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

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Project End Date: December 31, 2020

## Overall Objectives / Fiscal Year (FY) 2018 Objectives\*

- Demonstrate an atomic layer deposition (ALD) encapsulation matrix of magnesium borohydride that meets DOE targets for onboard hydrogen storage in light-duty vehicles by achieving a majority of the following (go/no-go):
  - Dehydrogenation/hydrogenation cyclability over three cycles
  - 3 wt% hydrogen delivery at 200°C
  - 3 wt% hydrogen uptake at 280°C, 120 bar hydrogen
  - 5x improvement on hydrogen absorption/desorption kinetics over neat  $\text{Mg}(\text{BH}_4)_2$ .
- Gain new insight to control hydrogen reaction pathways and kinetics (Barriers D, E, O).
- Develop ALD and vapor-phase processes that, if successful, can be scaled for manufacturing.

\* This project is a 1-year seedling with potential to be expanded in a Phase 2 pending meeting the

above objectives, available funding, and DOE mission.

## 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<sup>1</sup>:

- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (L) Lack of Understanding of Hydrogen 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 achieving or meet the following DOE 2020 hydrogen storage targets:

- System gravimetric and volumetric capacity: 0.045 kg  $\text{H}_2$ /kg system, 0.030 kg  $\text{H}_2$ /L system
- Charging time (5.6 kg): 3–5 min
- Minimum full flow rate: 0.004 (g/s)/kW
- Min./max. delivery temperature: -40/85°C
- Cycle life: 1,500.

## FY 2018 Accomplishments

- Developed a progression of coatings with ALD that met, surpassed, or showed a pathway to meeting individual components of the go/no-go criteria listed in overall objectives.
- Showed hydrogen cyclability over five cycles at low cycled capacity (0.5 wt%).
- Reduced hydrogen desorption temperature for  $\text{Mg}(\text{BH}_4)_2$  to 107°C from 220°C.

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

- Achieved a desorbed hydrogen capacity of 6.6 wt%, which exceeded the target of 3 wt%.
- Demonstrated a ~5x improvement on hydrogen absorption and desorption kinetics.

## INTRODUCTION

Domestic energy sources must be developed in order 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 DOE along with several automakers have led to significant advancement in hydrogen-based fuel cells for light-duty vehicles. While early market adoption of hydrogen vehicles has resulted from these advances, all systems rely on storage tanks of hydrogen pressurized to 700 bar. 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% hydrogen. Magnesium borohydride,  $\text{Mg}(\text{BH}_4)_2$ , offers a hydrogen storage *material* capacity of 113 g/L and 14.9 wt%. Both the volumetric and gravimetric capacity of  $\text{Mg}(\text{BH}_4)_2$  offer the potential to meet the *system* requirements DOE has identified. 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 completely new reversible hydrogen storage materials matrix based on encapsulation via ALD of nanostructured metal borohydrides. ALD is a vapor-phase method to grow thin films layer by layer. The metal borohydride-encapsulation architecture will include layers that will protect against loss of the nanostructure hydride and impart chemical additives to enhance kinetics and reversibility. The concept was motivated by substantial research where ALD coatings provided protective and catalytic properties to heterogeneous catalysts. ALD offers:

