density >0.055 kg H_2/L.
- Develop a scale-up plan of manufacturing the new composite at the cost <$333/kg H_2.
- Establish fundamental understanding on the improved dehydrogenation and rehydrogenation kinetics promoted by graphene.

Fiscal Year (FY) 2017 Objectives

- Deliver a hydride@graphene system with reversible >8 wt% total gravimetric and >0.03 kg H_2/L total volumetric hydrogen storage capacities at temperatures <400°C over at least five dehydrogenation (DH)–rehydrogenation (RH) cycles.
- Understand the structural changes in $NaBH_4$@graphene during DH and RH cycles.
- Improve $NaBH_4$@graphene dehydrogenation kinetics by exploring structural or chemical approaches.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

(A) System Weight and Volume

(B) System Cost

(C) Efficiency

(D) Durability/Operability

(E) Charging/Discharging Rates

(O) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project is to design and synthesize "graphene wrapped" complex hydride composites as the next generation hydrogen storage materials that meet the following DOE hydrogen storage targets.

- Excess gravimetric hydrogen storage capacity:
  - DOE 2025 Target: 5.5 wt% system basis
  - Project Target: 10 wt% on material basis
- Volumetric H_2 storage capacity:
  - DOE 2025 Target: 0.040 kg H_2/L of system
  - Project Target: 0.055 kg H_2/L of material total

FY 2017 Accomplishments

- Successfully synthesized a $NaBH_4$@graphene composite and demonstrated six DH and RH cycles with measured capacity between 7.4 wt% and 9 wt%.
- Successfully demonstrated the improvement in hydrogen release kinetics at lower temperature in $NaBH_4$@graphene over the bulk phase $NaBH_4$.
- Successfully demonstrated the regeneration of sodium borohydride in $NaBH_4$@graphene at 350°C and 40 bar by X-ray diffraction and other characterization techniques.

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INTRODUCTION

This project is focused on the development of a new class of hydrogen storage material, hydride@graphene, for next-generation hydrogen-powered fuel cell vehicles. The new approach is based on a recent breakthrough through the collaboration between Shanghai Jiao Tong University and Argonne National Laboratory [1]. Using a simple solvent-based method, we successfully synthesized a "nanoencapsulated" sodium borohydride–graphene composite, $NaBH_4$@graphene, in which $NaBH_4$

nanocrystallites are individually wrapped by single layer graphene. The new composite offers regenerable 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 will expand the method to prepare a broader range of hydride@graphene composites using the complex hydrides of higher intrinsic gravimetric and volumetric densities. We will explore various morphological and chemical approaches to improve the DH–RH kinetics, guided by computational modeling. We will collaborate with Hydrogen Materials–Advanced Research Consortium (HyMARC) in modeling, synthesis, measurement, and characterization.

APPROACH

The new approach we will apply in this project will focus on improving the hydrogen storage capacity of the hydride–graphene composites by reducing the amount of graphene while maintaining the nano-encapsulation. Phase I focuses on improving the synthesis of the $NaBH_4$@graphene system and initiating the investigation of Mg-based hydride@graphene systems. The $NaBH_4$@graphene composite in which sodium borohydride nanocrystallites are individually wrapped by single layer graphene, can be prepared from a solvent-based method (Figure 1). The new composite offers regenerable hydrogen storage capacity in multiple DH and RH cycles. The improved $NaBH_4$@graphene will be evaluated by a DOE designated lab for validation. Throughout the project, the new hydride composites will be characterized using various conventional and advanced characterization tools. The DH–RH capacities will be first evaluated in-house before delivering to other labs. Computational modeling and simulation will be carried out to provide insights for DH–RH kinetics improvement. We will also leverage the existing capabilities at HyMARC in computational modeling, structural characterization, and capacity measurement to facilitate the material development.

RESULTS

The project was initiated at the beginning of FY 2017. During this period, we accomplished the following tasks.

