HyMARC Seedling: Atomic Layer Deposition Synthesis of Novel Nanostructured Metal Borohydrides

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Project End Date: December 31, 2019

Overall Objectives / Fiscal Year (FY) 2019 Objectives

- Demonstrate improvement of absorption kinetics for an atomic layer deposition (ALD)-coated $Mg(BH_4)_2$ to 3 wt % reversible capacity over at least three cycles, and 5-fold (5x) improvement of the absorption kinetics with respect to neat $Mg(BH_4)_2$ (sourced from the same lot). Operational conditions are not to exceed 250°C temperature, 120 bar pressure.

- Gain new insight into the reaction pathways and kinetics ALD coatings enable for hydrogen discharging and charging.

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]:

- (D) Durability/Operability

- (E) Charging/Discharging Rates

- (O) Lack of Understanding of Hydrogen Physisorption and Chemisorption.

Technical Targets

This project is developing magnesium borohydride composites that will have improved reversibility (Durability/Operability) and kinetics (Charging/Discharging Rates) of hydrogen reactions. The new materials will show a path to achieve or meet the following DOE hydrogen storage targets:

- System gravimetric and volumetric capacity: 0.045 kg H_2/kg system, 0.030 kg H_2/L system

- Charging time (5.6 kg): 3–5 min

- Average flow rate: 0.004 (g/s)/kW

- Min./max. delivery temperature: -40/85°C

- Cycle life: 1,500.

FY 2019 Accomplishments

- Developed ALD-coated $Mg(BH_4)_2$ with 7.6 wt % hydrogen discharged, which exceeds previous results of 6.6 wt %.

- Identified a mechanism for ALD-coating-driven rapid hydrogen discharge rates.

- Developed and screened more than 12 new ALD coatings to improve hydrogen charging and cyclability.

INTRODUCTION

Domestic energy sources must be developed to reduce U.S. dependence on foreign fossil fuels and meet the growing demand for updated energy infrastructure with increased storage capacity. Over the past 15 years, U.S. energy policy has pursued research and development of hydrogen as a viable renewable fuel for light-duty transportation and energy storage applications. Efforts from the U.S. Department of Energy (DOE), along with several automakers, have led to significant advancement in hydrogen-based fuel cells for light-duty vehicles.

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

While early market adoption of hydrogen vehicles has resulted from these advances, all systems rely on storage tanks of hydrogen pressurized to 700 bar (~28 g/L). The pressure requirements present challenges in infrastructure and delivery that could limit widespread deployment of hydrogen vehicles. Hydride materials, specifically metal borohydrides, offer a strategy to significantly reduce the pressure while still achieving the needed storage capacity-to-weight ratios. The DOE 2020 hydrogen storage system capacity targets are 30 g/L and 4.5 wt %, and the ultimate goals are 50 g/L and 6.5 wt % H_2. Magnesium borohydride, $Mg(BH_4)_2$, offers a hydrogen storage *materials* capacity of 113 g/L and 14.9 wt %. Both the volumetric and gravimetric capacity of $Mg(BH_4)_2$ offer the potential to meet the *system* requirements DOE has identified. The development of metal borohydride technology has stalled due to the kinetics, cyclability, reaction pathways, and operating temperatures for hydrogen absorption and desorption. Prior DOE-sponsored research has shown that nanostructuring metal hydrides and the use of chemical additives can promote the necessary kinetics, control reaction pathways, and control the material phases. This project aims to incorporate these benefits into a materials hierarchy that can advance metal borohydride technology.

APPROACH

The goal of this project is to develop a reversible hydrogen storage material based on an ALD coating of nanostructured metal borohydrides. ALD is a vapor phase method to grow thin films layer by layer. ALD can coat a metal borohydride with layers that protect against loss of the nanostructured hydride and impart chemical additives. The concept combines well-known nanostructuring and chemical additives that improve hydride kinetics and reversibility with a growing body of research that shows ALD coatings improve similar nanoscale phenomena in catalysis and battery materials. In this project, ALD coatings generally have improved performance in various hydride discharging or charging properties and include the following:

- Oxide materials on $Mg(BH_4)_2$ like Al_2O_3, TiO_2, and CeO_2

- Elemental metals like palladium, ruthenium, and platinum on $Mg(BH_4)_2$

- Nitride-like materials with titanium and boron on $Mg(BH_4)_2$

- Oxide and nitride coatings on other hydrides magnesium, palladium, and sodium borohydride.

