NREL
Transforming ENERGY

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

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DOE Hydrogen and Fuel Cells Program
2020 Annual Merit Review and Peer Evaluation Meeting

Project ID #ST143

Overview

Timeline and Budget

- Project start date: 9/15/2017*
- Project end date: 3/31/2021

- FY18 DOE funding: $250k
- FY19 planned DOE funding: $375k
- FY20 planned DOE funding:
- $375k
- Total DOE funds received to date: $1,000,000

*Phase 3 Project Start: 4/1/2020

Barriers

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

Partners

H2Tech Consulting (cost share)

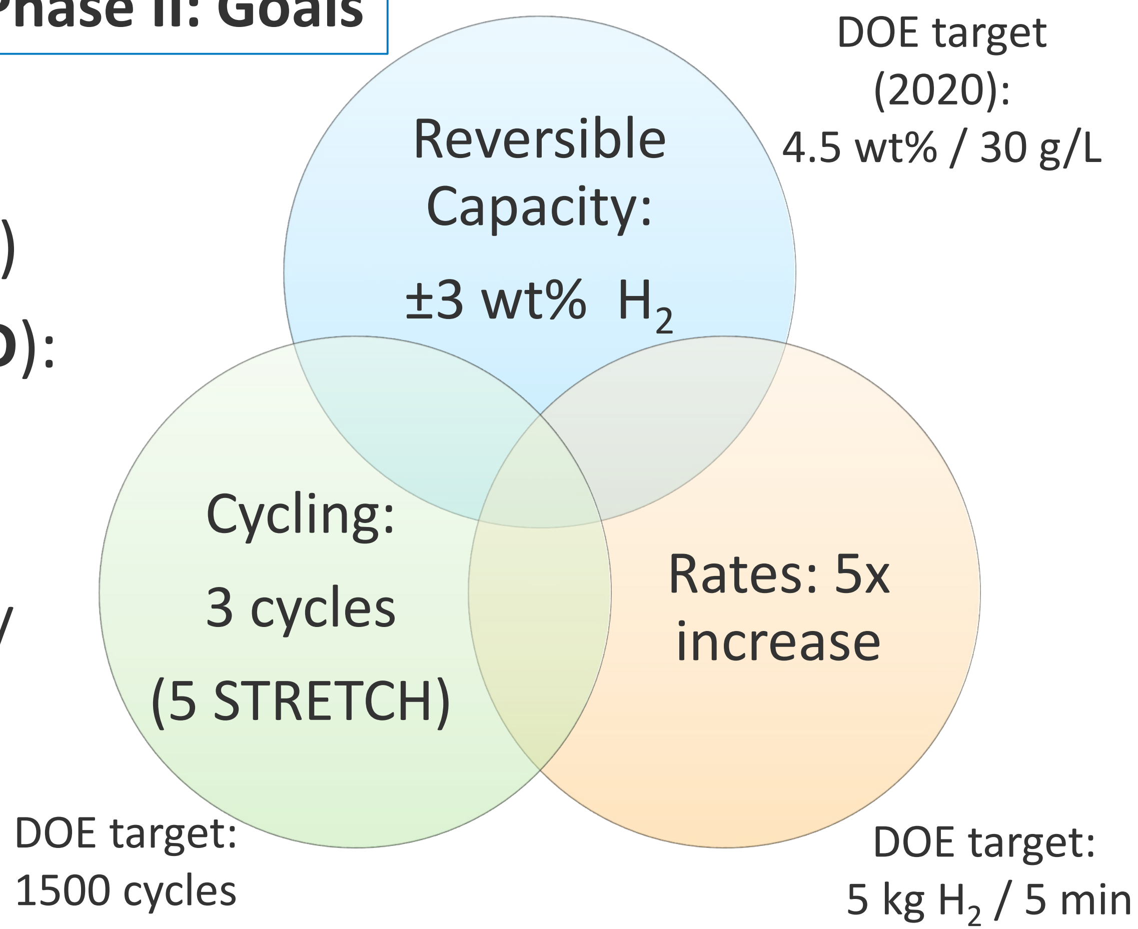
Colorado School of Mines (cost share)

HyMARC core team

Relevance: Improve H_2 cycling and rates

- Project objectives: Improve ***reversible capacity*** and ***rates*** (charging/discharging)
- Reversibility (Barrier **D**):
  - Increase cycle life
- *Rates* (Barrier **E**.):
  - Reduce H_2 charging / discharging time
  - Reduce Operating Temperatures

Phase II: Goals

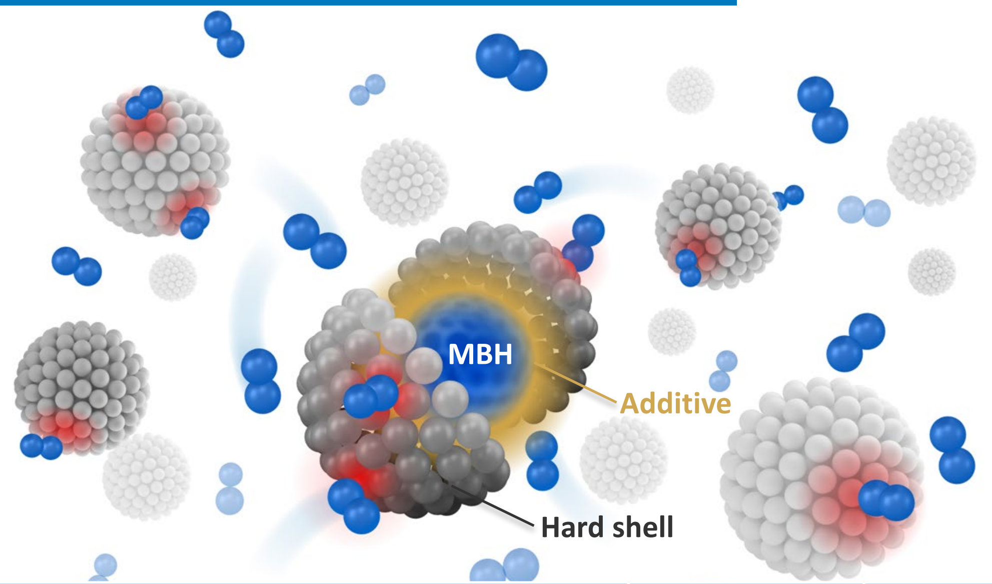


Complex metal hydrides like $Mg(BH_4)_2$, $NaAlH_4$ possess a high hydrogen storage capacity, but insufficient charging/discharging rates and cyclability for DOE targets.

