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

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Overall Objectives

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

Fiscal Year (FY) 2018 Objectives

- To 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 of <400°C over at least five DH–RH cycles.
- To reduce $NaBH_4$@graphene dehydrogenation temperature by exploring catalyst and structural 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[1]:

(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 hydrogen 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 2018 Accomplishments

- Successfully synthesized catalyst-doped $NaBH_4$@graphene composite and demonstrated five DH and RH cycles with measured gravimetric capacity >7.4 wt% at 406°C.
- Successfully demonstrated the improvement in hydrogen release kinetics by lowering the DH temperature by 320°C over bulk $NaBH_4$ or 138°C over $NaBH_4$@graphene at the beginning of the project.

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[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

INTRODUCTION

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 [1]. Using a simple solvent-based method, we successfully synthesized a "nanoencapsulated" sodium borohydride-graphene composite, $NaBH_4$@G, in which $NaBH_4$ 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 the Hydrogen Materials Advanced Research Consortium (HyMARC).

APPROACH

The approach we applied focused on improving the hydrogen storage capacity of the hydride–graphene composites by reducing the amount of graphene while maintaining the nanoencapsulation. We also focused on improving DH and RH kinetics of the $NaBH_4$@graphene system by incorporating catalytic additives within the graphene-wrapped solid mixture. The improved $NaBH_4$@graphene was evaluated by a DOE-designated lab. Throughout the project, the new hydride composites were characterized by various characterization tools. Computational modeling and simulation were carried out simultaneously to provide insights for DH–RH kinetics.

RESULTS

During FY 2018, we accomplished the following tasks.

To improve DH–RH kinetics, we prepared and evaluated a number of $NaBH_4$@G composites containing low concentrations of transition metals (typically around one percent) synthesized by wet chemistry. The transition metals explored were magnesium, vanadium, and nickel. These metals are known to form hydrides with lower DH temperatures. By incorporating them with $NaBH_4$, we anticipated that they could serve as catalysts to facilitate DH–RH reactions through solid-state interaction with $NaBH_4$ confined by graphene. Figure 1 shows hydrogen release as a function of temperature for a representative composite, $NaBH_4$+MgNiV@G, obtained from thermogravimetric analysis (TGA). For comparison, the hydrogen release from $NaBH_4$@G and bulk $NaBH_4$ are also included. The DH onset temperature for $NaBH_4$+MgNiV@G was lowered by 138°C compared to $NaBH_4$@G and 320°C compared to bulk $NaBH_4$, indicating significant improvement in DH kinetics by the catalysts. The challenge at this point is that a significant fraction of hydride still decomposes at temperatures above 400°C as shown by the second peak in Figure 1 for $NaBH_4$+MgNiV@G, which suggests that the catalyst has not interacted with the entire phase of the hydride. Better dispersion and mixing are needed to further improve the DH kinetics.

The catalyst-promoted DH kinetics are also reflected in the temperature-programmed hydrogen desorption in the hydrogen discharge capacity measurement. Figure 2 shows a side-by-side comparison between catalyst-added hydride ($NaBH_4$+MgNiV@G) and $NaBH_4$@G during step-wise hydrogen release from room temperature to 430°C at 100-degree intervals. Clearly, with the improved DH kinetics, the $NaBH_4$+MgNiV@G composite discharged more hydrogen than $NaBH_4$@G did at low temperature steps. For example, ~4 wt% hydrogen was already discharged at 300°C for $NaBH_4$+MgNiV@G, compared to ~1 wt% for $NaBH_4$@G under the same temperature. The total discharged hydrogen reached 8.2 wt% at 430°C for $NaBH_4$+MgNiV@G; in comparison, $NaBH_4$@G released a similar amount of hydrogen at 475°C.