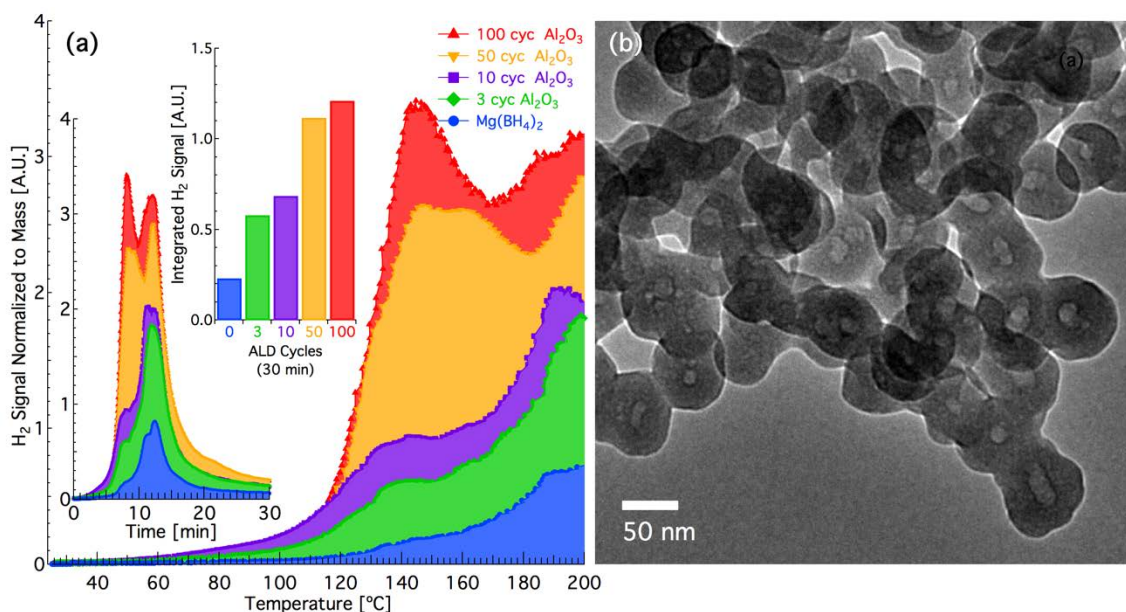
- Conformal coatings of materials like aluminum oxide that are inert to hydrogenation/dehydrogenation conditions
- A wide variety of chemical additives previously shown to enhance metal borohydride reversibility and kinetics like palladium or cerium oxide
- A facile means to combine these materials to tailor properties to performance.

Recent developments in ALD manufacturing have demonstrated >100 kg per day throughput on powders and other granular materials. Thus, ALD solutions to the challenges with metal borohydrides will bring to front new scientific knowledge with the potential to be scaled.

## RESULTS

The project first investigated the thickness of the aluminum oxide coatings on  $\text{Mg}(\text{BH}_4)_2$ . Hydrogen desorption measured by temperature-programmed desorption gave the first unexpected and compelling results: hydrogen desorption improves with increasing coating thickness. Figure 1 (a) shows temperature-programmed desorption of  $\text{Al}_2\text{O}_3$  coatings for 0, 3, 10, 50, and 100 ALD cycles. An ALD cycle is a sequence of two ALD precursor exposures (A, B) that are repeated to grow a film layer by layer. ALD of  $\text{Al}_2\text{O}_3$  is performed by alternating exposures of trimethylaluminum and water and has a growth rate of 0.11 nanometers per cycle on flat substrates. The results from Figure 1 (a) are based on total sample mass basis, which means that the 100-cycle  $\text{Al}_2\text{O}_3$  coating has the most inactive material ( $\text{Al}_2\text{O}_3$ ) but also desorbs the most hydrogen. Furthermore, the ALD coating promotes hydrogen desorption at a lower temperature, where again the 100-cycle case performs the best. Control experiments were performed to ensure that ALD of  $\text{Al}_2\text{O}_3$  alone does not desorb hydrogen under similar conditions. Figure 1 (b) shows an image from a transmission electron microscope of

the 100-cycle  $\text{Al}_2\text{O}_3/\text{Mg}(\text{BH}_4)_2$ . The image suggests that a core shell has formed, which is consistent with an encapsulated nanostructured phase. The thickness of the coating is on the order of 10–15 nanometers, which could be expected for the number of cycles performed on a granular material.



**Figure 1.** (a) Temperature-programmed desorption of  $\text{Mg}(\text{BH}_4)_2$  coated with 3, 10, 50, and 100 cycles of  $\text{Al}_2\text{O}_3$ . The hydrogen signal, derived from mass spectrometry, is plotted as function of temperature and time (inset). Also included as an inset is the time integration of the hydrogen signal over 30 minutes. (b) Transmission electron micrograph of  $\text{Mg}(\text{BH}_4)_2$  coated with 100 cycles of  $\text{Al}_2\text{O}_3$ .