Approach: Coatings by Atomic Layer Deposition (ALD)

Concept: Improve ***reversible capacity*** and ***rates*** by materials with:

1) Durable nanostructured phase
2) Chemical additives that enhance reaction rates



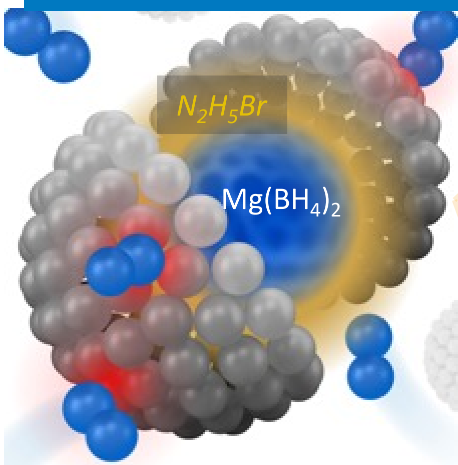
How: ALD coatings that:

- **Protect.** Hard-permeable coating to retain nano-hydride for cyclability.
- **Catalyze.** Thin layer of additives that enhance rates.

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

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

Accomplishments & Progress (A&P): Desorption mechanism for ALD BN/$Mg(BH_4)_2$



- Rapid H_2 discharging results $Mg(BH_4)_2$ + N_2H_5Br
- N_2H_5Br is a product of 'boron nitride' ALD
- Reaction driven by:
  - Heterolytic cleavage of B-H, N-H
  - Exothermic
- Irreversible Mg-O-Br-B-N products result