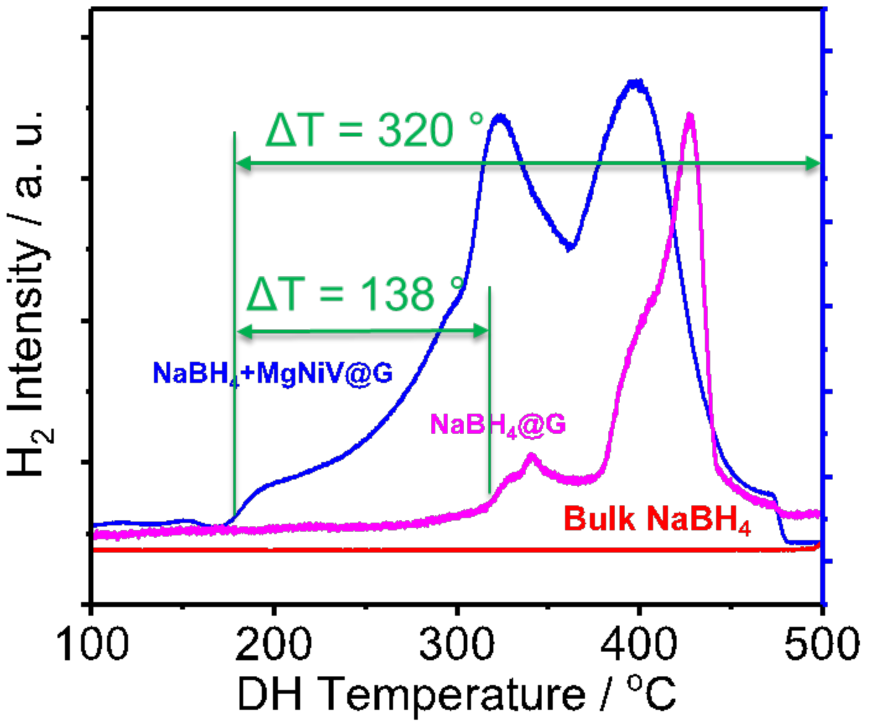

Figure 1. The hydrogen desorption as the function of temperature during TGA analysis on $NaBH_4$+MgNiV@G, $NaBH_4$@G, and bulk $NaBH_4$.

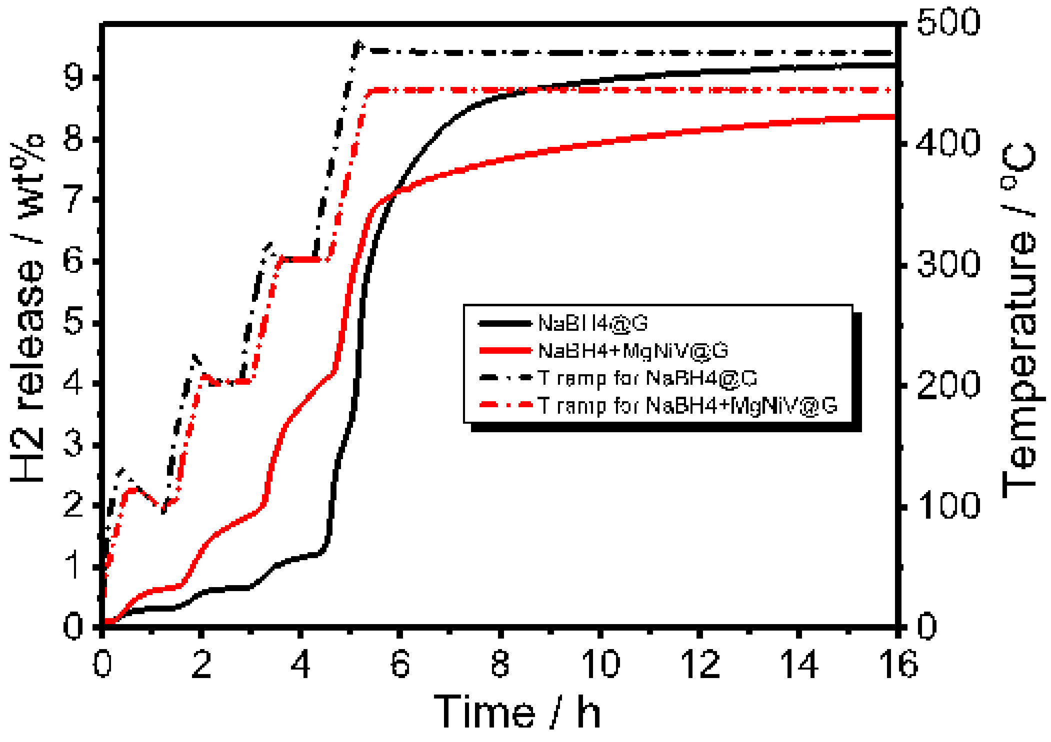

Figure 2. Comparison of hydrogen releases from $NaBH_4$+MgNiV@G and $NaBH_4$@G during step-wise temperature-programmed discharge