Current efforts focus on combing these layers into a coating that will capture the improvement of the materials for both discharging and charging hydrogen.

RESULTS

Rapid hydrogen discharging was obtained from a boron-nitride-like (BN) ALD coating on the gamma phase of magnesium borohydride, γ-$Mg(BH_4)_2$. This material released 6.6 wt % hydrogen in less than 10 seconds at 107°C. Figure 1 shows a comparison of hydrogen discharging for neat γ-$Mg(BH_4)_2$ and the two top performers: BN coated and boron nitride-titanium nitride (BN-TiN) coated γ-$Mg(BH_4)_2$. The BN coating produces rapid release up to 6.6 wt % and the BN-TiN coating produces the best discharged capacity at 7.6 wt %. These results reflect modest progress for the material hydrogen capacity released. DOE targets represent the total system hydrogen capacity that accounts for a tank and hardware for hydrogen delivery, and thus, the material capacity will need to exceed the system target of 4.5 wt %. The rate of hydrogen discharging of 6.6 wt % in less than 10 seconds at low temperature (107°C) shows significant steps toward meeting the DOE targets in discharge rate and operating temperature (60°C). A temperature of 300°C is typically required to discharge large amounts of hydrogen from $Mg(BH_4)_2$, and the time required for this is significantly longer than 10 seconds.
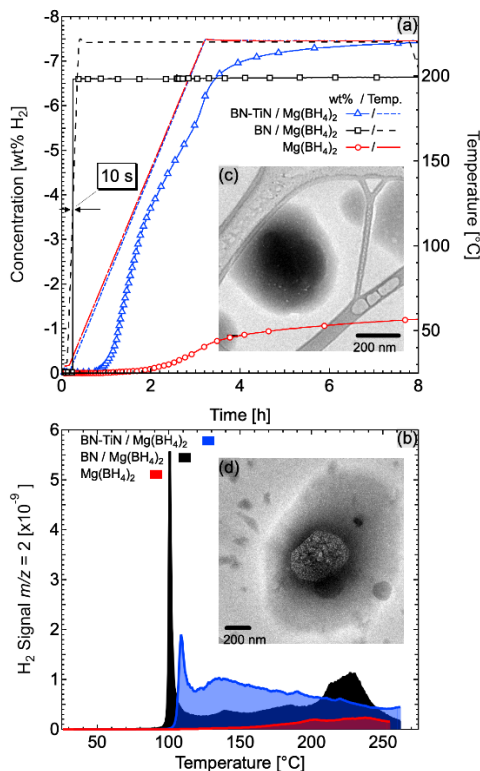
Figure 1. (a) Pressure-composition-temperature (PCT) discharging of hydrogen for BN/ Mg(BH$_4$)$_2$, BN-TiN/Mg(BH$_4$)$_2$, and neat Mg(BH$_4$)$_2$ where hydrogen release is denoted with a negative sign and hydrogen uptake is positive. (b) Temperature-programmed desorption (TPD) data showing the discharge rates for the materials in (a). (c), (d) Transmission electron micrographs for BN/Mg(BH$_4$)$_2$ after ALD and 250°C discharging, respectively.

