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

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DOE Hydrogen and Fuel Cells Program
2019 Annual Merit Review and Peer Evaluation Meeting

Project ID #ST143

Overview

Timeline and Budget

- Project start date: 9/15/2017*
- Project end date: 12/31/2020

- FY18 DOE funding: $250k
- FY19 planned DOE funding: $375k
- Total DOE funds received to date: $625,000

*Phase 2 Project Start: 1/1/2019

Barriers

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

Partners

H2Tech Consulting (cost share)

Colorado School of Mines (cost share)

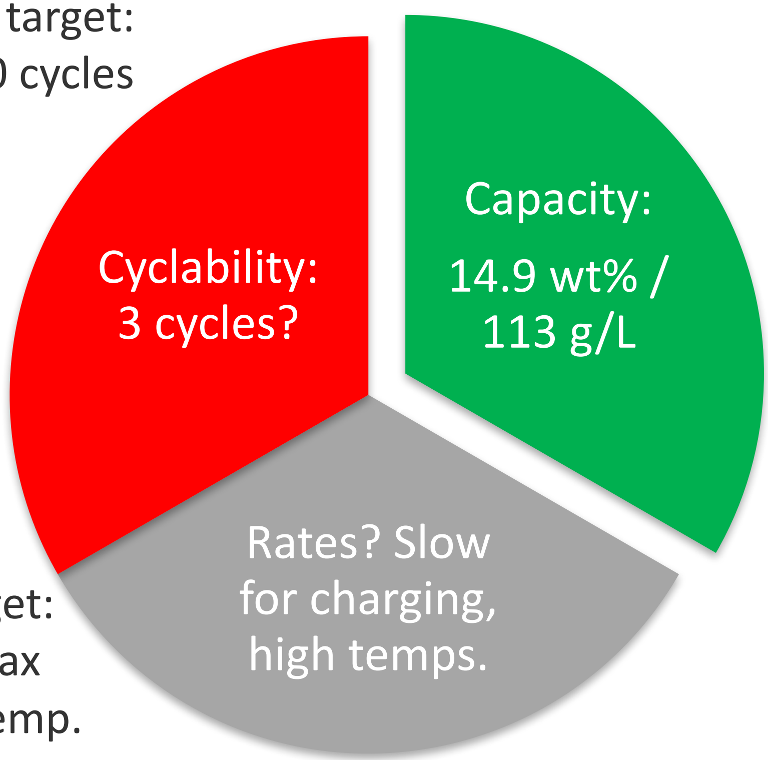
HyMARC core team

Relevance: Improve H_2 cycling and rates

- Project objectives: Improve ***reversibility*** and ***kinetics*** charging / discharging for $Mg(BH_4)_2$
- Reversibility (Barrier **D**):
  - Increase cycle life
- *Kinetics* (Barrier **E.**):
  - Reduce H_2 charging / discharging time
  - Reduce Operating Temperatures

DOE System (2020) target: 4.5 wt% / 30 g/L

DOE target: 1500 cycles



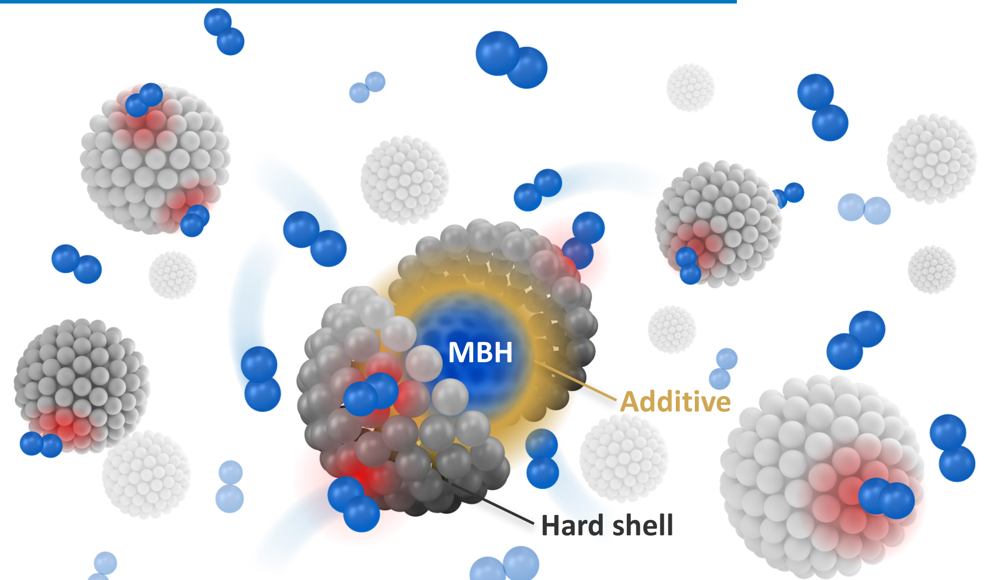
DOE target: 85 °C Max delivery temp.

Metal borohydrides (MBHs) like $Mg(BH_4)_2$ possess a high hydrogen storage capacity, but insufficient charging/discharging rates and cyclability for DOE targets.

Approach: Coatings by Atomic Layer

Concept: Improve hydrogen *charging / discharging rates* and *cyclability* by:

1) Durable nanostructured phase
2) Incorporate chemical additives that enhance reaction rates



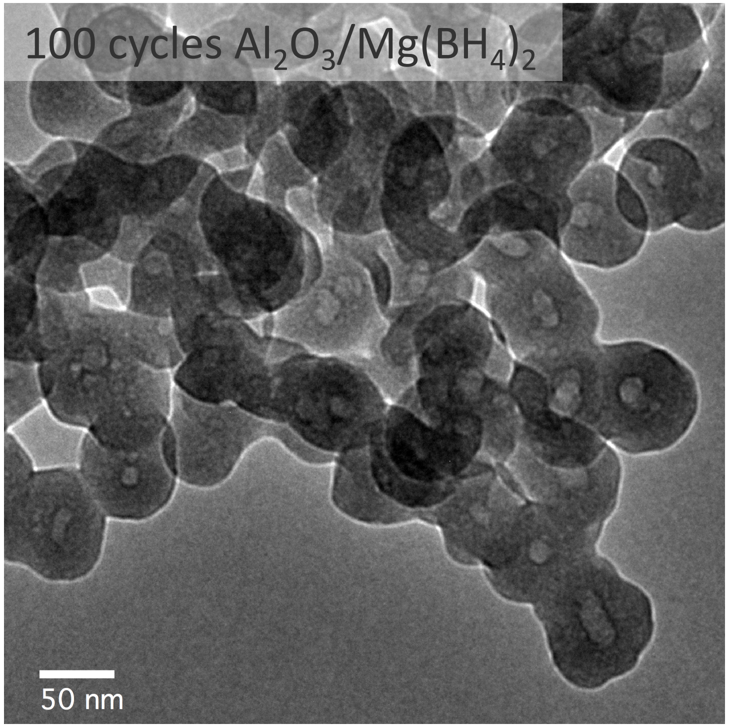
How: Coat MBHs via ALD to:

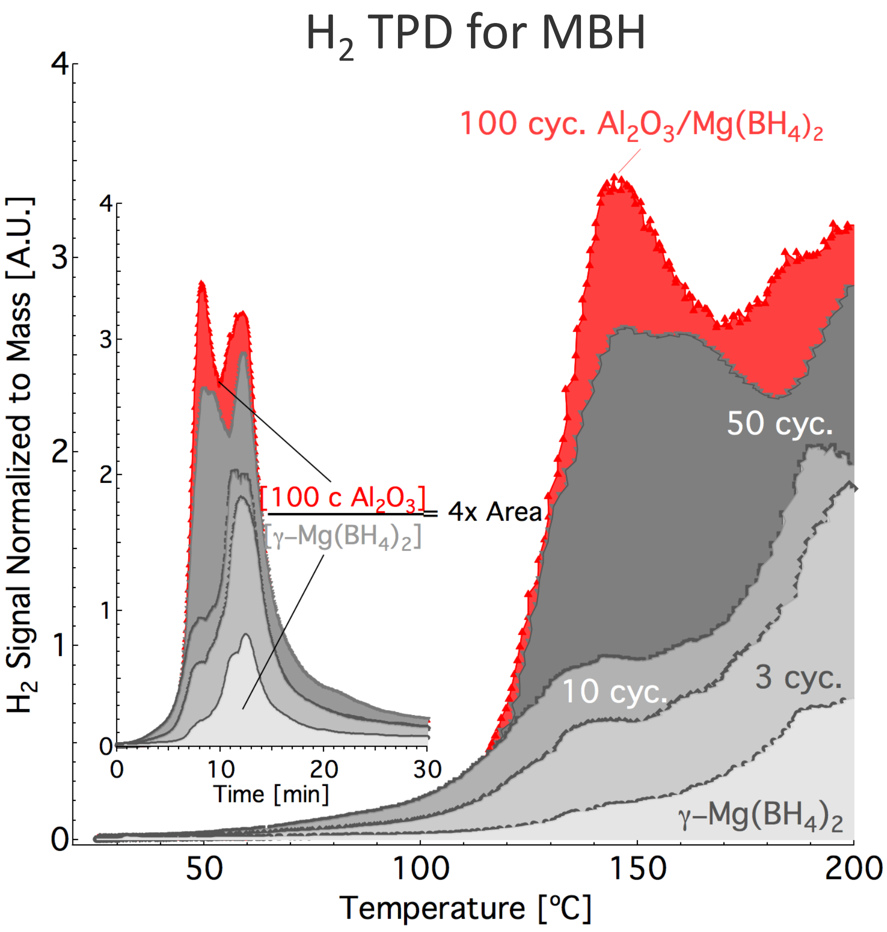
- **Protect:** Hard-permeable coating to retain nanostructured MBH phase for cyclability.
- **Catalyze:** Thin layer of additives that enhance rates.

Milestone Description	Due Date (FY19)	Progress
Determine the discharging reaction mechanism	Q2	75%
Determine charging rates/cyclability of neat $Mg(BH_4)_2$	Q1	100 %
Determine the charging reaction mechanism	Q3	25%
Characterize coatings with advanced microscopy	Q4	10%
Go/No-go: Three H_2 cycles at 3 wt% H2 + 5x improved charging. (Conditions: 250°C, 120 bar H_2)	Q4	15%

ALD coatings on $Mg(BH_4)_2$ developed in FY18 improved discharge rates and showed potential for charging and cyclability.

Accomplishments and Progress: Recap of FY18 Oxide ALD for $Mg(BH_4)_2$



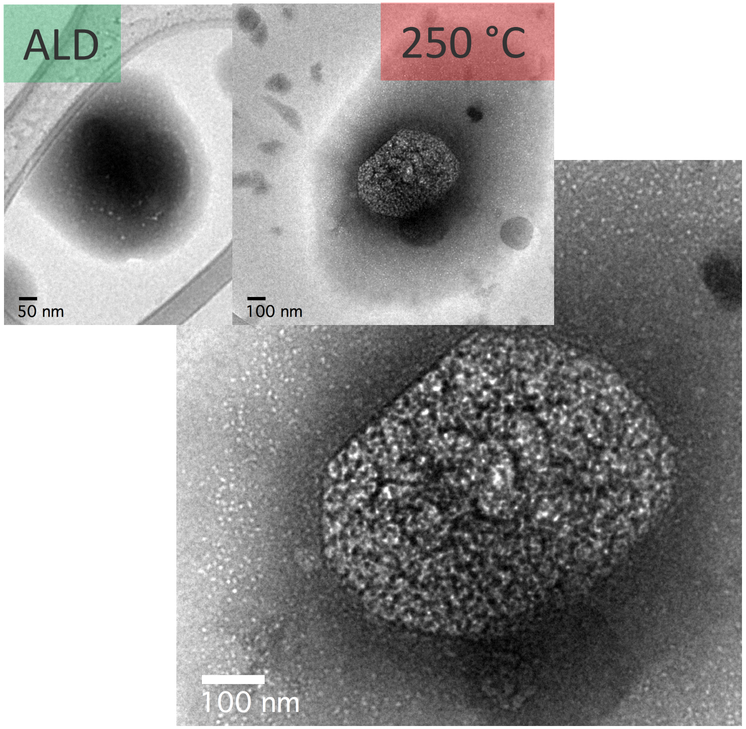


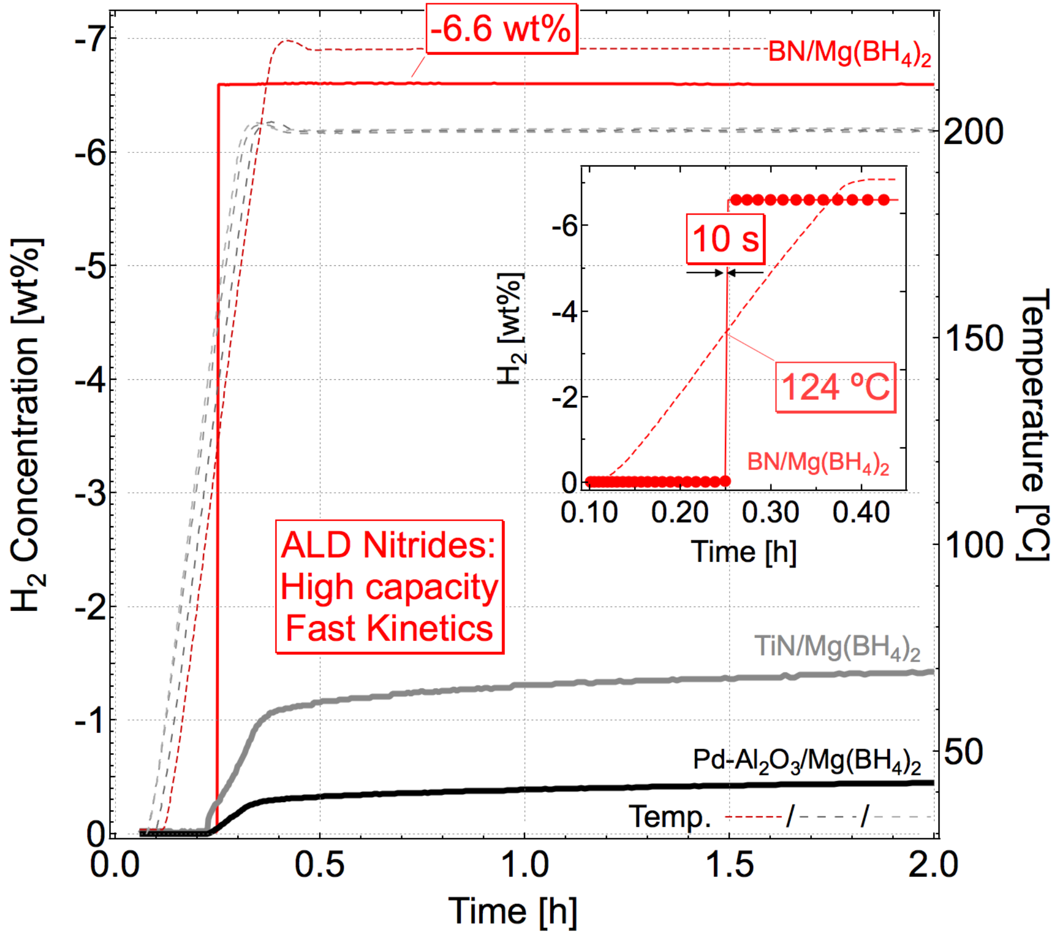
- Temperature programmed desorption (TPD) ALD Al_2O_3 series on $Mg(BH_4)_2$: 3, 10, 50, 100 cycles
- H_2 desorption improves (up to 4x) with increasing ALD cycles

Al_2O_3 on nano-$Mg(BH_4)_2$ enhances discharge rate for thicker coatings.