$Mg(BH_4)_2 + N_2H_5Br$

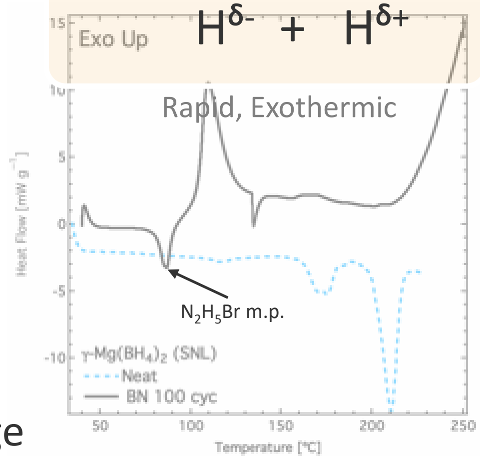
$H^{\delta-}$ + $H^{\delta+}$

Rapid, Exothermic

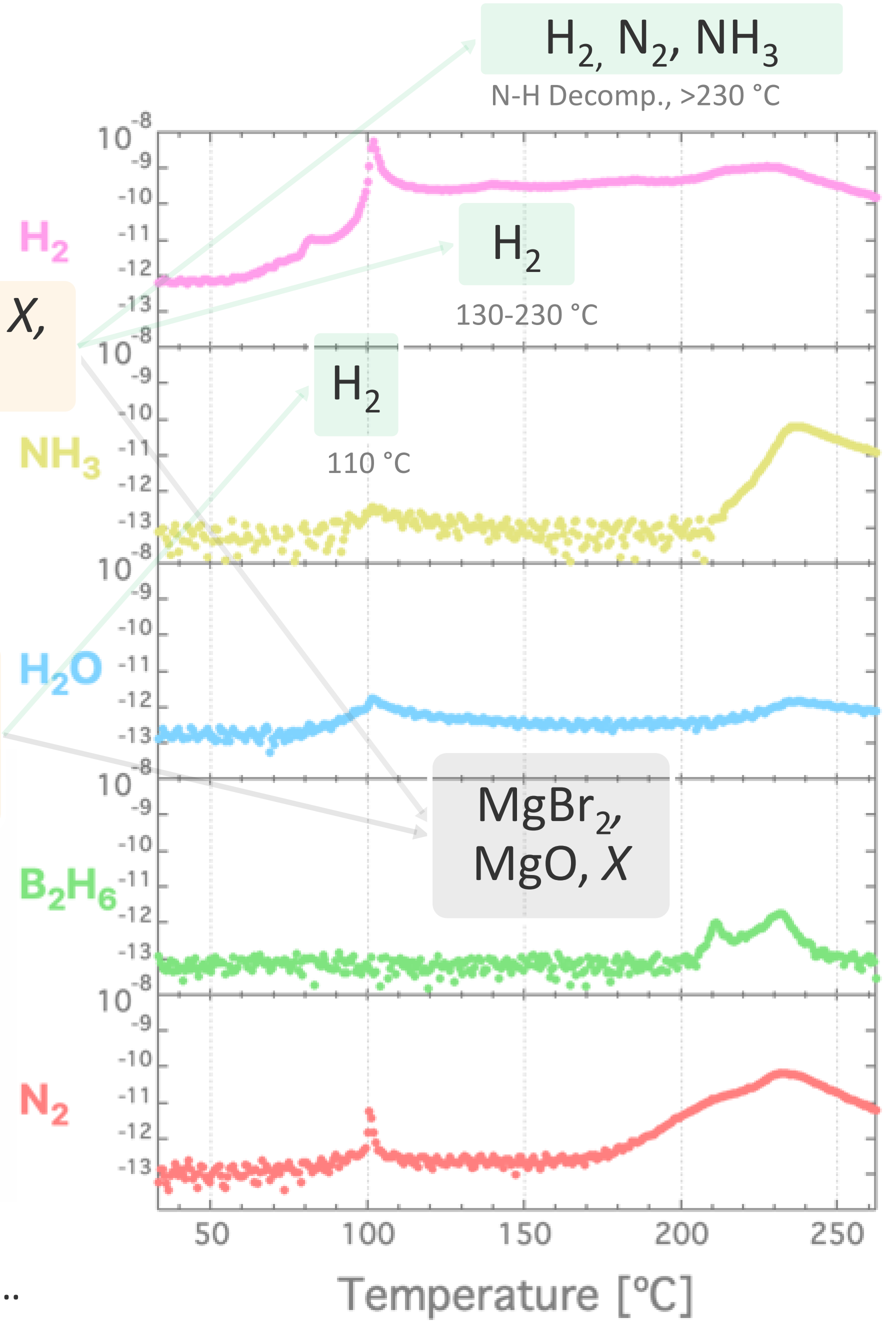
Δ Exo →

$Mg(BH_4)_2$ + *X*, *MgH_2*

X Suppresses B_2H_6



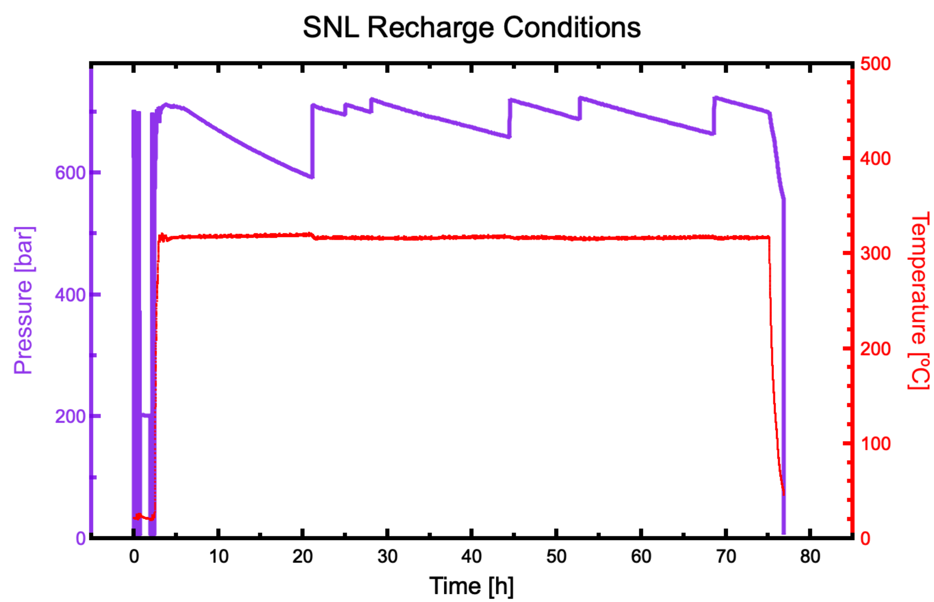
X = Amorphous B-N-O…



A&P: High pressure recharge of ALD-$Mg(BH_4)_2$

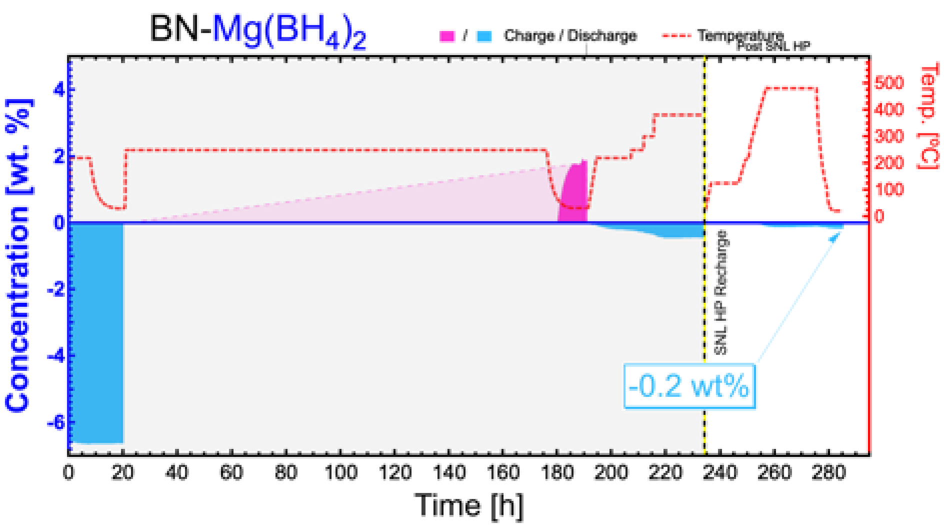
- High Pressure Recharge / Sandia National Lab:
  - Year 1 materials: ALD on $Mg(BH_4)_2$:
    TiO_2-Al_2O_3-CeO_2,
    Pd-Al_2O_3,
    BN, TiN
  - Pre-desorbed to high temperature
  - Recharge: 700 bar H_2 / 320 °C / 72 h
  - All 4 samples recharged at the same time

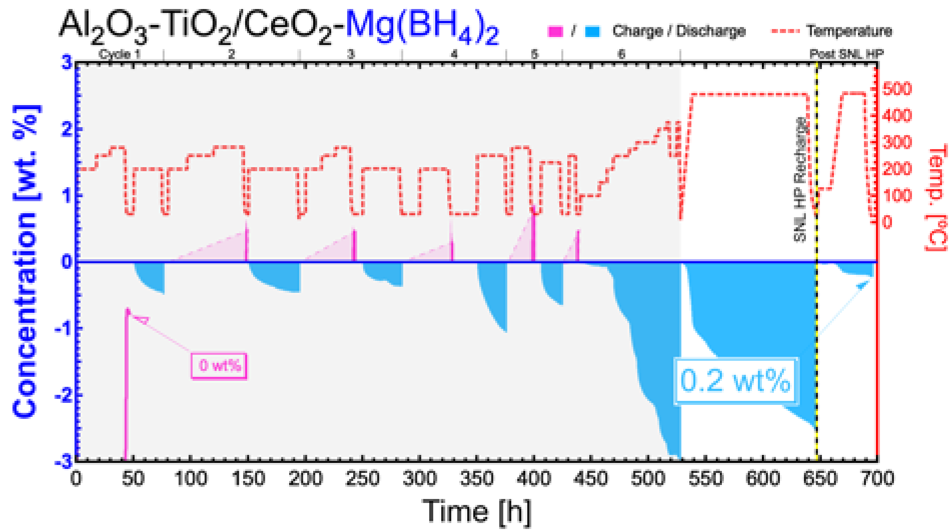
Sandia high pressure charging apparatus can reach up to 1000 bar H_2 and 400 °C.