Analysis of Figure 1 can provide more information about the desorption phenomena. The hydrogen concentration in Figure 1a is from PCT manometric measurements taken during discharging of BN-TiN, BN, and neat γ-Mg(BH$_4$)$_2$. Also included are the corresponding temperature profiles. In PCT data, discharged hydrogen is denoted by a negative sign, whereas hydrogen uptake during charging is denoted by a positive sign. Comparing these data to the TPD data in Figure 1b provides some insight into the discharge rate. TPD measures a hydrogen discharge rate and is related to the PCT curve by the integral of that rate. The TPD data shows an extremely strong discharge rate at 107°C from BN/Mg(BH$_4$)$_2$ and no subsequent discharging until temperatures are above 200°C. This translates to the rise in the PCT curve for hydrogen concentration that then plateaus for BN/Mg(BH$_4$)$_2$. The TPD for BN-TiN/Mg(BH$_4$)$_2$ in Figure 1b shows strong discharging near 115°C, followed by a second weaker discharge event from 130°C to 200°C. The corresponding PCT data reflects the different discharge events by slope changes in the curve. Similar discharge behavior for all three materials has been reproduced in different ALD batches on different lots of source Mg(BH$_4$)$_2$ material. Figures 1c and 1d show transmission electron micrographs of the BN/Mg(BH$_4$)$_2$ after ALD and after 250°C discharging, respectively. The micrographs indicate a change in the center of the particles after discharging is also seen on many other particles after discharging.

The second discharge event in the BN-TiN/Mg(BH$_4$)$_2$ from 130°–200°C may arise from hydrogen release from the more dense alpha phase of Mg(BH$_4$)$_2$. X-ray diffraction data (not shown) indicates the α-Mg(BH$_4$)$_2$ may form from the titanium nitride (TiN) ALD process. The discharging from α-Mg(BH$_4$)$_2$ may be triggered by the initial first BN/ Mg(BH$_4$)$_2$ mechanism. The higher density of the alpha phase results in sustained hydrogen discharging in the temperature range 130°–200°C. This indicates that blends of magnesium borohydride phases could be used to tune the desired hydrogen release. The role ALD has on Mg(BH$_4$)$_2$ phase transformations is being investigated further.

The goals of this year are to understand the mechanism ALD coatings enable for this unprecedented result and to use this knowledge to improve hydrogen charging and cyclability. At the time of the report, the latter effort is in progress and results will be forthcoming. A significant amount of materials characterization has been directed at understanding the mechanism of discharging. The mechanism for hydrogen discharge results from the ALD process modifying a finite layer at the interface of the $Mg(BH_4)_2$ and ALD coating. This layer has a high concentration of nitrogen-hydrogen (N-H) bonds. The electronegativity of nitrogen induces a polar bond resulting in a positive charge localized on hydrogen. The opposite happens for boron-hydrogen (B-H) bonds leaving hydrogen with a negative charge. These subtle differences in charge on hydrogen for N-H and B-H bonds result in energetically favorable formation of the H_2 molecule and rapid discharging. Figure 2 sums up all the materials characterization by showing the evolution of the N-H and B-H species. Figure 2 shows diffuse reflectance Fourier transform infrared spectroscopy results for $BN/Mg(BH_4)_2$ after ALD, discharging at 150°C, and discharging to 250°C. Also included is neat $Mg(BH_4)_2$ for comparison and several indicators for N-H, B-H, and other bonds bending and stretching modes. After ALD, a significant amount of N-H has been added to the $Mg(BH_4)_2$. Discharging at 150°C results in large losses of the N-H and some B-H, and the N-H are largely gone at 250°C.
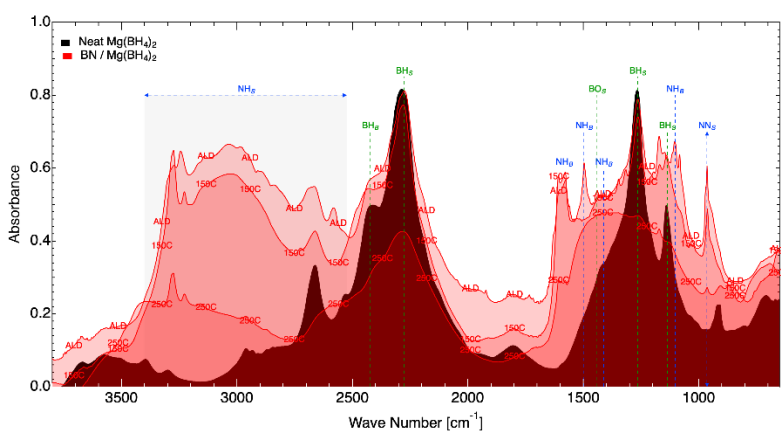

Figure 2. Infrared absorbance of ALD boron nitride coated $Mg(BH_4)_2$ after ALD, discharging to 150°C, and discharging to 250°C. Also included is neat $Mg(BH_4)_2$. Bending (*B*) and stretching (*S*) modes for various boron, nitrogen, and hydrogen bonds are also indicated.