$Mg(BH_4)_2$ provided by Sandia National Laboratory

A&P: Improving hydrogen discharging capacity and rates

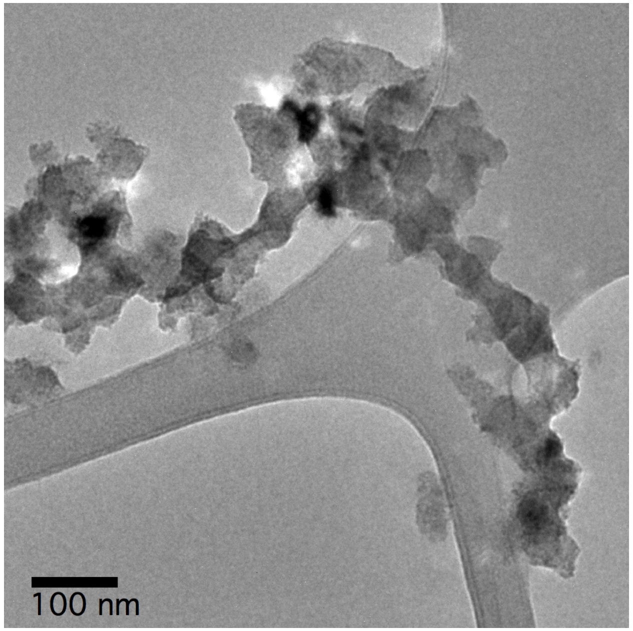


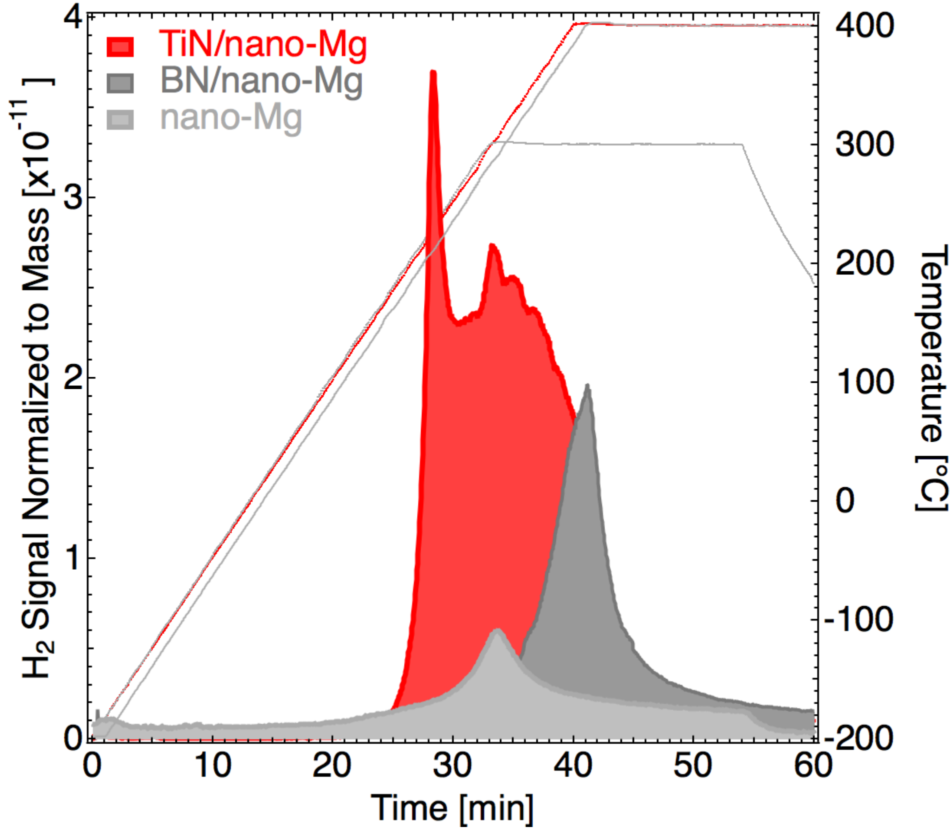


- Best performing ALD oxide did not meet goals
- Developed boron nitride (BN) and titanium nitride (TiN) coatings for $Mg(BH_4)_2$

Nitride coatings gave performance that exceeded the project goals and show promise for DOE system targets.

A& P: ALD coatings on other metal hydrides: nano-Mg





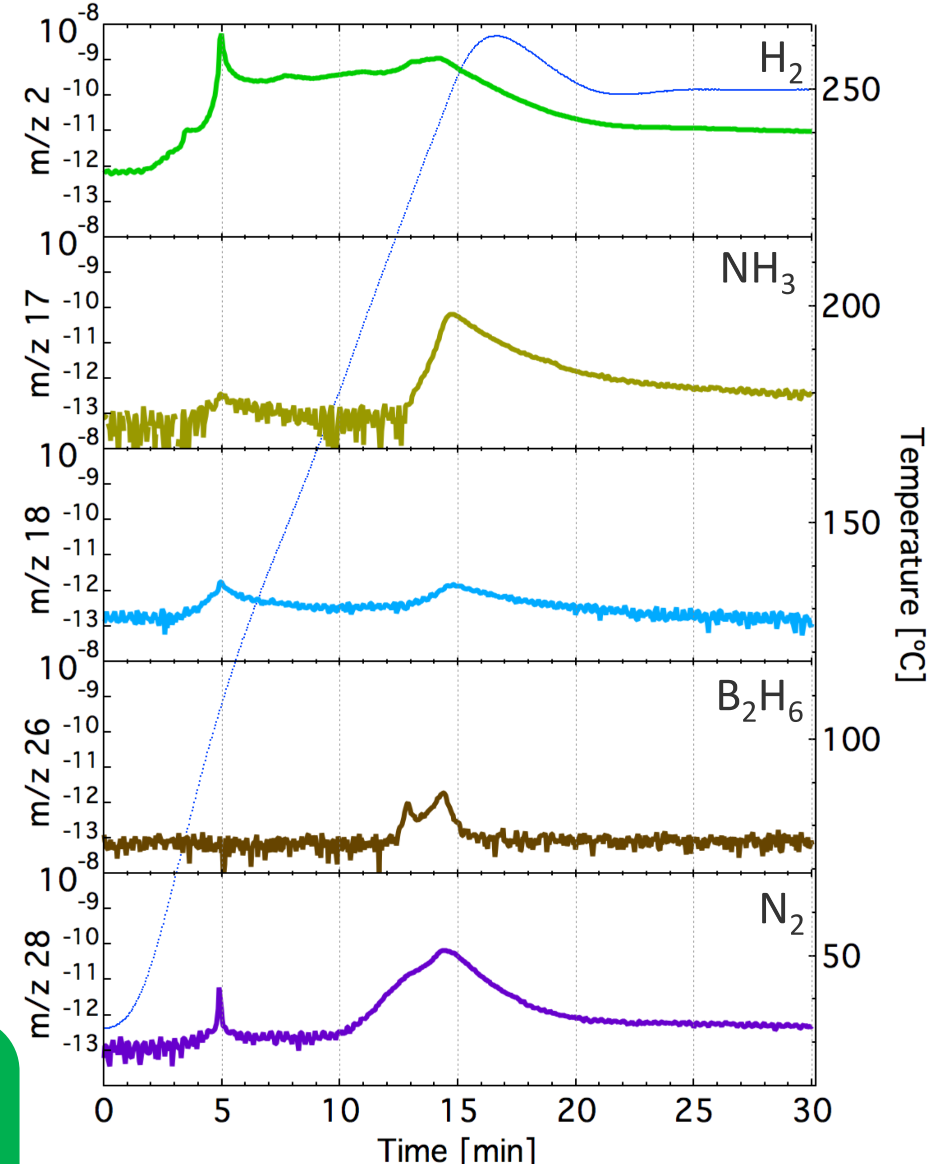
- nano-Mg -provided by HyMARC
- Prior to TPD: 1 bar H_2, 300˚C, 12 h.