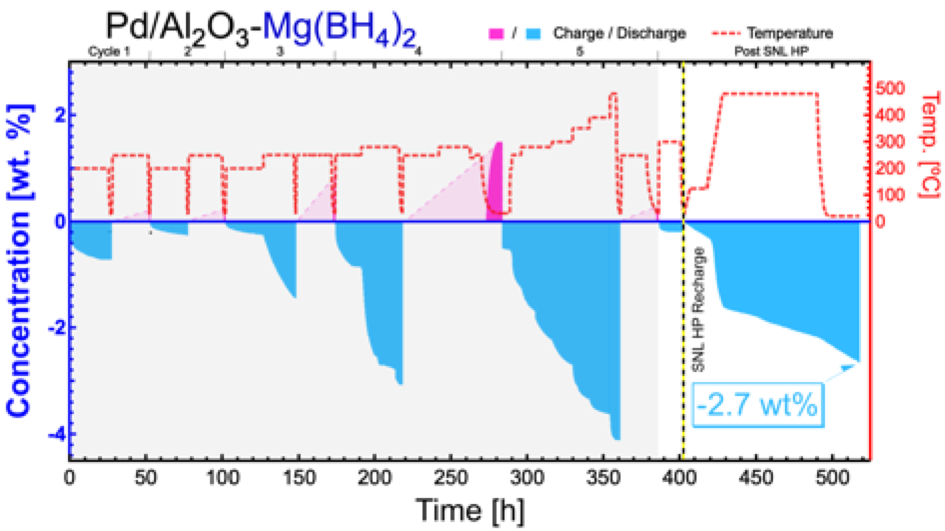


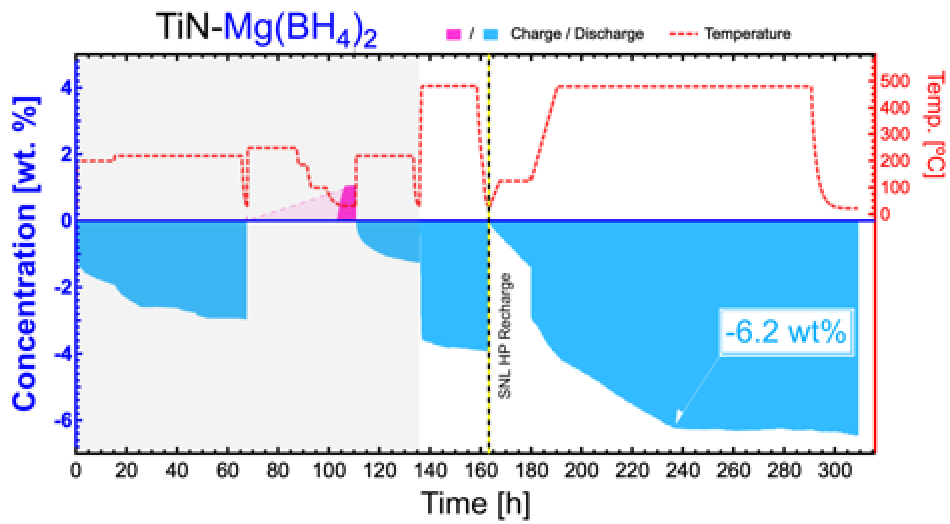
Recharge conditions of 700 bar H_2 /320°C/ 72h should not result in $Mg(BH_4)_2$ without active additives present.

