NATIONAL RENEWABLE ENERGY LABORATORY

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

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Project ID # ST143

Overview

Timeline and Budget

- Project start date: 9/15/2017
- Project end date: 9/30/2018†
- Total project budget: $278k
  - Total recipient share: $153k
  - Total federal share: $250k
  - Total DOE funds spent*: $168k

*As of 3/31/18

†Phase I; Phase II (proposed)

Barriers

- **D** – Durability/Operability
- **E** – Charging/Discharging Rates
- **O** – Lack of understanding of hydrogen chemisorption

Partners

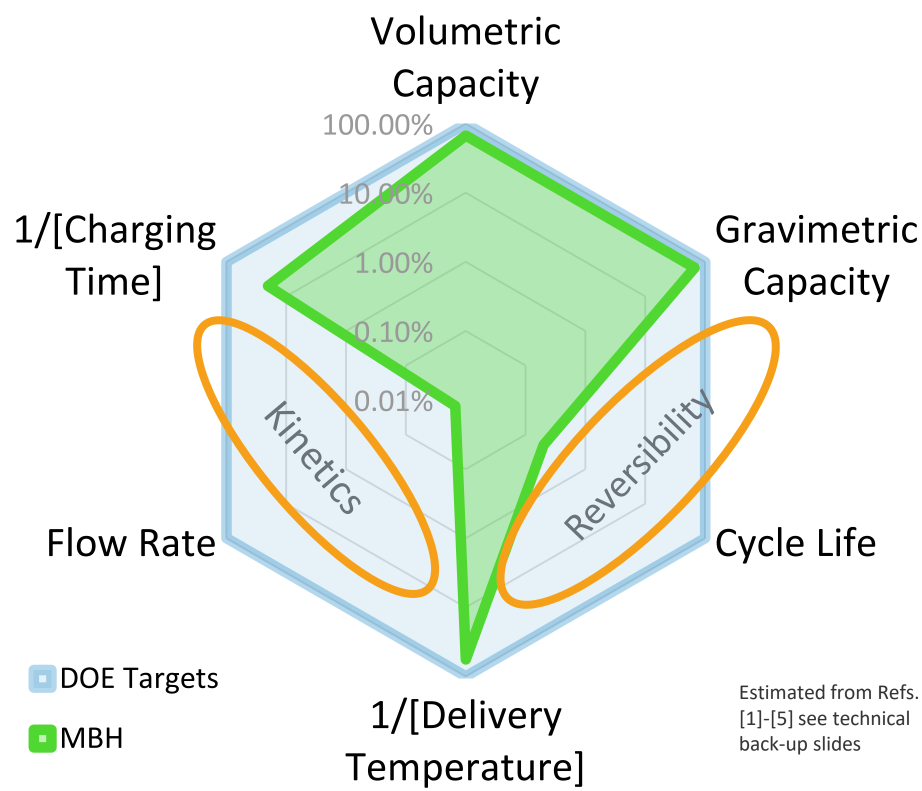
- H2Tech Consulting (cost share)

Relevance

Metal borohydrides (MBHs) such as $Mg(BH_4)_2$ possess a high hydrogen storage capacity, but absorption and release of hydrogen is slow and has poor reversibility.

- Project objectives: improve ***reversibility*** and ***kinetics*** of hydrogen absorption and release for $Mg(BH_4)_2$
- *Reversibility* addresses Barrier **D**. Goals:
  - Increase H_2 cycling
  - Reduce cycling temp.
- *Kinetics* addresses Barrier **E**. Project Goals:
  - Increase H_2 delivery (Flow rate, Temp.)
  - Reduce H_2 charging time

Selected System Targets Relevant to MBHs

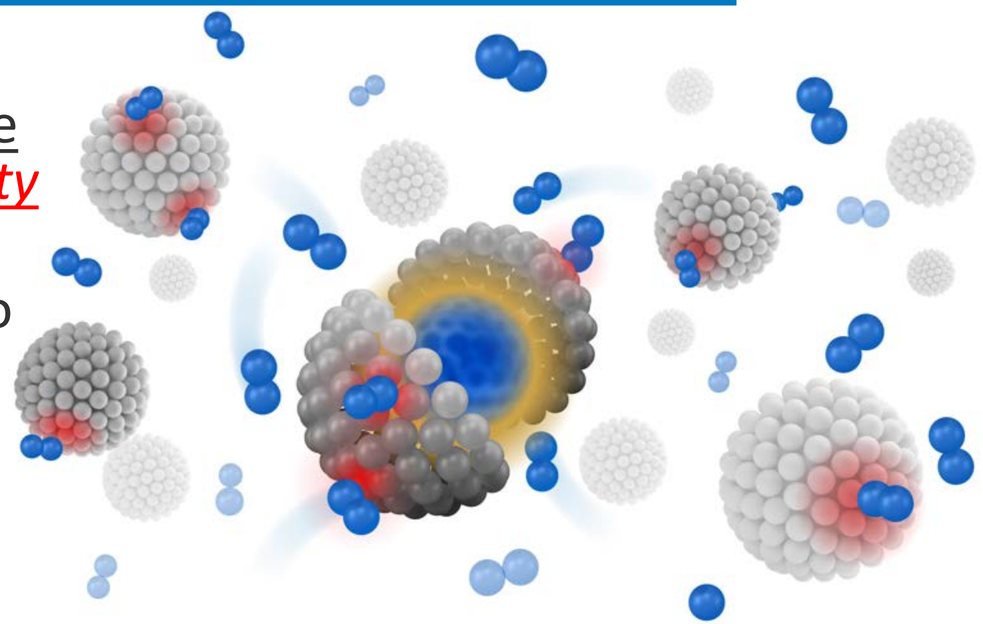


Estimated from Refs. [1]-[5] see technical back-up slides

Approach

Concept: Improve hydrogen uptake and release *kinetics* and *reversibility* by:

1) Decrease hydride particle size to Increase diffusion and reaction rates.
2) Coat particles to maintain separation and short reaction distances.
3) Coat with monolayer catalysts to enhance reaction rates.
4) Maintain high storage capacity by creating atomically thin coatings.