We prepared several batches of $NaBH_4$@graphene with theoretical gravimetrical capacities ranging from 7 wt% to 9 wt% on the composite basis. These samples were tested under multiple DH and RH cycles. The DH tests were completed through temperature-programmed discharge while the RH cycles in between were achieved by recharging the composite at elevated pressure (40 bar) and temperature (350°C). Figure 2a shows the hydrogen releases in six consecutive cycles measured by a Sievert apparatus over an $NaBH_4$@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, a gravimetric capacity of 9 wt% was reached at the end of the first discharge. After the regeneration, the gravimetric capacity was reduced but maintained above 7.3 wt% during the following five cycles, shown by Figure 2b,

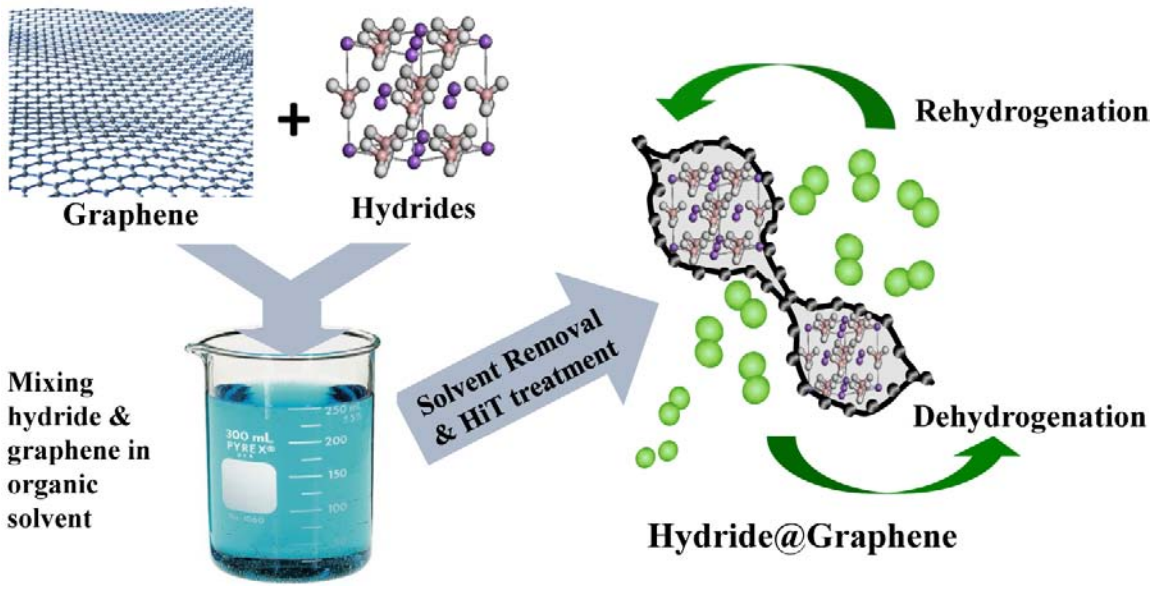


FIGURE 1. Schematics of solution-based synthesis of hydride wrapped by graphene

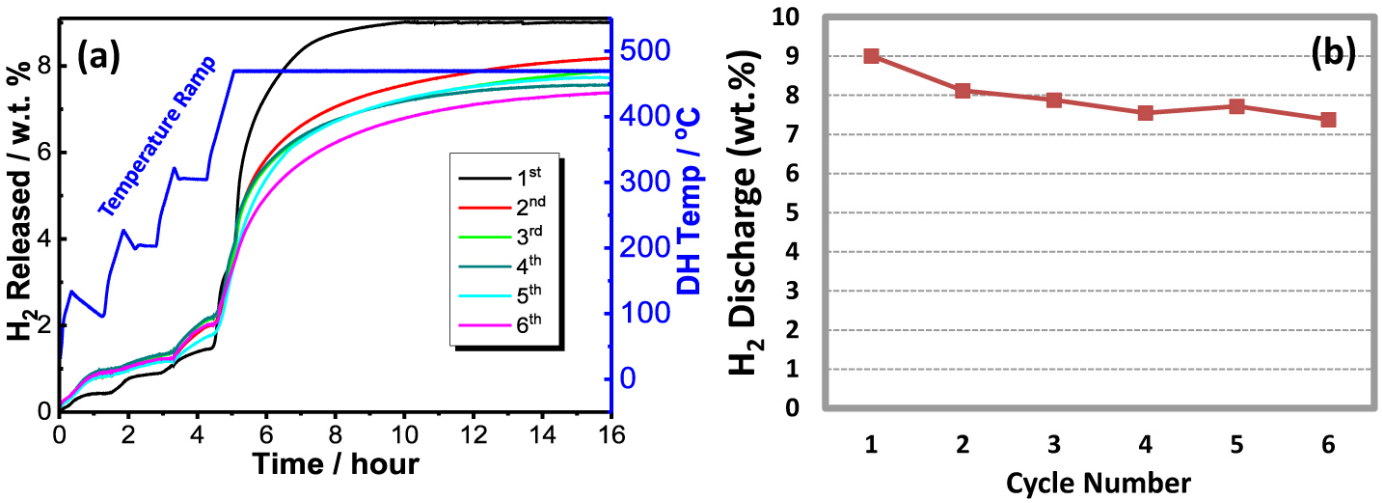


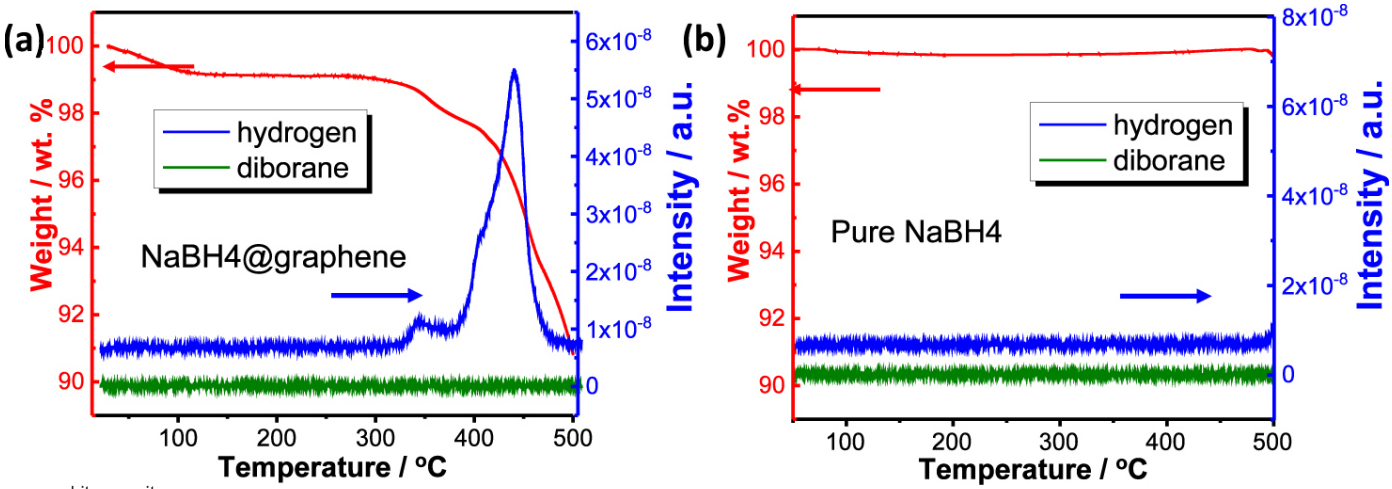
FIGURE 2. (a) Temperature-programmed hydrogen release from $NaBH_4$@graphene; (b) the hydrogen discharge gravimetric capacity as a function of cycle number

representing the retention of >81% of the theoretical value. These values are also listed in Table 1. Compared to previous studies on bulk or nano-confined complex hydrides, the graphene encapsulated hydride developed by our approach show significant improvements in capacity, cyclability, and reversibility [2].