A&P: Post High-Pressure Recharge Desorption









Shaded Area: Data From Phase 1

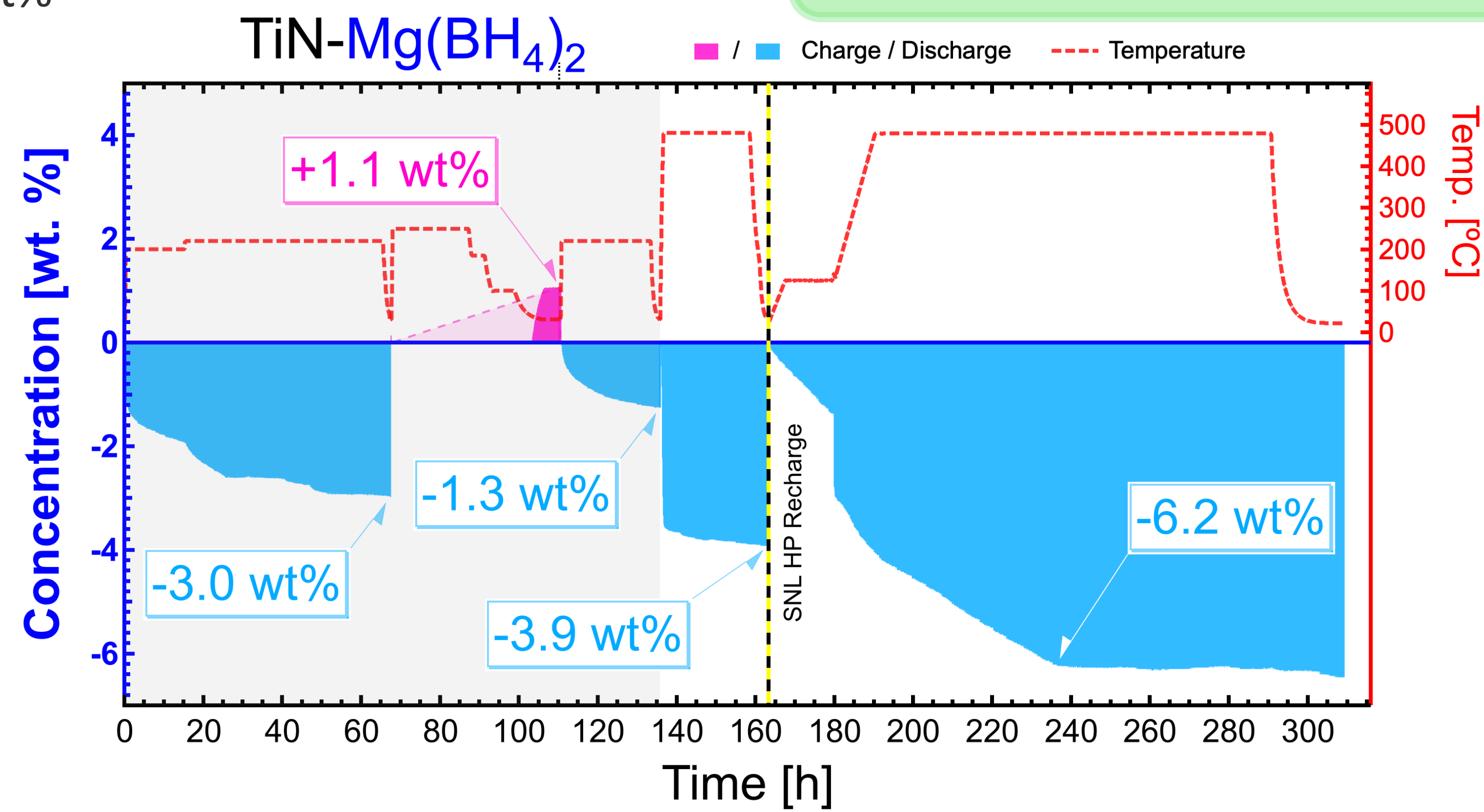
Clear Area: Results SNL HP charging

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

- $Mg(BH_4)_2$: 14.9 wt% H_2
- (-3.0) + (+1.1) + (-1.3) + (-3.9) = - 7.1 wt% H_2
- $TiN/Mg(BH_4)_2$: 7.1 / 14.9 = 50% Capacity
- Reversibility $TiN/Mg(BH_4)_2$ = 6.2 wt%

- @ 6.2 / 7.1 = 87 % efficiency! (?)
- Desorbed H_2 >> Binary hydrides (e.g. MgH_2 at 7.6 wt%)

ALD titanium nitride (TiN) is a promising new hydride additive!



A&P: Reversibility via TiN coating shows a path to cycling (and *Phase 3)*

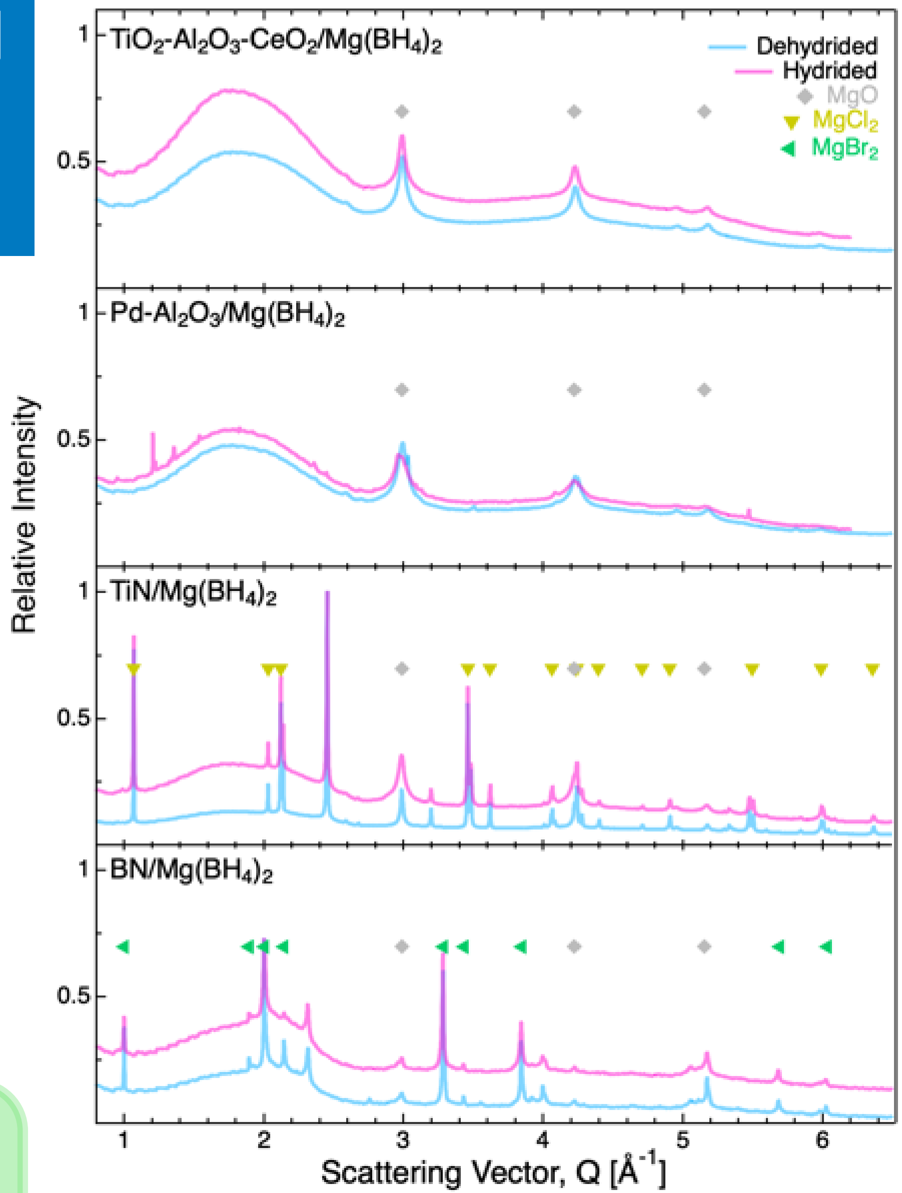
– No crystalline $Mg(BH_4)_2$
(or other hydrides)

– Lots of irreversible $MgCl_2$, MgO, etc.