How: Encapsulate MBHs via atomic layer deposition with:

Protective Matrix Layer (**PML**). Retain nanostructured MBH phase. (Reversibility)

Kinetic Matrix Layer (KML). Enhance H_2 processes w/chemical additives. (Kinetics)

ALD coatings have improved the physical and chemical properties of other nanostructured architectures. Similar benefits will be realized for MBHs.

Approach: Milestones

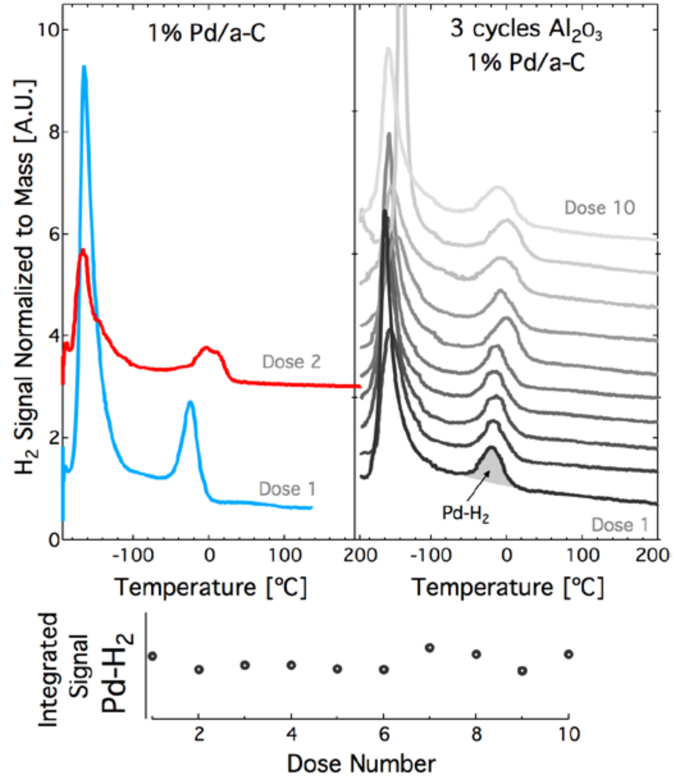
Milestone	Description (as of 03/31/18)	Complete
MS 1.2.1	**(1)** Dehydriding/hydriding cyclability over 3 cycles; **(2)** H_2 desorption will be tested at 200 °C against initial vacuum for a 24 h period; **(3)** H_2 absorption will be tested at 280 °C, 120 bar H_2 overpressure, and 24 h. Materials characterization will be performed to help identify structure-property relationships. (XRD, TEM, NMR, etc.)	100 %
MS 2.1.1	H_2 storage testing will be performed to demonstrate ALD Al_2O_3 coatings on nanostructured Pd (1wt%Pd/activated carbon) to enhance cyclability. TPD measurements will be performed to show consistent H_2 uptake/delivery over 5 cycles after heat treatments exceeding 400 °C.	100 %
MS 2.2.1	H_2 storage testing will be performed to demonstrate ALD Al_2O_3 coatings on nanostructured $Mg(BH_4)_2$ to enhance cyclability for 3 cycles. H_2 desorption will be tested at 200 °C against initial vacuum for a 24 h period. H_2 absorption will be tested at 280 °C, 120 bar H_2 overpressure, and 24 h.	100 %
MS 3.1.1	MgB_2 and $Mg(BH_4)_2$ will be coated with Al_2O_3, TiO_2 and CeO_2 by ALD and tested for H_2 adsorption to show improved hydriding temperatures, pressures, and kinetics. H_2 absorption at 200, 250, and 280 °C will be performed at 120 bar H_2 overpressure.	25%
Go/No-Go	A functional ALD encapsulation of $Mg(BH_4)_2$ will demonstrate a majority of the following significant hydrogen storage improvements: **(1)** Dehydriding/hydriding cyclability over 3 cycles; **(2)** 3 wt% H2 delivery at 200 °C; **(3)** 3 wt% uptake at 280 °C and 120 bar H_2 overpressure; (4) a 5x improvement in Dehydriding and Hydriding kinetics when compared to bulk $Mg(BH_4)_2$ under the same conditions and same initial material (particles size, purity, manufacturer, etc).	25%

A&P: Enhanced thermal cyclability of Al_2O_3/nano-Pd

MS 2.2.1

- ALD Al_2O_3/nano-Pd:
  - Temperature Programmed Desorption (TPD)
  - Nano-Pd: 1% Pd dispersed on activated carbon (1%Pd/a-C)
  - Thermal cycling: 450 °C, Dose H_2 at 23 °C
- Pd-H_2 signal at ~0 °C remains constant over many cycles for ALD coated material

H_2 TPD for nano-Pd



H_2 desorption after thermal cycles for 1%Pd/a-C: uncoated and 3 ALD cycles of Al_2O_3. The integrated signal for the Pd-H2 peak is plotted versus the H_2 dose number.