TiN, BN ALD coatings enhance H_2 desorption for nano-Mg and show that ALD coatings can improve other hydride materials..

nano-Mg provided by Lawrence Berkeley National Laboratory

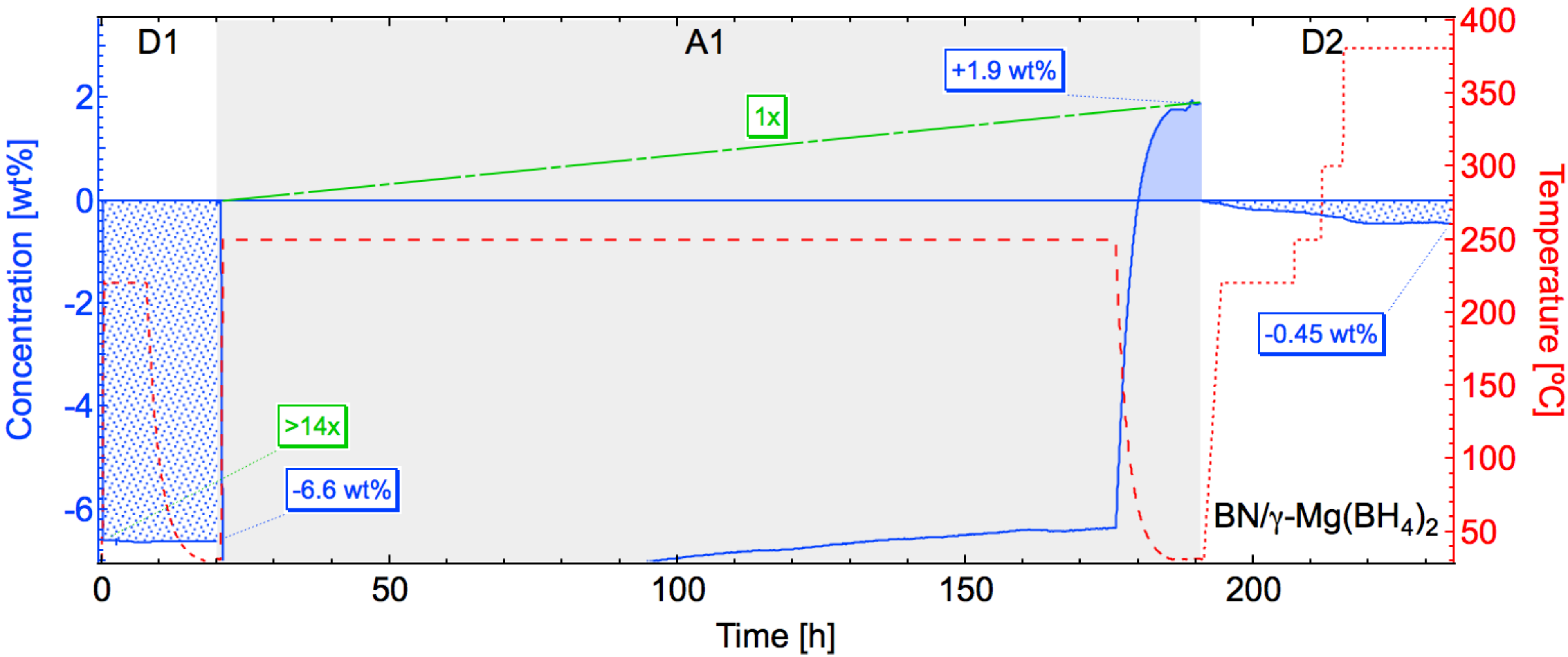
A&P- Discharging details of $BN/Mg(BH_4)_2$

- Desorption onset
  - PCT - 124 °C
  - TPD - 107 °C
- TPD Reaction Products:
  - Below 230 °C: H_2
  - Above 230 °C: NH_3, N_2, B_2H_6 (trace)
- Confirmed batch-to-batch reproducibility w/TPD



$BN/Mg(BH_4)_2$ rapidly discharges substantial amounts of clean H_2 at low temperature.

A&P: BN/$Mg(BH_4)_2$ cyclability

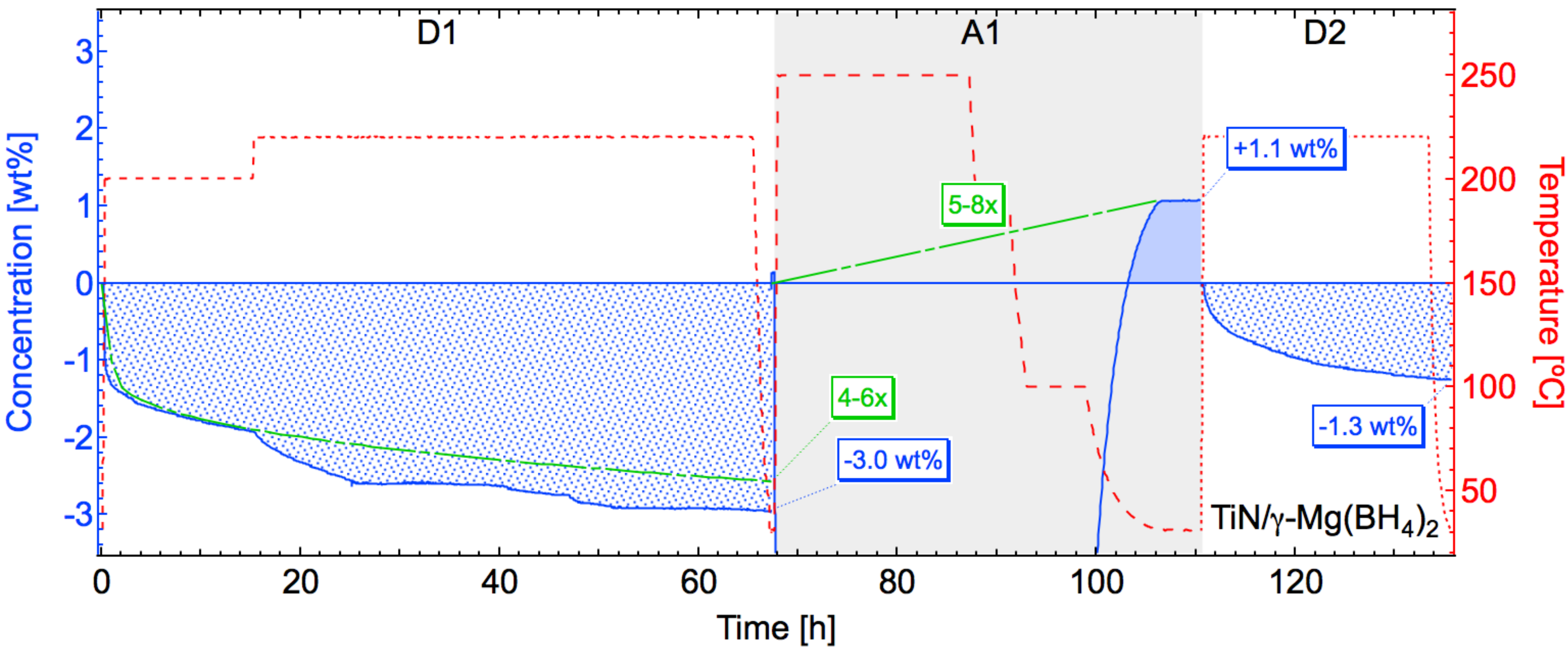


PCT: BN/$Mg(BH_4)_2$ does not cycle under mild conditions.