– Rates Needed 480 °C and it still took a long time

- $TiN/Mg(BH_4)_2$ reversibility at high cycling efficiency

- *GNG & Phase 3:* **Find the metal hydride that TiN will enable cycling**

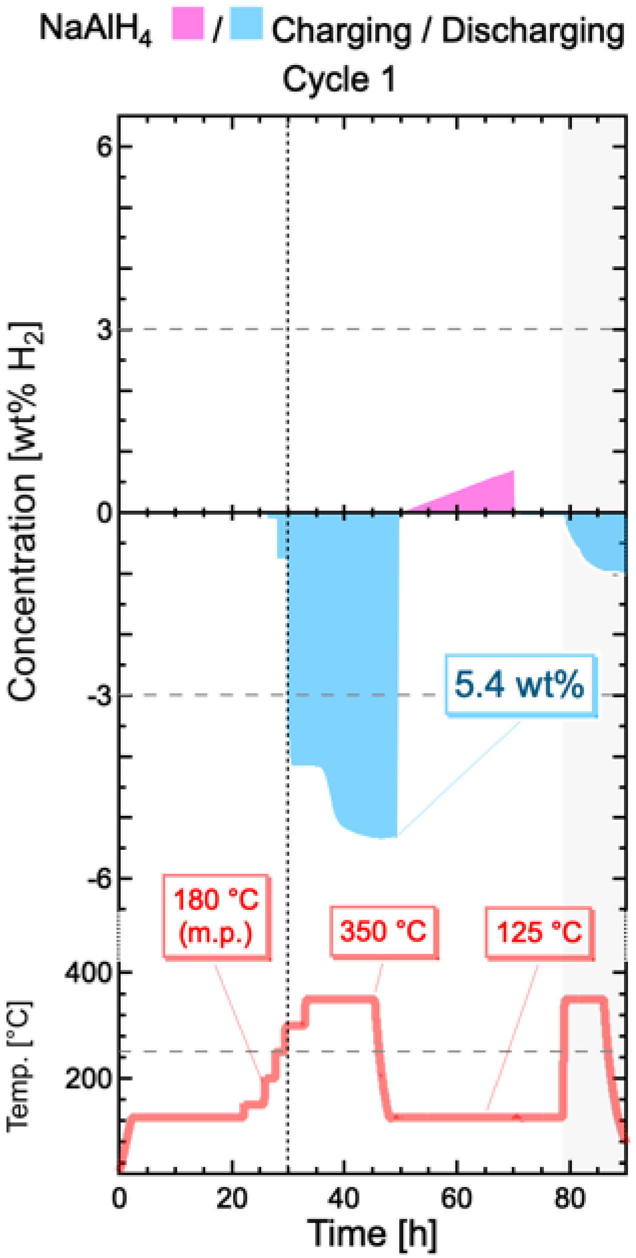


XRD: Metal Hydride Peaks: ⛔
$MgCl_2$ ($MgBr_2$), MgO, Amorphous: ✓
(SSRL – N. Strange, M. Toney)

A&P: Unmodified 'Neat' $NaAlH_4$ has Poor Rates

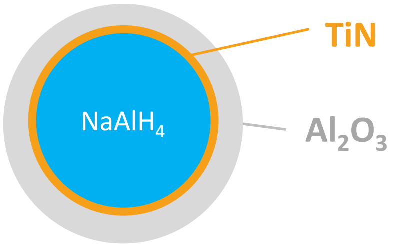
- Without additives (e.g. Ti) $NaAlH_4$ kinetics are too slow:
  - 5.4 wt% H_2 desorbed only after heating > 300 °C
- Absorption thermodynamics requires lower temperatures
  - Very little reversible cycling capacity observed
- **Can an ALD TiN get $NaAlH_4$ to cycle?**