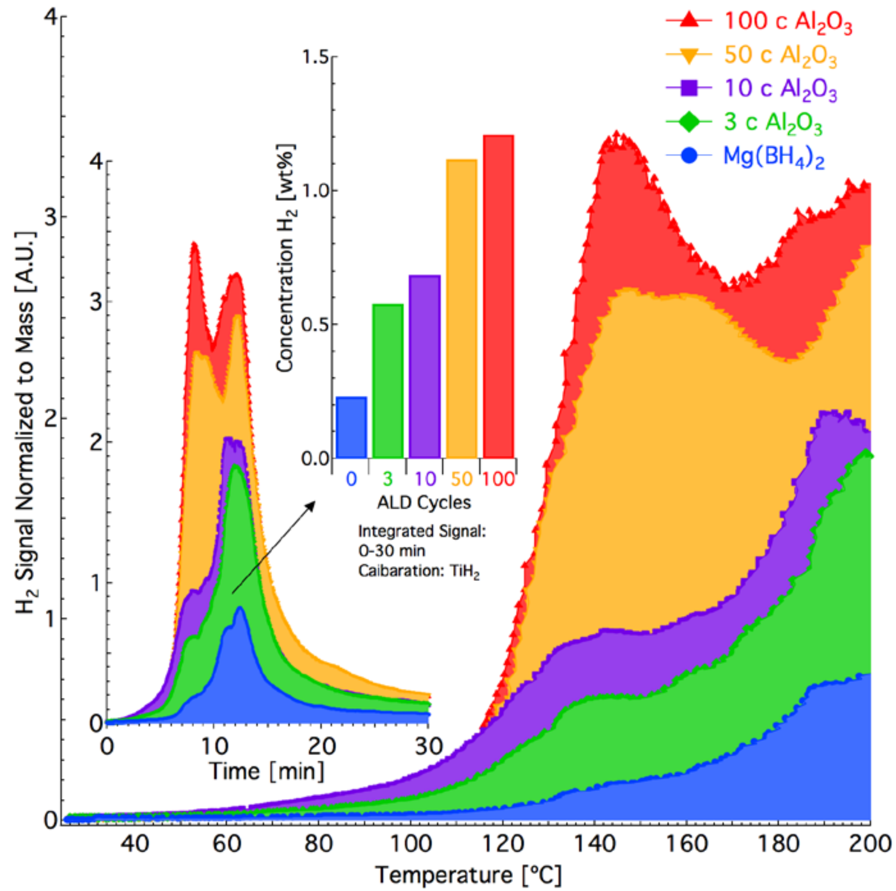
We demonstrated a functional PML coating of Al_2O_3 on nano-Pd that is permeable to H_2 and improves durability/cyclability.

A&P: Temperature programmed desorption Hydrogen desorption of $Al_2O_3/Mg(BH_4)_2$

MS 2.2.1

- TPD for a series of ALD Al_2O_3/nano-$Mg(BH_4)_2$: 3, 10, 50, 100 cycles
- ALD coatings reduce desorption temperature: 140 °C
- Time-integrated TPD signal shows increased H_2 desorption with increasing ALD
- Control sample (not shown): No significant H_2 desorption from ALD Al_2O_3 film only
- Reversibility is qualitatively demonstrated with a PML
- TPD data is normalized to mass

H_2 TPD for MBH



The PML coating of Al_2O_3 on nano-$Mg(BH_4)_2$ shows enhanced desorption that suggests improved kinetics for H_2 delivery (flow rate, temperature).

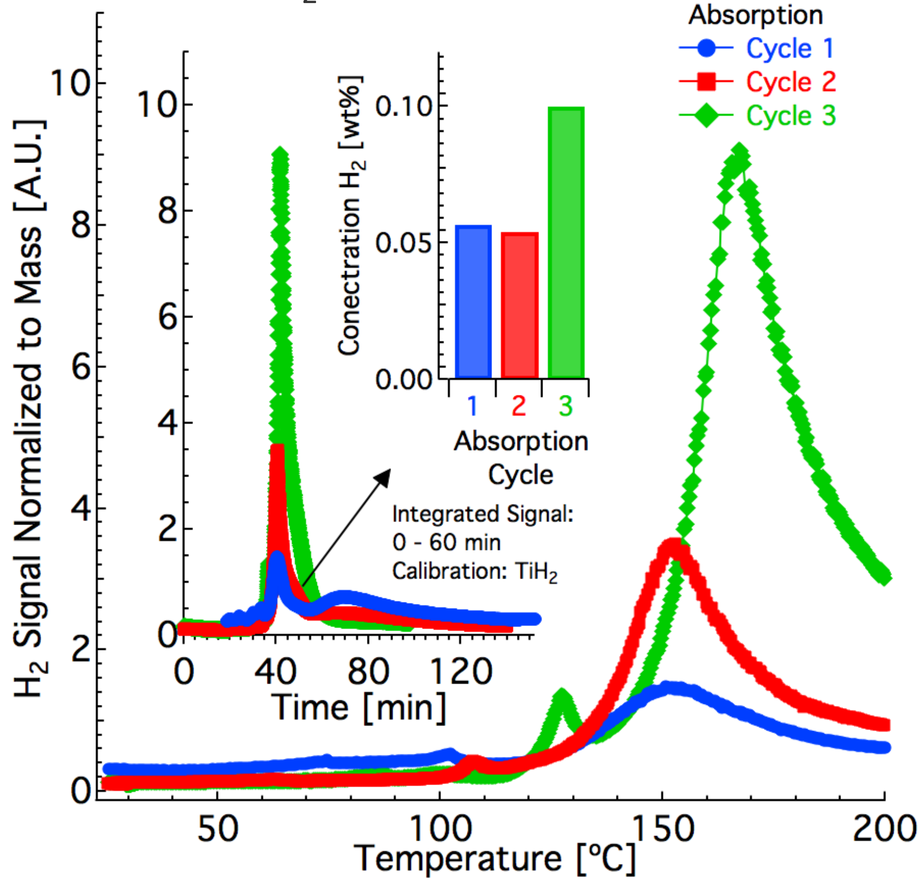
MBH provided by Sandia National Laboratory

A&P: Hydrogen reversibility of $Al_2O_3/Mg(BH_4)_2$

MS 2.2.1

- ALD Al_2O_3/nano-$Mg(BH_4)_2$ cycled (3x) between:
  - TPD
  - Absorption, 120 bar H_2, 285 °C, 24 h
- Reversibility is qualitatively demonstrated with a PML
- H_2 desorption increases after each absorption cycle
- Increased desorption at each cycles indicates that the PML leads to enhanced H_2 uptake.

H_2 TPD for cycled MBH



We demonstrated a functional PML coating of Al_2O_3 on nano-$Mg(BH_4)_2$ with reversible H_2 absorption and desorption.