Cycle	H_2 wt%	Rate*
D1 – 220 °C, vacuum	-6.6	> 14x
A1 – 250 °C / 120 bar H_2	+1.9	1x
D2 – Desorption 2	-0.45	-

*Relative to neat $Mg(BH_4)_2$

A&P: TiN/$Mg(BH_4)_2$ cyclability

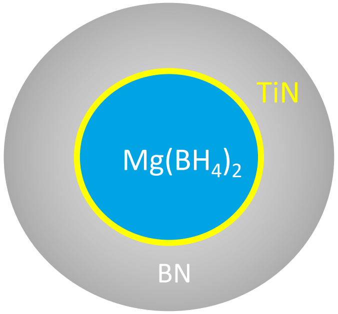


PCT: TiN/$Mg(BH_4)_2$ shows promise to cycle under mild conditions.

Cycle	H_2 wt%	Rate*
D1 – 220 °C, vacuum	-3.0	4-6x
A1 – 250 °C / 120 bar H_2	+1.1	5-8x
D2 – Desorption 2	-1.3	-

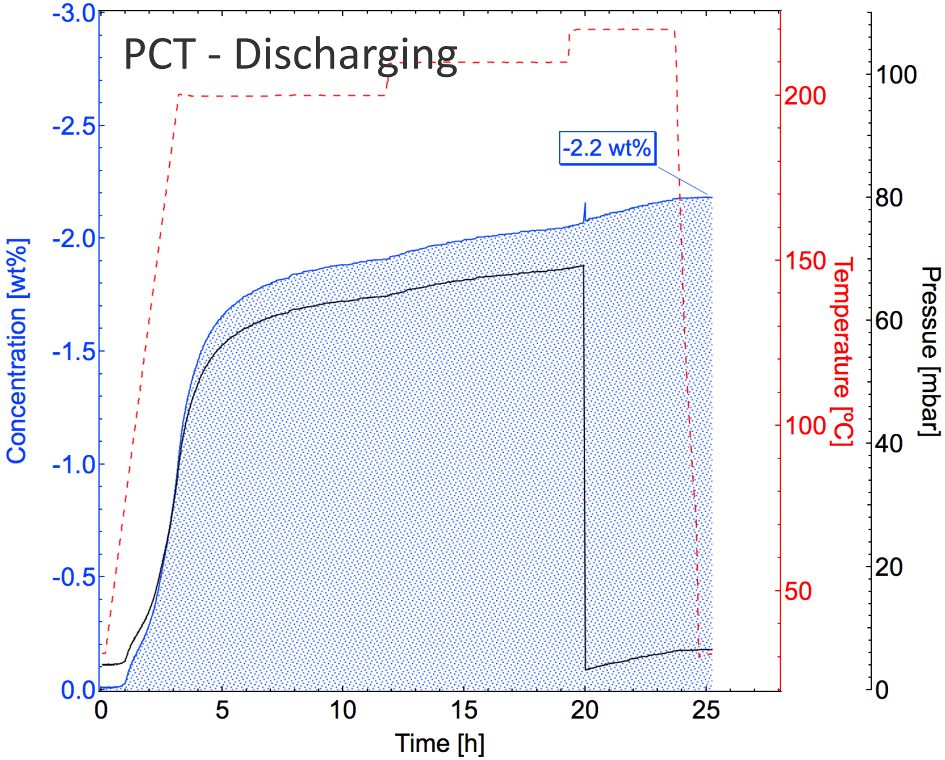
*Relative to neat $Mg(BH_4)_2$

A&P: Boron additive effects



Schematic of TiN-BN/$Mg(BH_4)_2$ Architecture

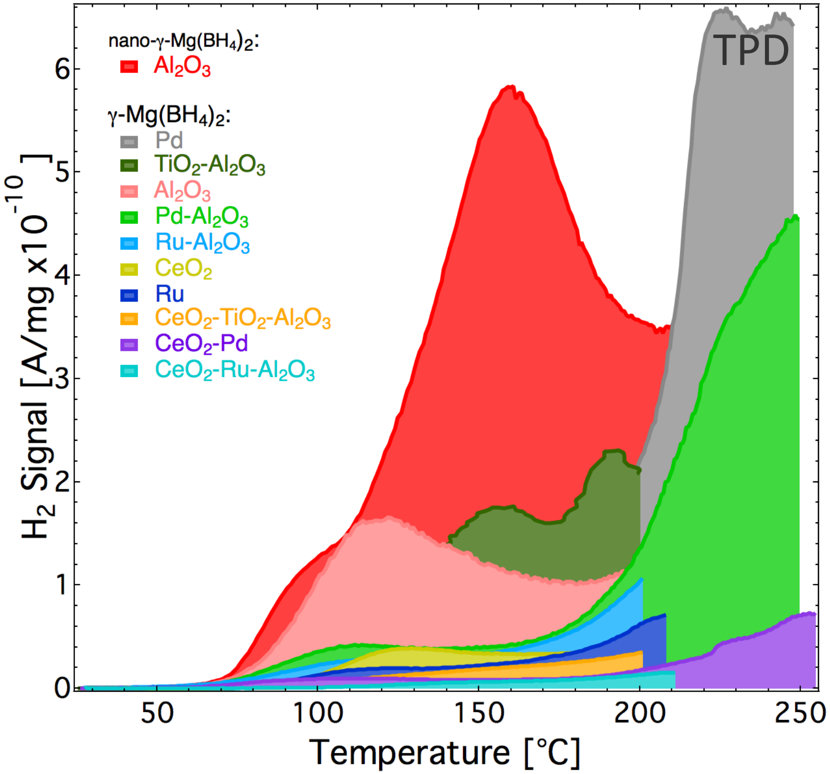
- TiN-BN/$Mg(BH_4)_2$:
  - Ultra-thin TiN layer between $Mg(BH_4)_2$ and BN
- PCT: Desorption resembles TiN/$Mg(BH_4)_2$



Results suggest chemical additive effects for BN-$Mg(BH_4)_2$ interface may result in the improved H_2 discharging.

A&P: Building the materials database for the HyMARC Data Hub

- FY18 ALD coatings on $Mg(BH_4)_2$
- > 14 different coating formulations (CeO_2, Pd, TiN…)
- TPD, TEM, XRD, PCT, …
- 100s of GB of data acquired!