TABLE 1. Gravimetric Capacities and Their Percentage against Theoretical Value During DH Cycles for $NaBH_4$@Graphene

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%

We also investigated the reactivity and structural changes of $NaBH_4$@graphene during hydrogen discharge and through the DH–RH cycle. To demonstrate the chemistry and kinetics affected by graphene, the investigations generally included bulk $NaBH_4$ for comparison. Figure 3 shows a side-by-side study on the hydrogen release as the function of DH temperature between NaBH4@graphene and bulk $NaBH_4$ using a thermogravimetric analysis method. In this study, discharged hydrogen was detected by mass spectrometer in tandem of thermogravimetric analysis while the sample weight loss was measured by the gravimetric balance. For bulk $NaBH_4$, no decipherable amount of hydrogen release was found until the temperature nearly reached 500°C. The $NaBH_4$@graphene, on the other hand, started to release a significant amount of hydrogen at a temperature as low as 330°C. Two peaks near temperatures of 340°C and 435°C represent the hydrogen detachment from two different intermediate species during hydride decomposition. Clearly,



a.u. – arbitrary units

FIGURE 3. Thermogravimetric analysis study on dehydrogenation from (a) $NaBH_4$@graphene and (b) bulk $NaBH_4$ as a function of temperature

the interaction between graphene and $NaBH_4$ has facilitated the hydrogen release from the NaBH4@graphene composite. We also investigated the hydride structural reversibility in $NaBH_4$@graphene during a DH and RH cycle using X-ray diffraction (XRD). Three samples, including fresh composite, dehydrogenated and rehydrogenated $NaBH_4$@graphene, and bulk $NaBH_4$ were studied. Their XRD spectra are shown in Figure 4. The pattern of fresh $NaBH_4$@graphene matches well with that of bulk $NaBH_4$, suggesting that sodium borohydride retained its crystal structure after being encapsulated inside of graphene. After the DH reaction, the peaks associated with $NaBH_4$ all disappeared, as was anticipated due to the loss of hydrogen and therefore the crystal structure. The XRD peaks reappeared after the RH reaction, indicating the recovery of hydride crystallites. We calculated the hydride crystallite size using the Scherrer equation and found that the average hydride particle size in $NaBH_4$@graphene is about 32 nm for both fresh and RH samples, which is about two-thirds of that found in bulk $NaBH_4$ (48 nm).

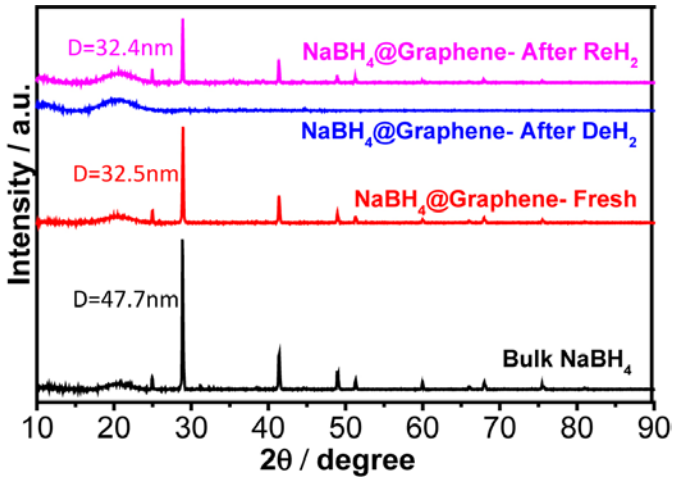


FIGURE 4. Comparison of XRD pattern and particle size for fresh, dehydrogenated and rehydrogenated $NaBH_4$@graphene samples using bulk $NaBH_4$ material as reference

CONCLUSIONS AND UPCOMING ACTIVITIES

We successfully demonstrated hydride cyclability in $NaBH_4$@graphene during multiple DH–RH cycles, measured by temperature-programmed desorption/isotherm regeneration and characterized by a variety of analytic tools. The kinetics of DH was clearly improved for the hydride wrapped by graphene in comparison to its bulk phase. We will continue to improve $NaBH_4$@graphene preparation and testing to reach the capacity and cyclability goals during the reminder of Phase I.

FY 2017 PUBLICATIONS/PRESENTATIONS

1. "Research on novel reversible hydride-graphene based hydrogen storage materials," Lina Chong and Di-Jia Liu, poster presentation at 2017 Gordon Research Conference in "Hydrogen-Metal Systems," July 16–21, 2017, Stonehill College, Easton, MA, USA.

REFERENCES

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. Recent progress in metal borohydrides for hydrogen storage, H.-W. Li, Y. Yan, S. Orimo, A. Züttel, and C.M. Jensen, *Energies,* **2011**, *4*, 185–214.