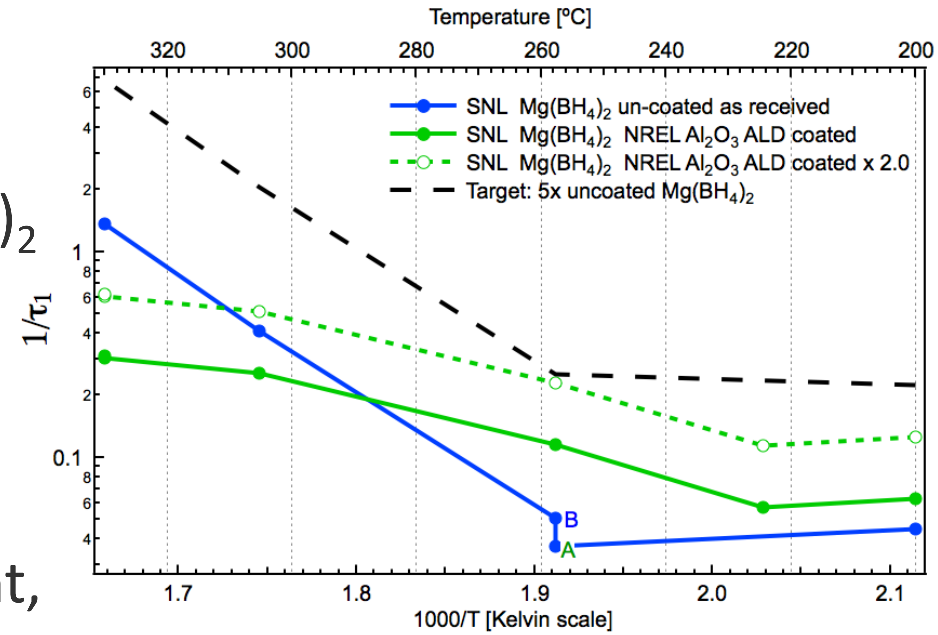
MBH provided by Sandia National Laboratory

A&P: Quantitative measurements of H_2 desorption kinetics

MS 2.2.1

- Desorption measured by manometric method for $Al_2O_3/Mg(BH_4)_2$ and uncoated MBH
- H_2 capacity for coated Mg $(BH_4)_2$ about ½ of uncoated MBH as expected.
- Desorption rates ($\approx 1/\tau_1$) are faster for Coated MBH at low temperatures.
- Based on active material weight, kinetics are projected to be 2x better for $Al_2O_3/Mg(BH_4)_2$ than uncoated MBH.

Arrhenius desorption plot



Data from fits to raw kinetics obtained with PCT (technical backup slides) and tested at milestone criteria.

Intrinsic desorption kinetics, on Mg $(BH_4)_2$ weight basis only, are significantly better for Al_2O_3 coated MBH at T < 305°C.

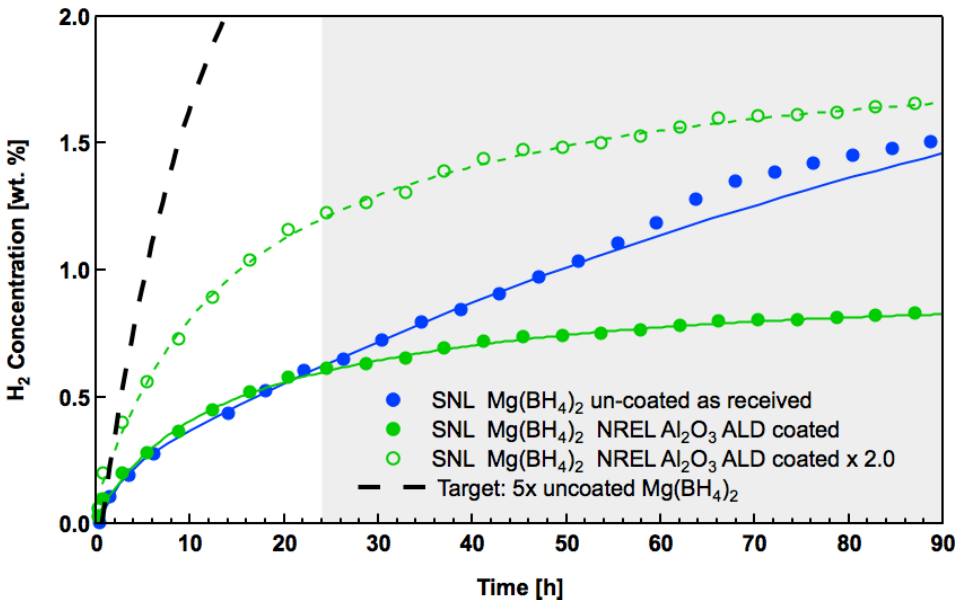
MBH provided by Sandia National Laboratory

A & P: Measurement of H_2 absorption for $Al_2O_3/Mg(BH_4)_2$

MS 2.2.1

- First PCTPro H_2 absorption after desorption for $Al_2O_3/Mg(BH_4)_2$ and uncoated MBH.
- Intrinsic absorption kinetics (on MBH weight basis only) are significantly better for $Al_2O_3/Mg(BH_4)_2$ under first 24h period (milestone conditions).
- H_2 uptake capacity are > 1.2wt.% in first 24h indicating only partial re-hydriding under these conditions.
- Based on active material weight, kinetics are projected to be 2x better for $Al_2O_3/Mg(BH_4)_2$ than uncoated MBH.

Manometric H_2 absorption



Data from fits to raw kinetics (technical back-up slides) obtained with PCT and tested at milestone criteria.

ALD coating improves H_2 reversibility due to increased desorption and absorption kinetics. Improved reversible capacity can be addressed through coating thickness.