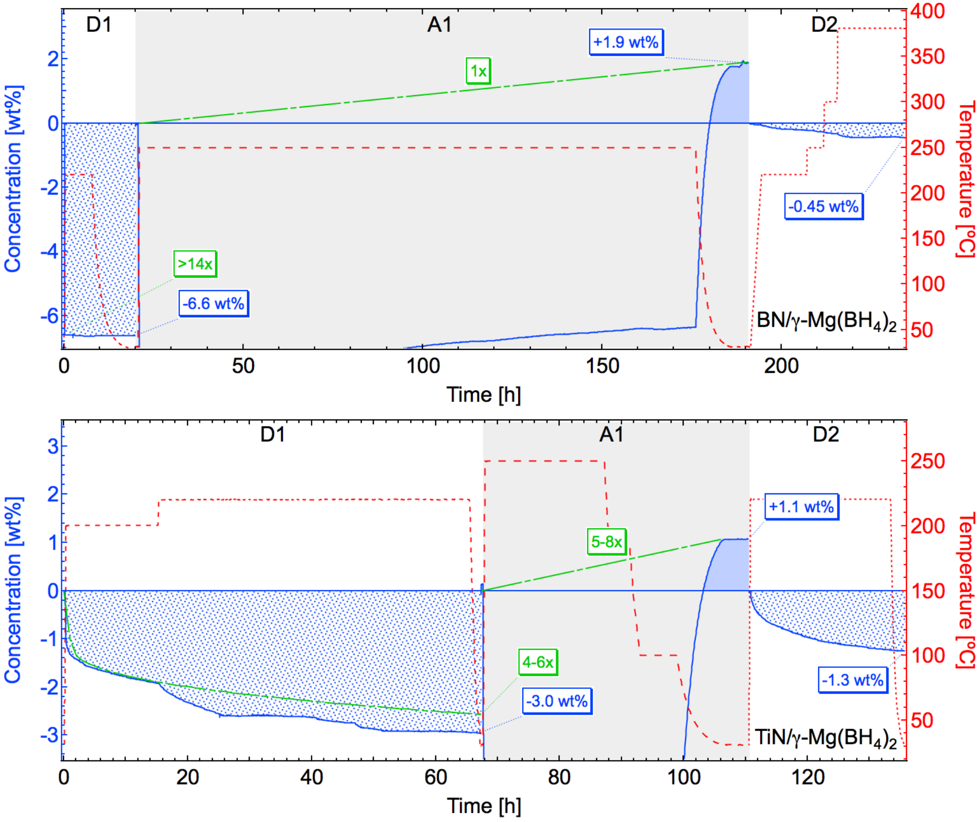
FY18 resulted in a significant number of new coatings for $Mg(BH_4)_2$ where data is being shared w/HyMARC via the data hub

Collaboration and Coordination

- H2 Technology Consulting LLC, prime partner, subcontractor, industry
  - Quantitative PCT measurements; Subject matter expertise
- Colorado School of Mines, Chemistry Department, subcontractor
  - Advanced materials characterization: atom probe tomography, TEM composition mapping
- HyMARC EMN, DOE FCTO
  - SNL: Nanostructured $Mg(BH_4)_2$, Subject matter expertise; high pressure experiments
  - NREL: Materials characterization, equipment, facilities, subject matter expertise
  - SLAC: X-ray scattering and spectroscopy
  - LLNL: Theory
  - PNNL: Advanced materials characterization; Subject matter expertise
- Forge Nano, ALD manufacturing company
  - Potential industry partner, letter of support

Remaining Challenges and Barriers

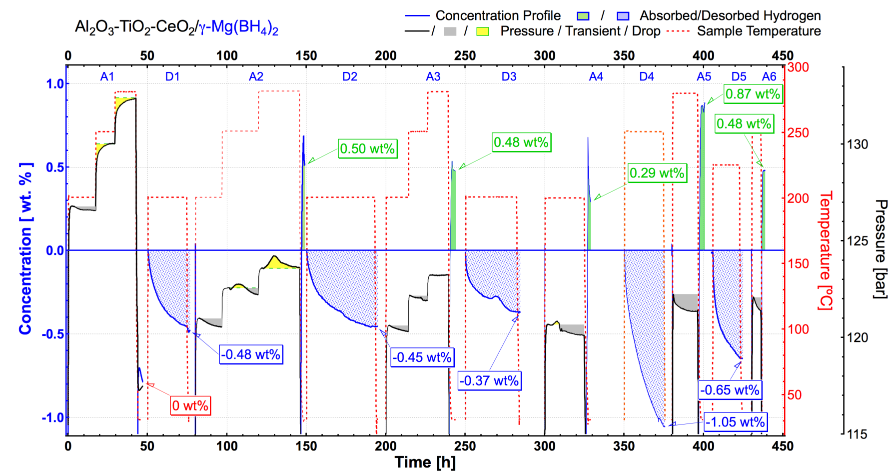
- Challenges/Barriers:
  - Cyclability
  - H_2 absorption rate
- Determine ALD driven mechanisms
  - What is the role of coating thickness?
  - What interfaces improve performance?



Improving hydrogen absorption rates and cyclability is the primary focus for FY19.

Proposed Future Work

- Meet criteria for FY19 Go/No Decision point:
  - Three H_2 discharge/charge cycles at 3 wt% with 5x improvement of charging rate
- Meet quarterly milestones
- Determine ALD driven mechanism



Year 1: Titanium and cerium oxides showed potential to improve cyclability (above). New ALD nitride coatings inspired by these results will be developed.

ALD enables rapid development and screening of new additives that can enhance cyclability and charging rates for $Mg(BH_4)_2$ to meet project deliverables.

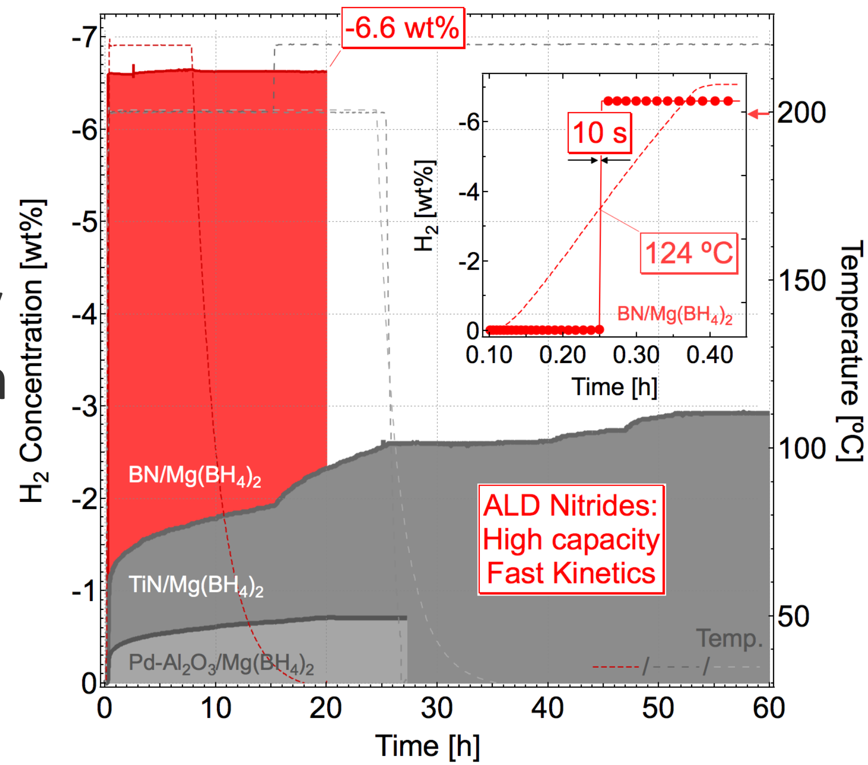
Proposed future work is subject to change based on funding levels and program needs

Technology Transfer Activities

- 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.
- Pursuing potential partners for ALD scale-up (ForgeNano)
- Identifying other applications where this technology would solve technical problems

Summary

- ALD coatings on $Mg(BH_4)_2$ led to unprecedented hydrogen discharging
- ALD offers the ability to rapidly develop new additives that can help metal hydrides meet DOE targets
- Cyclability and hydrogen charging need improvement



Deliverable Summary Table	FY 18 (Best Result)	FY 19 Target
H_2 Cycles / Cycled capacity	5 / 0.5 wt%	3 / 3 wt*
H_2 Discharging: Capacity /Rate / Temp.	7 wt% / > 14x / 107 °C	-
H_2 Charging: Capacity / Rate / Temp.	0.5 wt% / 5x / 250 °C	3 wt% / 5x / 250 °C