These initial results confirm several important elements of our approach:

1. ALD coatings can produce a conformal core-shell structure
2. The coating does not inhibit hydrogen mass transport
3. Thicker coatings promote hydrogen desorption and reduce desorption onset temperature.

The latter of these addresses project and DOE goals for operability and discharge rates. This also provides the basis for the design of the materials later in the project.

Chemical additives to enhance kinetics and reversibility were next explored. Figure 2 shows the hydrogen cycling of an ALD coating on  $\text{Mg}(\text{BH}_4)_2$  consisting of  $\text{Al}_2\text{O}_3\text{-TiO}_2\text{-CeO}_2$ . The cycling was performed with a pressure-composition-temperature (PCT) manometric apparatus. Figure 2 contains a series of hydrogen absorptions (A1, ...) and desorptions (D1, ...) measured under the criteria listed above in the overall objectives. The figure includes the hydrogen concentration (blue), system pressure (black), and sample temperature (red). The text boxes in the figure give the desorbed (blue) and absorbed (green) hydrogen quantity. Desorption is negative on the concentration scale whereas absorption is positive. The gray shaded regions on the pressure curves indicate the sample is absorbing hydrogen whereas the yellow shaded regions are transients where absorption does not occur. Absorption 1 (A1) was performed after ALD and shows little to no hydrogen uptake. Thereafter, the cycled hydrogen capacity is roughly proportional to the desorption steps. While the cycled capacity is low (0.5 wt%), the five cycles surpassed the go/no-go criteria of three cycles. The data also illustrate the aggressive goal to desorb 3 wt% hydrogen at 200°C: without the significant progress in desorption kinetics, this will not be possible. Indeed, neat  $\text{Mg}(\text{BH}_4)_2$  does not desorb hydrogen until 220°C. The data from Figure 2 compared to other absorption/desorption cycles for  $\text{Al}_2\text{O}_3/\text{Mg}(\text{BH}_4)_2$  and other materials indicate the Ce-based additives were important in improving cyclability and absorption.