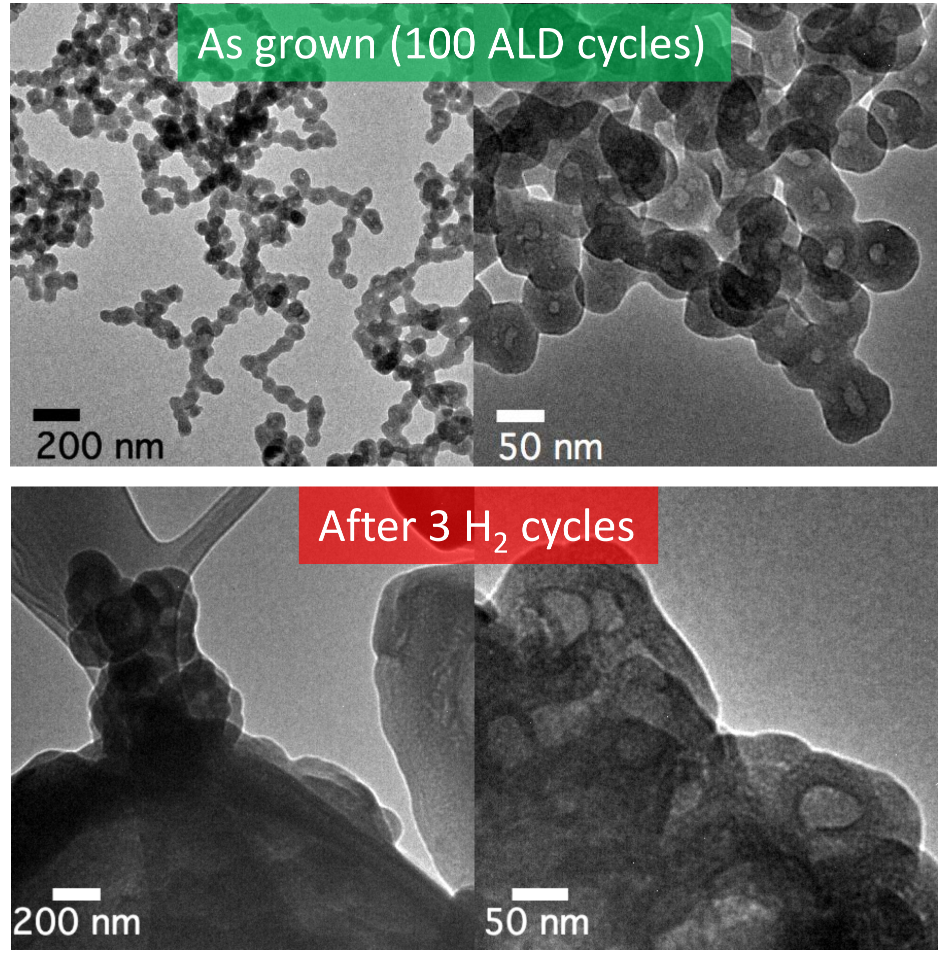
MBH provided by Sandia National Laboratory

A&P: Characterizing the Materials Architecture

MS 1.2.1

Transmission electron microscope (TEM) images show:

- Nanoparticles encapsulated with a shell structure
- Core/shell structure is retained after 3 cycles:
  - H_2 desorption 200 °C, vacuum, 24 h
  - H_2 absorption , 280 °C, 120 bar H_2, 24 h
- H_2 cycling condenses open, dendritic core-shells

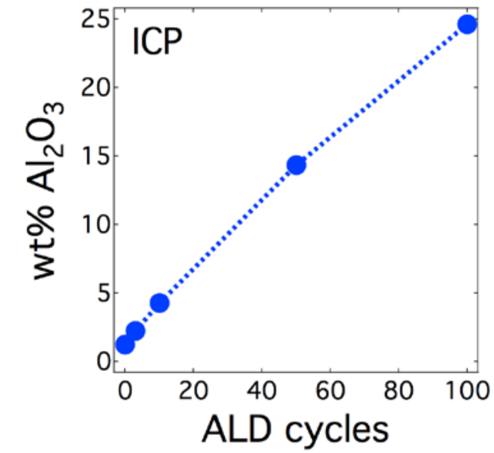


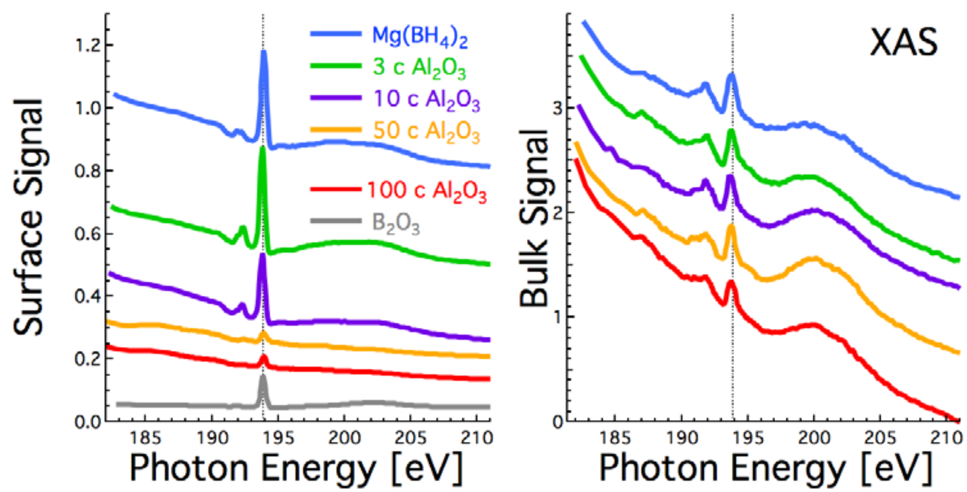
We show a PML architecture of Al_2O_3/nano-$Mg(MBH_4)_2$ with conformal encapsulation that is retained after H_2 desorption/absorption cycling.