Thank You

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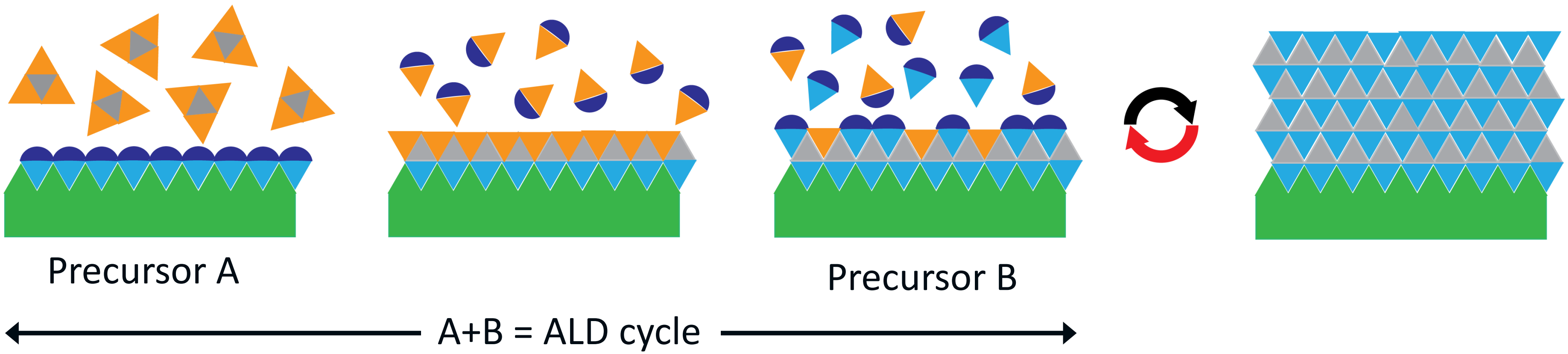
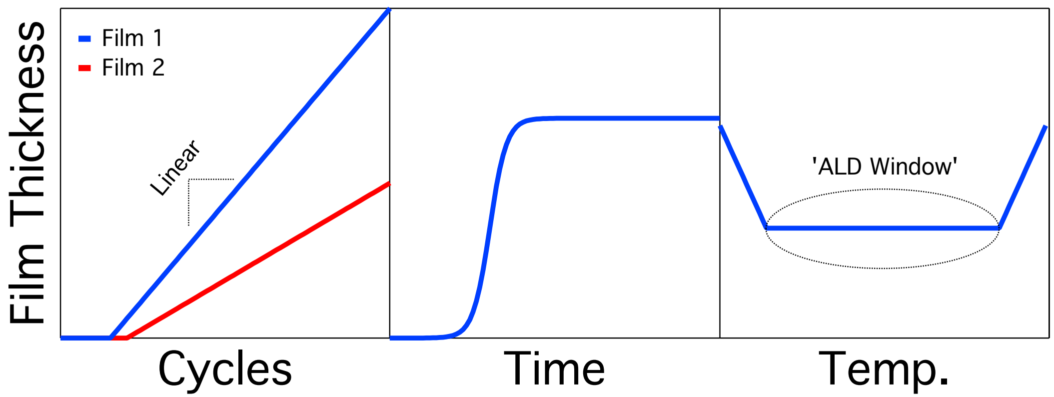
Technical Back-Up Slides

Accomplishments and Progress: Responses to Previous Year Reviewers’ Comments

- This project was not reviewed in FY18.

Atomic Layer Deposition





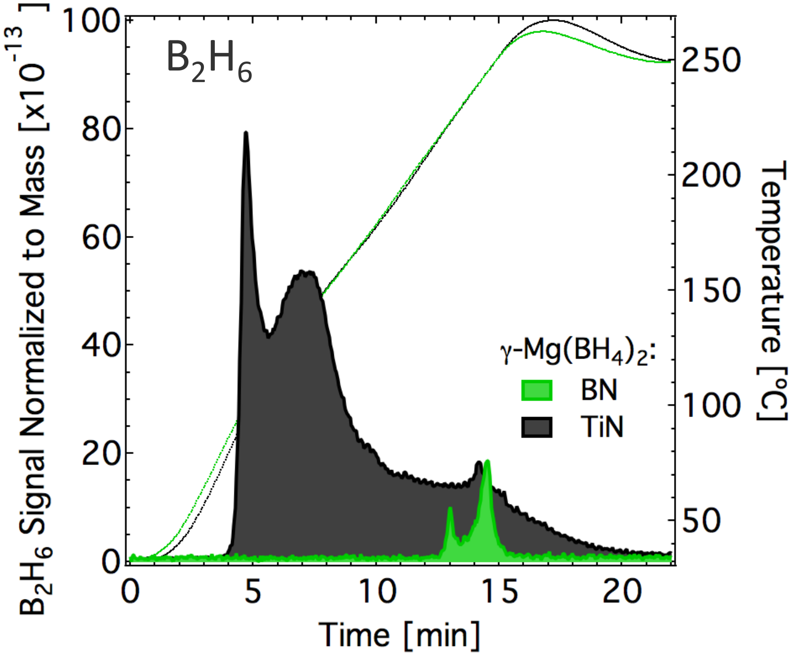
Nucleation and growth rate determined by surface chemistry and precursor molecular size.

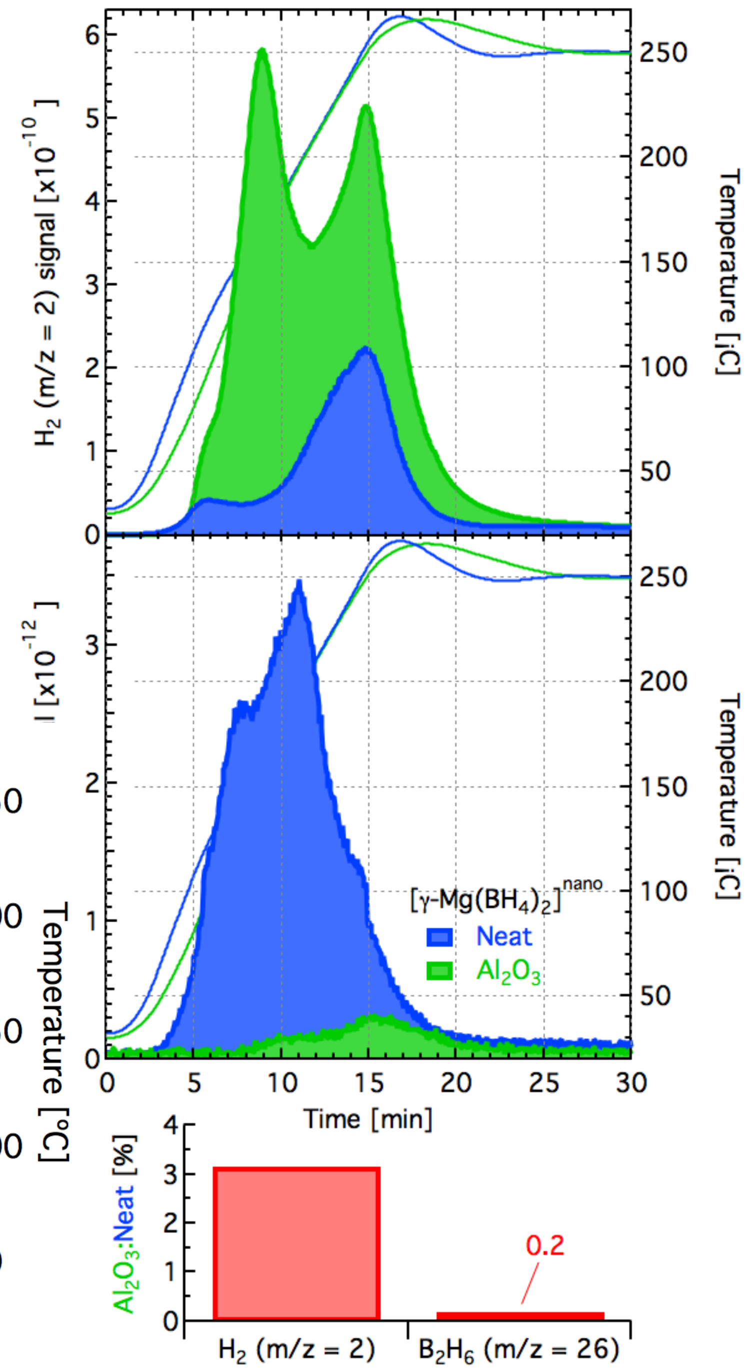
Operating principles:

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

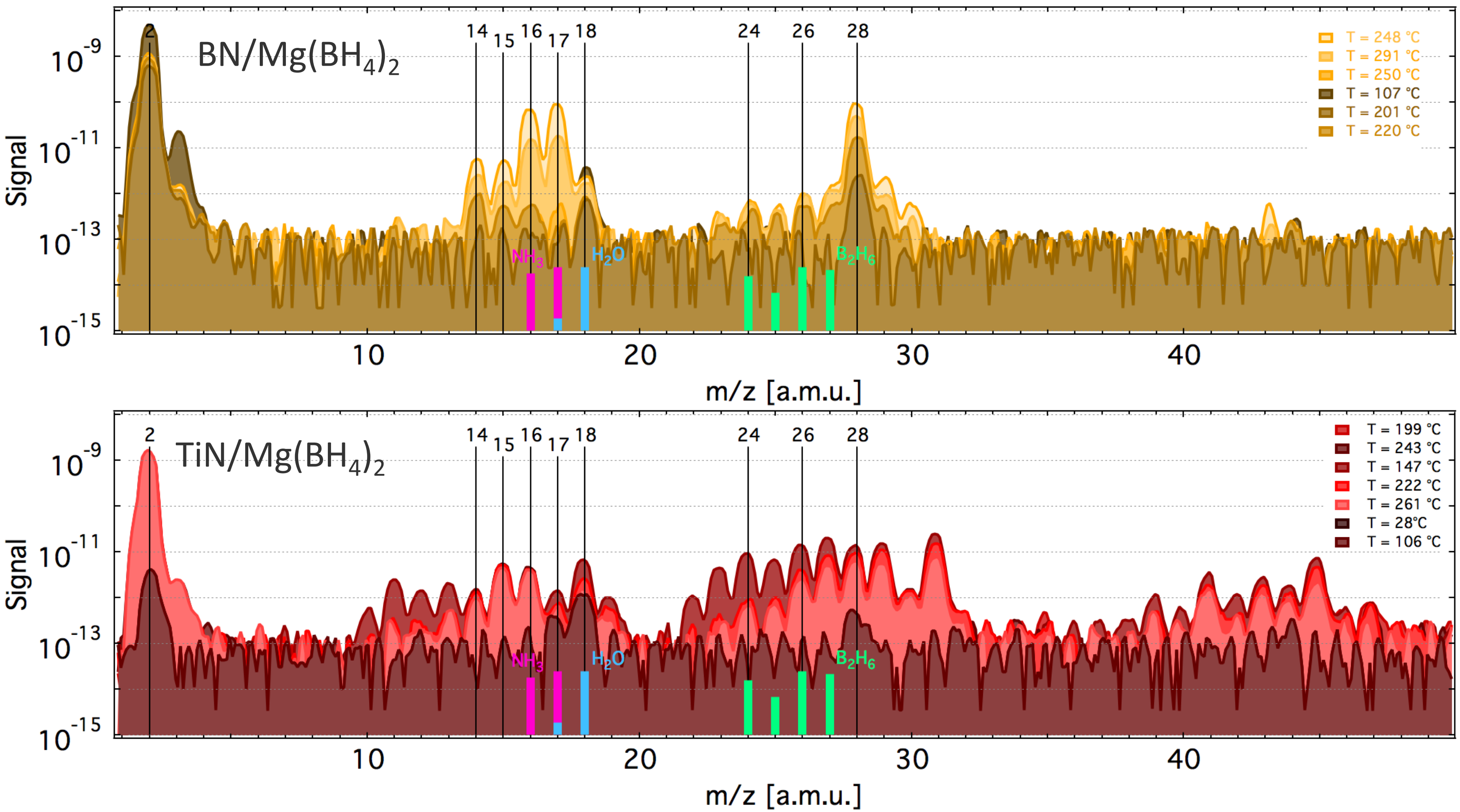
B_2H_6 Suppression

- Temperature programmed desorption showing suppression of B_2H_6:
  - BN coatings
  - Al_2O_3 coatings



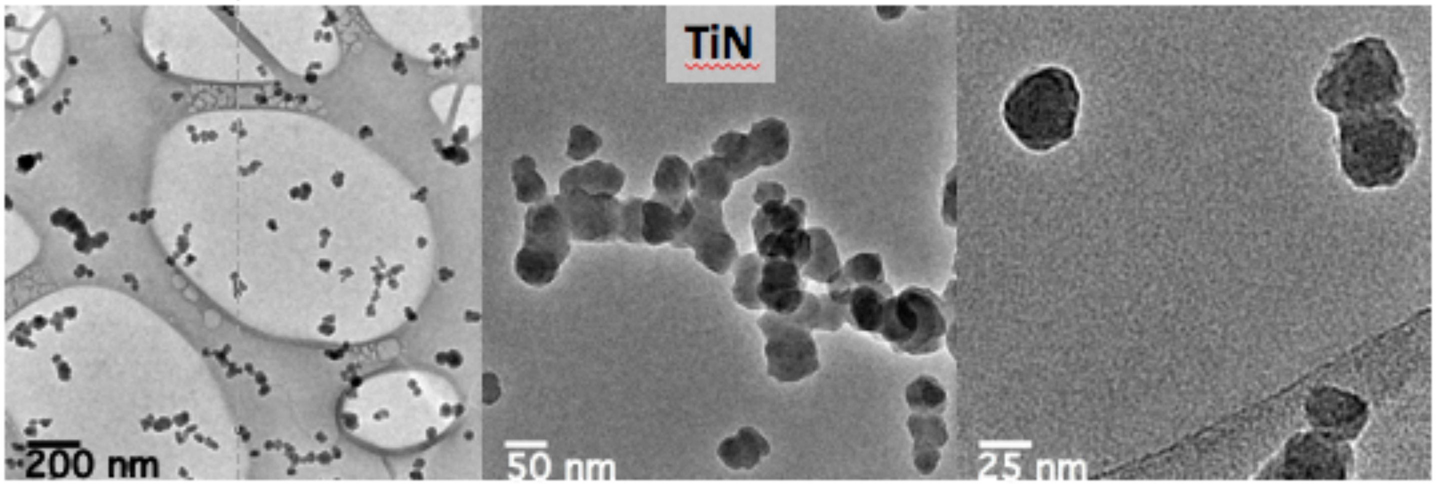


Desorption mass spectra



- $BN/Mg(BH_4)_2$: Cleaner desorption reaction – H_2 >> NH_3, N_2; minimal B_2H_6
- $TiN/Mg(BH_4)_2$: Complex desorption reaction – with some B_2H_6

TEM of TiN/$Mg(BH_4)_2$



- Similar to previous oxide coatings: small particles discreet particles
- Coated powders show a gold color consistent w/TiN
- XRD shows now crystallinity as deposited