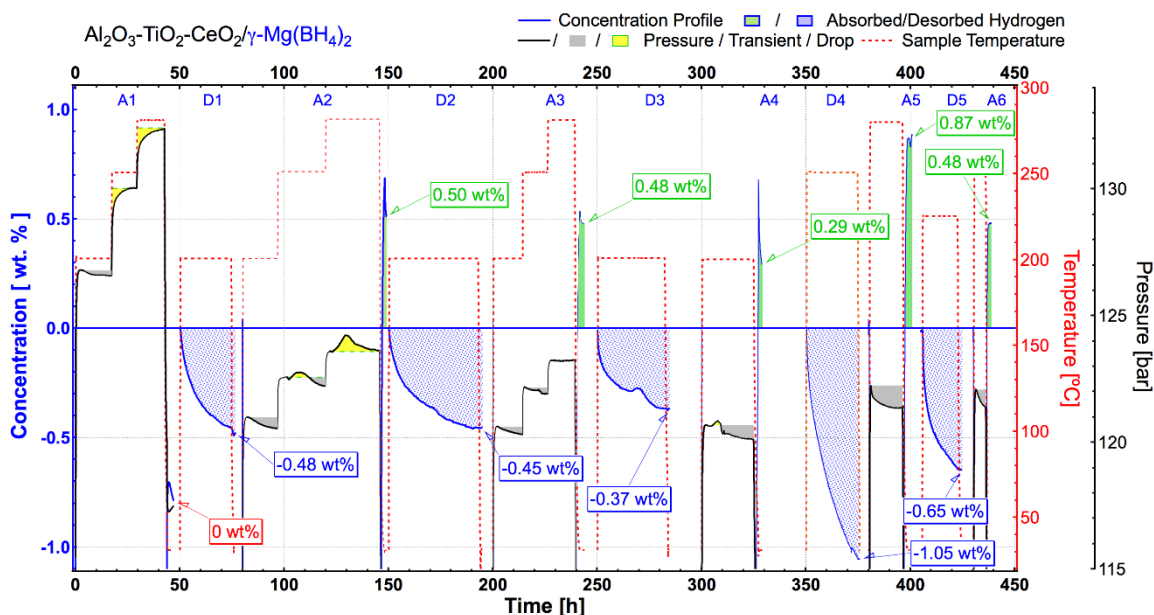


Figure 2. Hydrogen absorption (A1, A2, ...) and desorption (D1, D2, ...) cycling measured with pressure-composition-temperature manometry for  $\text{Mg}(\text{BH}_4)_2$  coated with  $\text{Al}_2\text{O}_3\text{-TiO}_2\text{-CeO}_2$ . Represented here are hydrogen concentration (blue), sample temperature (red), and system pressure (black) where gray shaded regions indicate active hydrogen absorption. The text boxes give the hydrogen concentration after each absorption or desorption step. Absorbed hydrogen is positive on the concentration profile and desorbed hydrogen is negative.

Progress was made to increase the desorption kinetics for  $\text{Mg}(\text{BH}_4)_2$  by chemical additives and new ALD processes. Screening a series of additives—including  $\text{CeO}_2$ ,  $\text{TiO}_2$ , Pd, Ru,  $\text{Al}_2\text{O}_3$ , and combinations of these—identified Pd/ $\text{Al}_2\text{O}_3$  as the leading candidate for improving desorption kinetics. The result is plotted in Figure 3, which shows 0.71 wt% hydrogen was desorbed in 24 hours, which was the best desorption result to that point but well short of the 3 wt% goal. In efforts to accelerate toward the project goals, new ALD processes were developed. The details of the ALD process and the nature of the coating are not yet ready for public disclosure. Figure 3 does show one of the results, coating X, which showed significant progress by desorbing 1.9 wt% at 200°C in 15 hours and ultimately 3 wt% after the sample temperature was raised to 220°C. Coating X/ $\text{Mg}(\text{BH}_4)_2$  also showed significant progress in absorption: 1.1 wt% was absorbed in 24 hours, making it the best so far. Figure 4 shows the progress in desorption kinetics for these new materials. The kinetic models are based on power law fits to the desorption data. A second new ALD process and coating produced even better desorption results: 6.6 wt% hydrogen, ~10 s, at 126°C. The current understanding for these new and exciting materials is unfolding and will be explored in the next phase.