MBH provided by Sandia National Laboratory

A&P: Characterizing the Materials Composition

- Linear mass uptake of Al_2O_3
- H_2 capacity measurement:
  - Inactive material ~ 50%
- X-ray absorption spectroscopy (XAS):
  - B_2O_3 at MBH interface
  - Constant bulk signal vs. decreasing surface signal



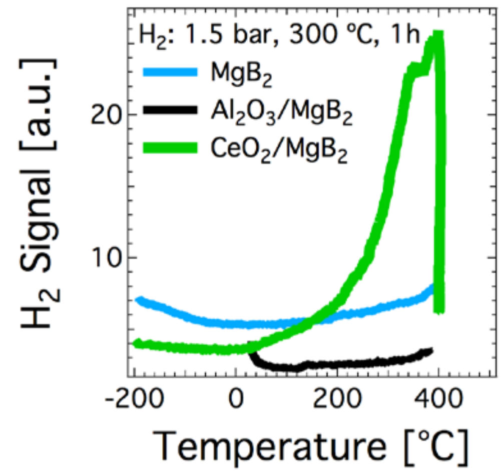


ALD of Al_2O_3 grows linearly on $Mg(MBH_4)_2$ with a B_2O_3-like interface.

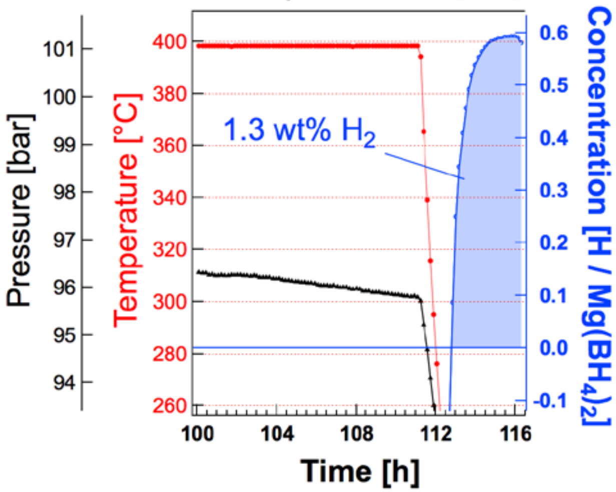
Accomplishments and Progress: Kinetic matrix layer materials selection for H_2 absorption.

MS 3.1.1

- ALD CeO_2 on MgB_2 is investigated as a kinetic matrix layer for H_2 absorption.
- TPD after low pressure H_2 treatment indicates H_2 absorption due to CeO_2. (1.5 bar H_2, 300 °C, 1 h)
- H_2 uptake quantified (1.3 wt%) for high pressure hydrogen absorption (100 bar, 390 °C, 116h)



TPD



PCT

We quantify H_2 update on MgB_2 using CeO_2 as part of a kinetic matrix layer for H_2 absorption.

Collaboration and Coordination

- H2 Technology Consulting LLC, partner, subcontractor, industry, works with DOE Fuel Cell Technologies Office (FCTO)
  - Essential partnership that provides quantitative measurements and subject matter expertise; daily interactions
- HyMARC EMN, DOE FCTO
  - Key collaborator that provides nanostructured MBH, materials characterization, theory, and subject matter expertise; weekly interactions
- HyMARC - HySCORE, DOE FCTO, Federal Laboratory
  - NREL: Key collaborator that provides materials characterization, equipment, facilities, subject matter expertise; daily interactions
  - PNNL: Collaborator that provides advanced materials characterization and subject matter expertise; biweekly interactions
- HyMARC – Support DOE FCTO, Federal Laboratory
  - SLAC: Advanced synchrotron measurements: X-ray emission spectroscopy, X-ray Raman scattering at 100 bar H_2

Remaining Challenges and Barriers

- Increase the H_2 desorption kinetics for ALD coated materials beyond the result demonstrated. Goal: 5x increase over uncoated MBH.
- Accurately determine the mass loading of ALD coatings to validate the performance improvements.
- Increase the quantity of H_2 adsorbed to show improved reversibility. Goal: 3 wt%.
- Identify a chemical additive that performs best as a KML and in cooperation with the PML improvements.

Proposed Future Work

Develop a functional ALD encapsulation of $Mg(BH_4)_2$ will demonstrate:

(1) Dehydriding/hydriding cyclability over 3 cycles;

(2) 3 wt% H2 delivery at 200 °C;

(3) 3 wt% uptake at 280 °C and 120 bar H_2 overpressure;

(4) 5x improvement in dehydriding and hydriding kinetics.

Any proposed future work is subject to change based on funding levels.

Technology Transfer Activities

- Subcontract with H2 Technology Consulting LLC, a small business developing hydrogen storage technology
- Conducted early stage discussions and obtained a letter of support from ForgeNano, a start-up developing ALD processes for powders at industrial scale
- Provisional patent filed: “Nanostructured Composite Metal Hydrides”, USPTO Application No. 62/507,354.

Summary

- ALD encapsulation with a protective layer (Al_2O_3) improves H_2 absorption and desorption kinetics.
  - This is validated in two ways from temperature programmed desorption and PCT.
  - Improvements to desorption kinetics (determined on a total mass basis) indicate that ALD coated MBH releases more H_2 at a given temperature despite having a lower H_2 capacity.
  - Improvements to absorption kinetics are encouraging.
- ALD encapsulation with Al_2O_3 improved reversibility of hydrogen cycles with respect to improved kinetics with moderate H_2 cycle capacity.
- Demonstrated a fully encapsulated architecture of $Al_2O_3/Mg(BH_4)_2$.
- All of the results are based on the first attempts at both materials synthesis and measurement which is encouraging for the next steps.