The layer of N-H modified $Mg(BH_4)_2$ does not extend throughout the entire material. X-ray diffraction and nuclear magnetic resonance spectroscopy show that the starting $Mg(BH_4)_2$ is present in large quantities after ALD and the ALD coating is amorphous. Calorimetry measurements show that the discharging at 107°C is exothermic. This result is consistent with the N-H, B-H discharging mechanism described above, and is well known in the literature. A key difference is the partial modification of $Mg(BH_4)_2$ with N-H bonds.

The effort to understand the ALD driven discharging mechanism was aided in part by developing new coatings on $Mg(BH_4)_2$. These coatings were developed to investigate the effects of coating thickness or mass (e.g., number of ALD cycles); ALD coating-hydride interface via the ALD sequence of coatings; and the coating on the alpha phase of $Mg(BH_4)_2$. Figure 3 accounts for these efforts by plotting the discharged hydrogen wt % up to 250°C from calibrated TPD against a figure-of-merit (FOM) that ranks the expected coating thickness. A larger FOM indicates a thicker, heavier coating. It is interesting to note that there does not appear to be a trend where the larger FOM shows dead weight penalties for thicker coatings. This is likely due to the N-H modified layer being the dominant mechanism. From the data in Figure 3, the top performer of BN-TiN was obtained.
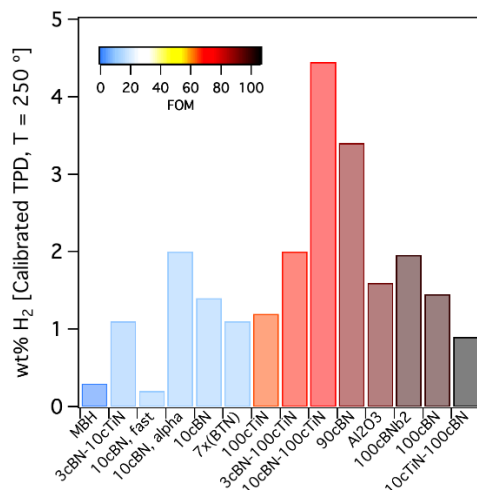
Figure 3. Discharged hydrogen concentration up to 250°C from calibrated TPD data from various ALD coatings on Mg(BH$_4$)$_2$. The FOM ranks expected thickness of the ALD coating with thickest, heaviest coatings having larger FOM values. (x-axis abbreviations: *c* = number of ALD cycles; BTN is a BN-TiN alloy or superlattice; b2 = batch 2)

Addressing the hydrogen charging and cyclability is being pursed with the knowledge that the ALD coatings modify the Mg(BH$_4$)$_2$. This knowledge can be leveraged to potentially change the hydrogen charging pathways that favor milder pressures and temperatures.

SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

1. Provisional patent: "Nanostructured Composite Metal Hydrides," USPTO Application No. 62/507,354 was converted to a non-provisional patent USPTO Application No. 15/982,232.

2. Filed provisional patent: "Encapsulated Hydrogen Fuels," USPTO Application No. 62/839,807.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. S. Christensen, poster presentation at the DOE Hydrogen and Fuel Cells Program 2019 Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., April 2019.

2. S. Christensen, presentation at Fuel Cell Technologies Office Hydrogen Storage Program face-to-face meeting, Richland, Washington, July 2019.

3. N. Leick, invited talk presented at ALD 2019–AVS, Seattle, Washington, July 2019.

4. S. Christensen, presentation to the DOE Hydrogen Storage Tech Team, Southfield, Michigan, September 2019.