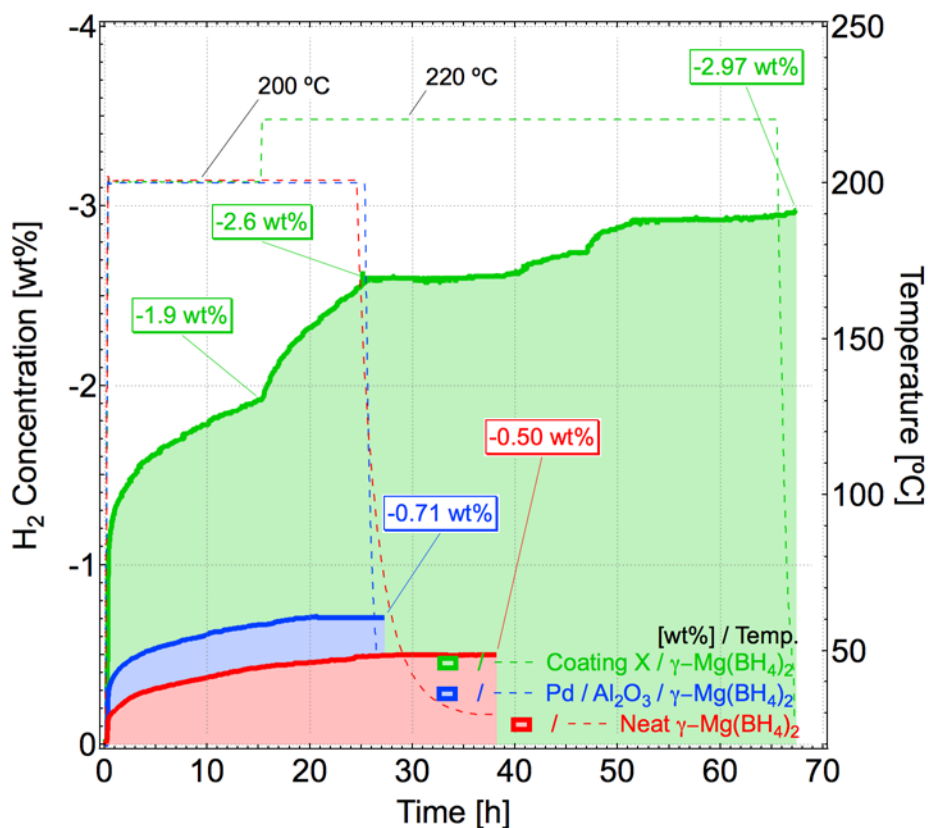


Figure 3. Hydrogen desorption progress for ALD coatings with chemical additives

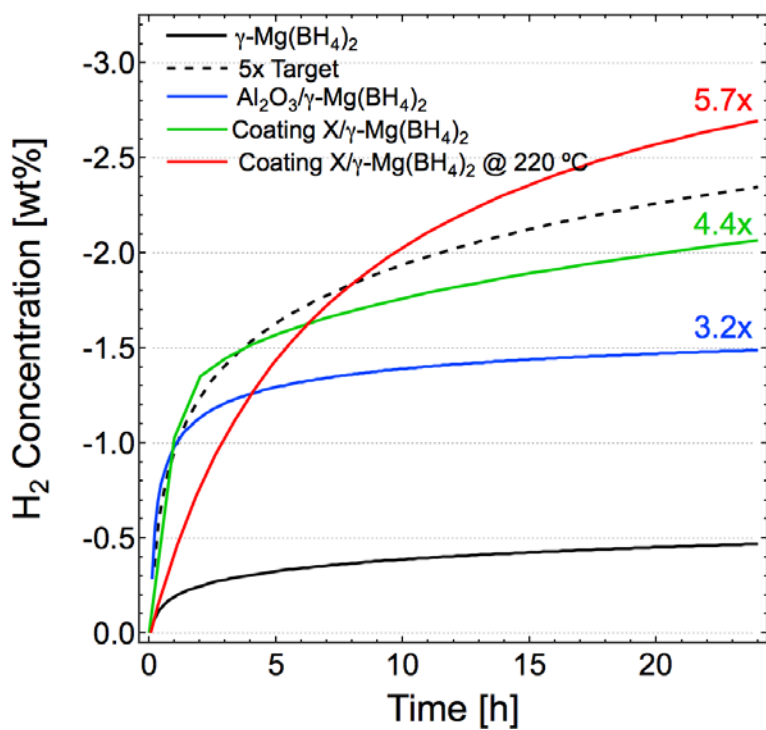


Figure 4. Hydrogen desorption kinetics for the ALD materials compared to neat Mg(BH4)2

## CONCLUSIONS AND UPCOMING ACTIVITIES

The project has successfully demonstrated a new pathway to meet DOE targets for hydrogen storage. Recent developments in ALD processes and materials were key to this progress. With these progress indicators, new scientific knowledge, and synergistic activities with the Hydrogen Materials Advanced Research Consortium Energy Materials Network node, the project has been selected to Phase 2, which will focus on the using the new ALD results to improve hydrogen absorption and cyclability.

## 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.

## FY 2018 PUBLICATIONS/PRESENTATIONS

1. Presented a poster at the DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, Washington, DC, June 2018, ST143.
2. Presented a progress report to the DOE Hydrogen Storage Tech Team, Southfield, Michigan.