Deliverable Summary Table *	Goal	Status
H_2 Cycles	3	3
H_2 Desorption: wt% / kinetics	3 / 5x / 200 °C	1.5 / 2x
H_2 Absorption: wt% / kinetics	3 / 5x / 285 °C	1.2 / 2x

*24 h period, desorption @ vacuum/200 °C, absorption @ 120 bar H_2, 285 °C

Thank You

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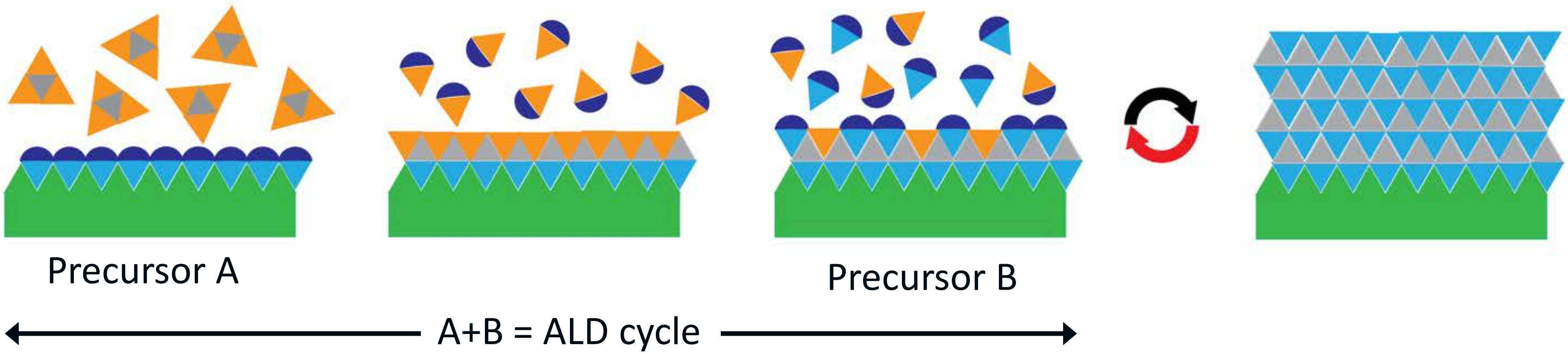
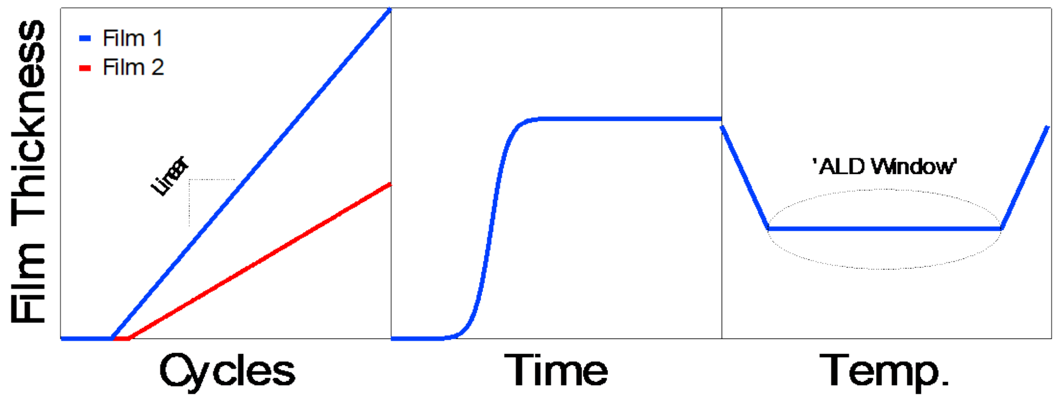
Technical Back-Up Slides

(Include this "divider" slide if you are including back-up technical slides [maximum of five]. These back-up technical slides will be available for your presentation and will be included in Web PDF files released to the public.)