Neat $NaAlH_4$ from Sigma Aldrich

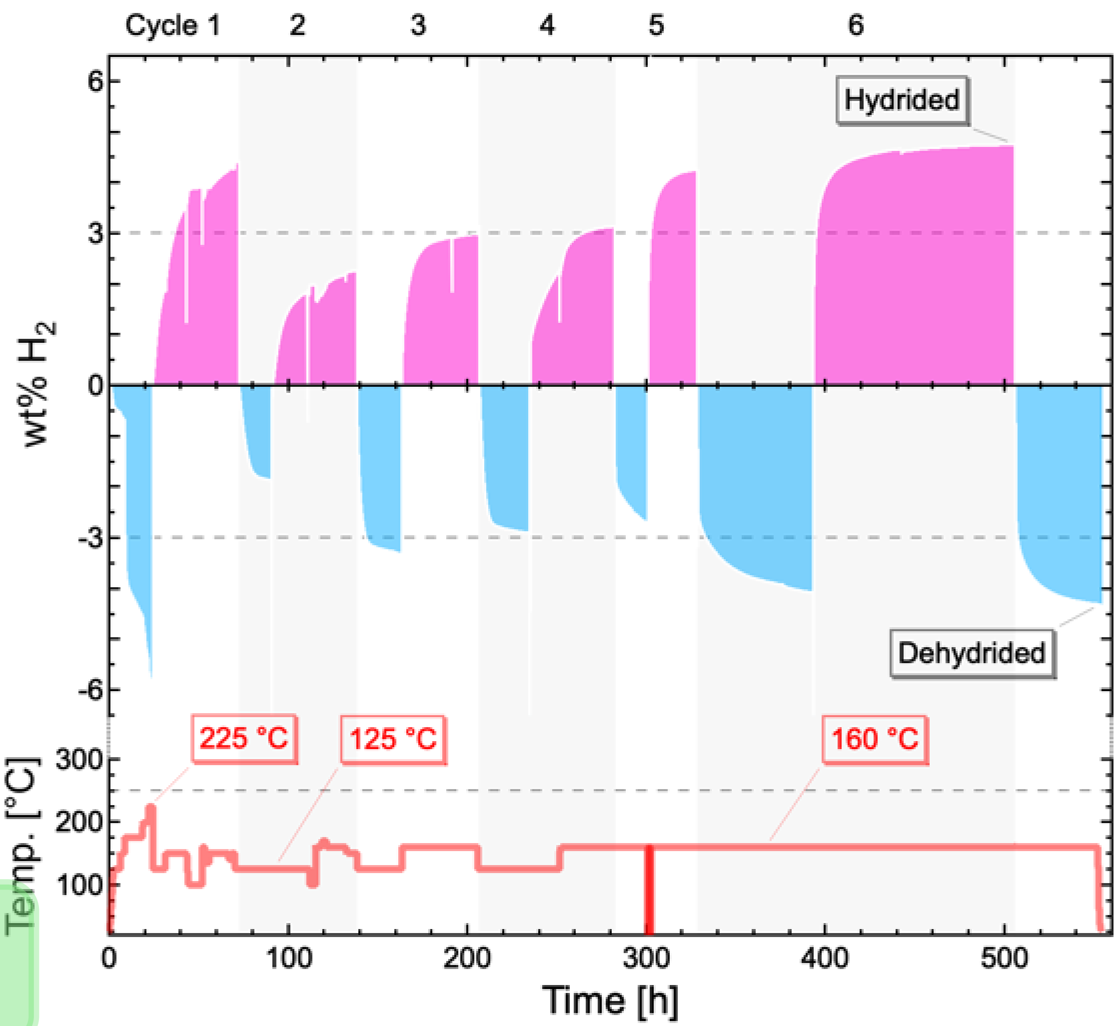


A&P: H_2 cycling ALD-$NaAlH_4$ surpasses Phase 2 goal

ALD on $NaAlH_4$ (Sigma):
1 nm TiN + 10 nm Al_2O_3



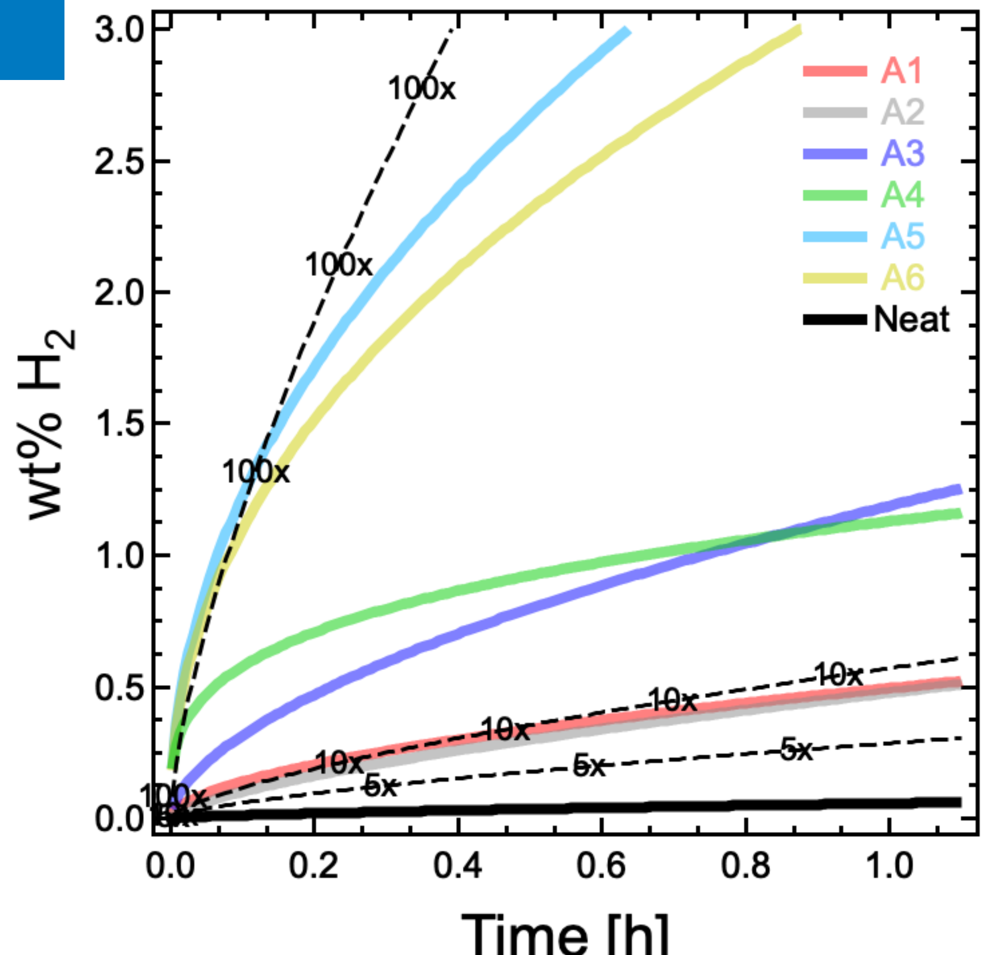
- PCT cycling:
  - 120 bar H_2
  - 225 °C: -5.7 wt%: Full theoretical capacity
  - 160 °C (from 350 °C)
  - 6.5 cycles
- Reversibility:
  - -3.6/+3.8 wt% avg.
  - -4.3/+4.8 wt% best ✓



- Goal: 3 wt% @ 3 cycles

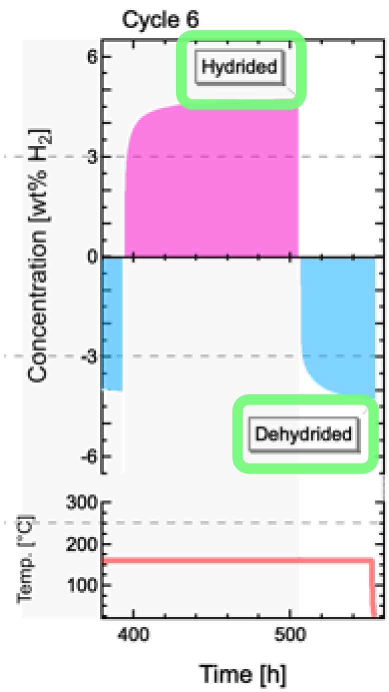
A&P: Rates for ALD-$NaAlH_4$ exceed Phase II Goal