We also performed five DH–RH cycles for the $NaBH_4$+MgNiV@G composite. The DH temperature was controlled at 407°C with background hydrogen pressure less than one bar while the RH temperature was set at 350°C under charging pressure of 40 bar. Figure 3 shows the gravimetric and volumetric hydrogen storage capacities obtained during the five cycles. The very high capacity achieved during the first cycle represents an artifact from 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, which were proved from purity analysis. At the end of the fifth cycle, the net gravimetric capacity was 7.3 wt% and the volumetric capacity was 0.042 kg/L.

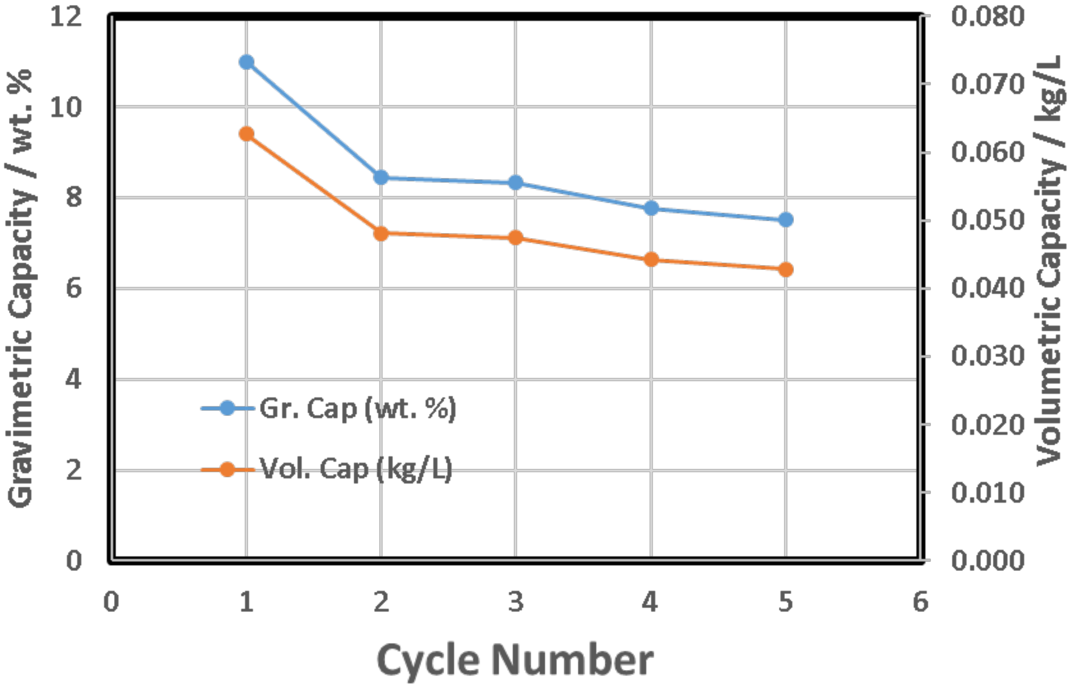

Figure 3. The hydrogen gravimetric and volumetric storage capacities as the function of cycle number over $NaBH_4$+MgNiV@G measured during a five-cycle DH–RH test

CONCLUSIONS AND UPCOMING ACTIVITIES

A significant improvement in DH kinetics was demonstrated in a catalyst-added $NaBH_4$@graphene composite. The new catalyst additive lowered initial the hydrogen discharge temperature from >500°C in bulk $NaBH_4$ to 180°C in $NaBH_4$+MgNiV@G, representing a 320°C reduction. Hydrogen release under a fixed-temperature DH cycle was achieved for $NaBH_4$+MgNiV@G through a five-cycle DH–RH test. The gravimetric capacity was retained at 7.5 wt% at the end of the fifth cycle.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. Lina Chong and Di-Jia Liu, "Hydride@graphene Composites for Hydrogen Storage with Improved Kinetics and Cyclability," Oral presentation at the 255th ACS National Meeting, New Orleans, LA, March 18–22, 2018.

REFERENCES

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