Atomic Layer Deposition



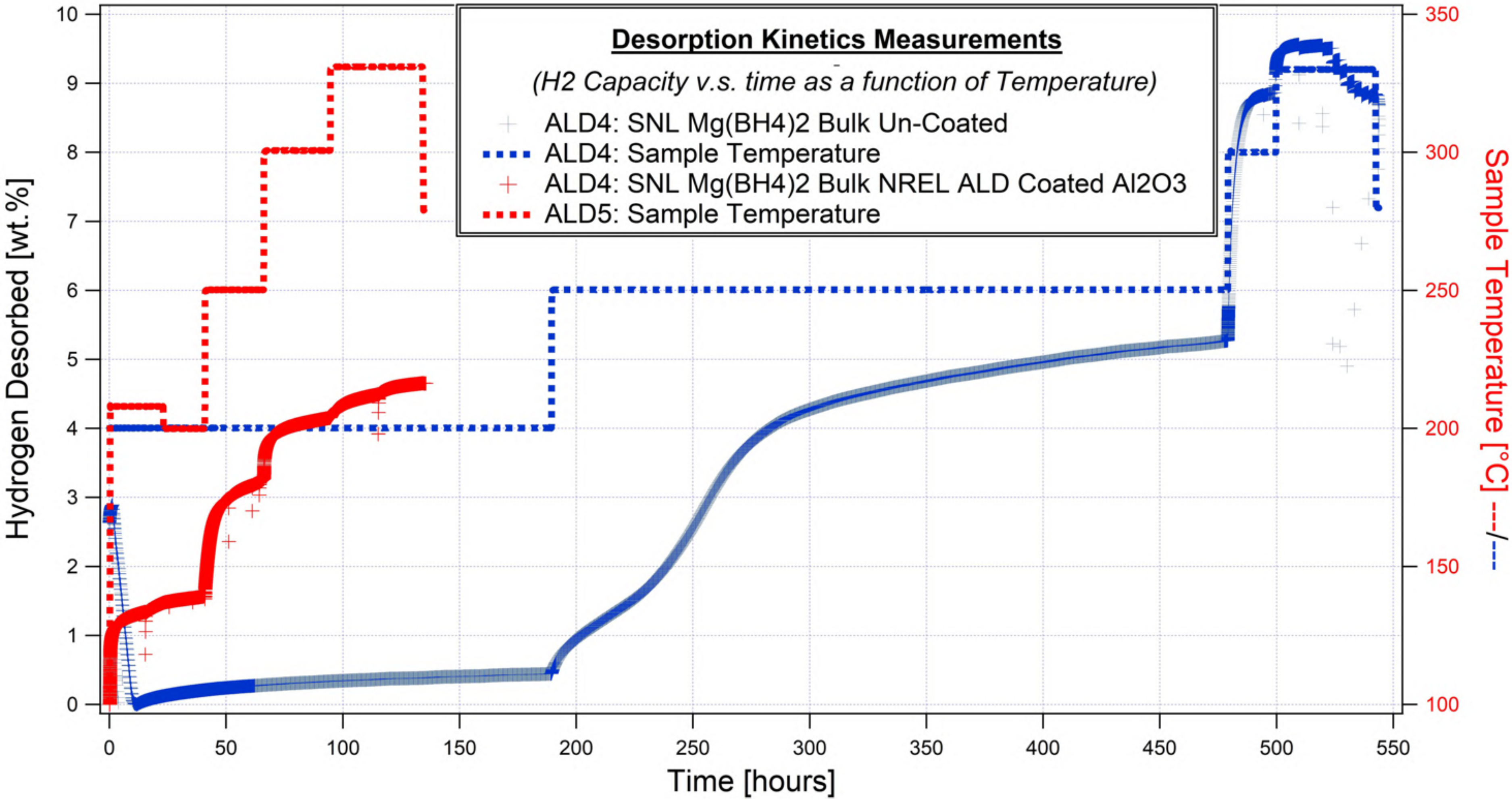


Nucleation and growth rate determined by surface chemistry and precursor molecular size.

Operating principles:

- ALD: sequential, self-limiting reactions at a surface
- Linear growth rate, saturating precursor adsorption, temperature-defined process window

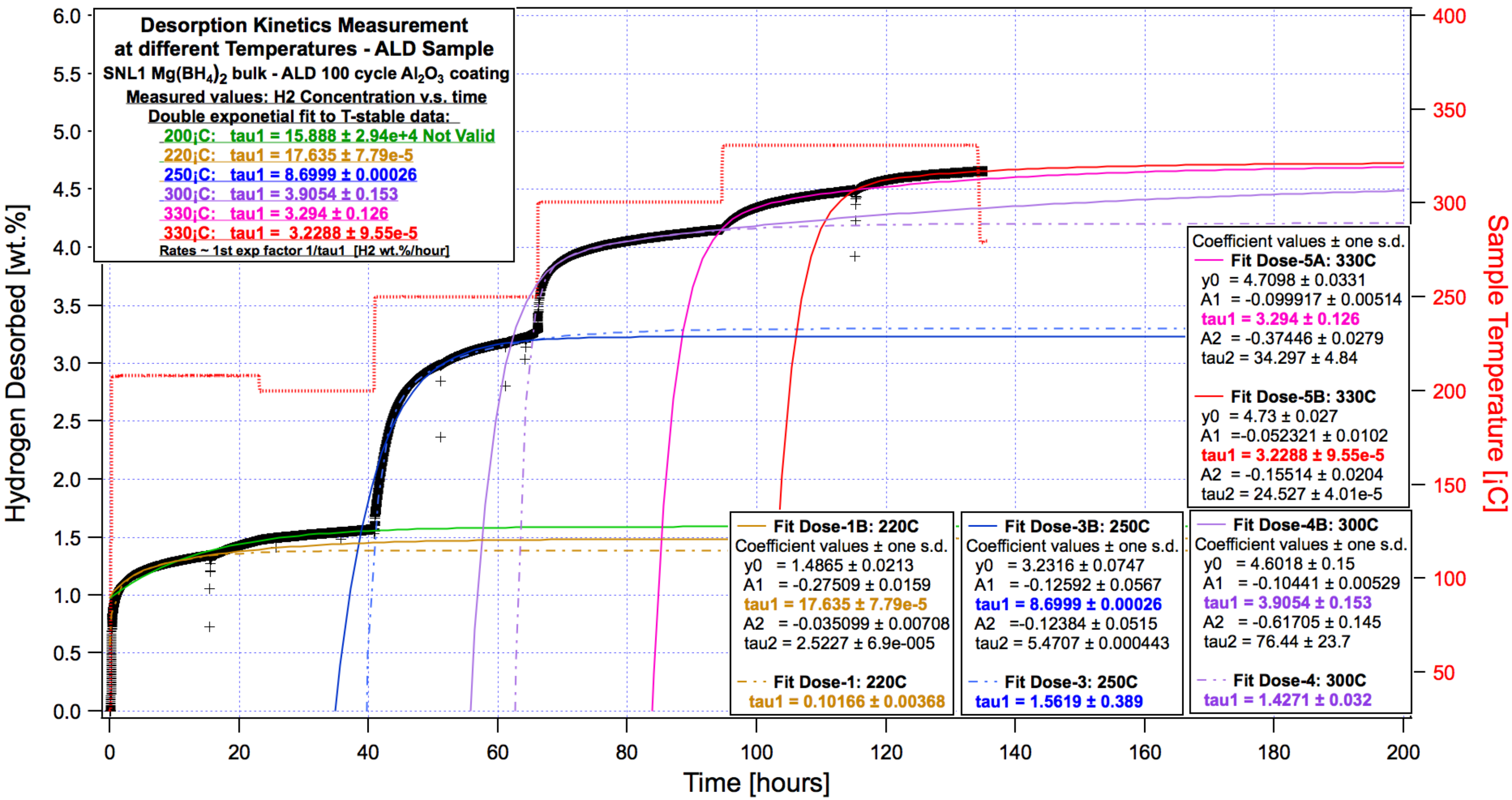
H_2 desorption data



- PCT data for H_2 desorption data for MBH materials. ALD: 100 cycles Al_2O_3 / $Mg(BH_4)_2$.

MBH provided by Sandia National Laboratory

H_2 desorption data analysis for ALD coated MBH



- Fitting analysis of PCT data H_2 desorption to extract Arrhenius rate constants. ALD 100 cycles Al_2O_3 / $Mg(BH_4)_2$.

MBH provided by Sandia National Laboratory