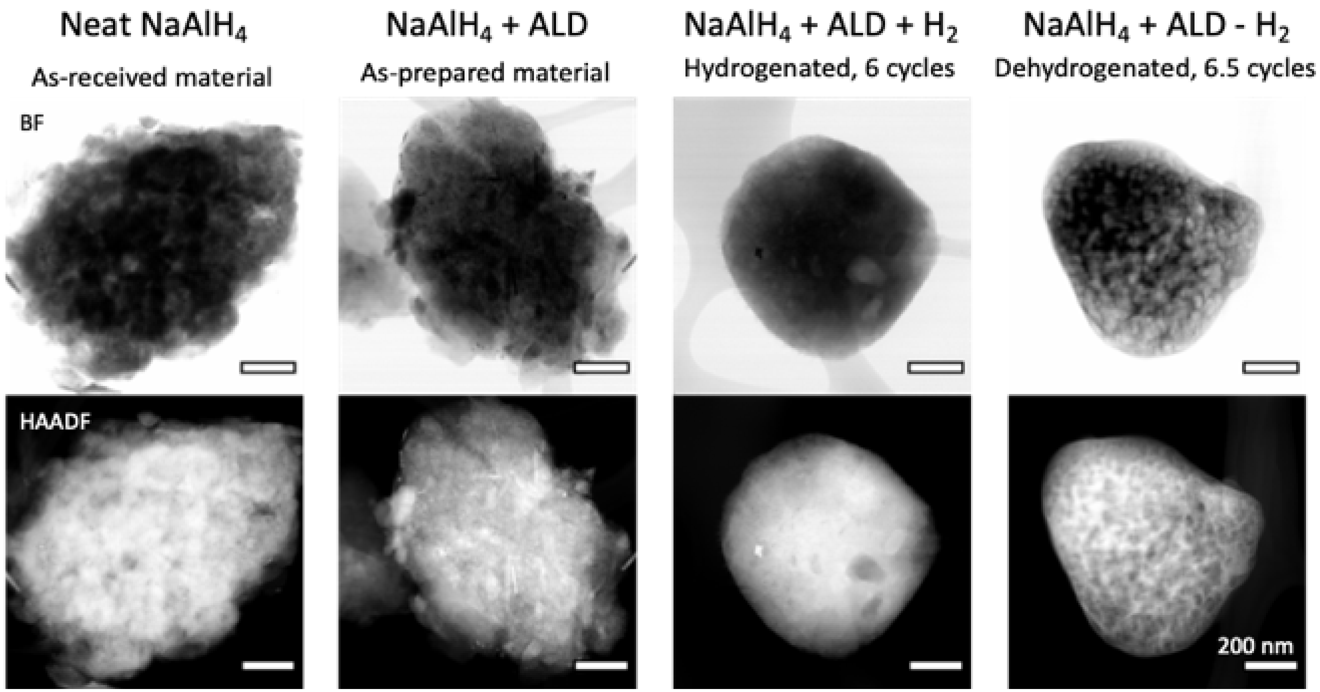
- Power Law Fits to H_2 absorption rate ***v***:
  - $v = k[H_2]^p$
  - Fitting for first 0.5 h
- Scalar multipliers to rate law of neat $NaAlH_4$
  - 5x, 10x, 100x
- ALD coatings improve Absorption rates by **10-100x**



Rate analysis of absorption steps A1-6 for ALD-$NaAlH_4$ compared to Neat exceed the goal of 5x improvement. Temps. ***125 °C****: Neat, A1, A2;* ***160 °C****: A3, A4, A5, A6.*

A&P: Smooth, clean morphology evolves from cycling ALD-$NaAlH_4$





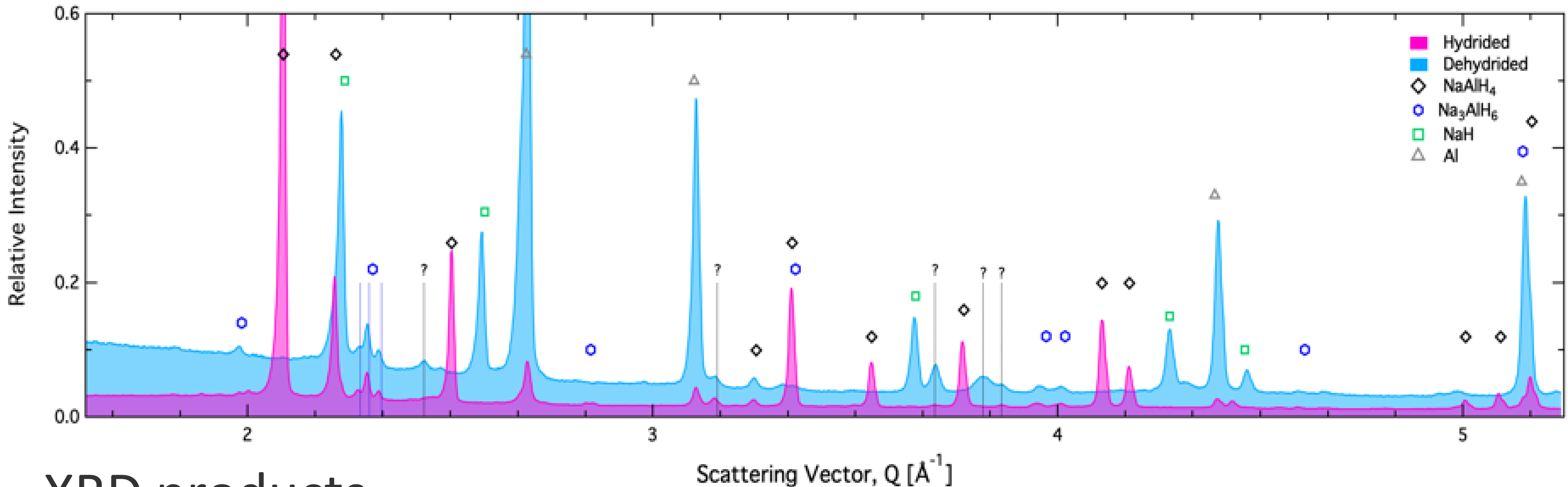
TEM

- Desorption 1 > 180 °C (melting point)!
- Cycling → smooth morphology
- **Particle size: 100s of nm**, low particle agglomeration

XRF (not shown)

- Neat $NaAlH_4$, Ti? No
- Ti on ALD-$NaAlH_4$? Yes!
- **No detectable Cl**

A&P: Efficient Cycling ALD-$NaAlH_4$ with high reversibility



XRD products

- Dehydrided: Rxn {2}
- Hydrided: Rxn {1}
- **No Cl products (e.g. NaCl)**
- Reversibility: **80-85% of 5.6 wt%** Cycling {1} + {2}

$NaAlH_4$ (7.5 wt% H_2 / 3.7 + 1.9 = 5.6 wt% reversible)					
	Reaction	wt% H_2 (theoretical)	Sample	XRD	wt% H_2 (measured)
{1}	$NaAlH_4 \rightleftharpoons$ ⅓Na_3AlH_6 + ⅔Al + H_2	3.7	Hydrided	**$NaAlH_4$**; Al, Na_3AlH_6 (trace)	+4.8
{2}	$Na_3AlH_6 \rightleftharpoons$ NaH + Al + 3/2H_2	1.9	Dehydrided	**NaH, Al**; $NaAl_3H_6$ (trace)	-4.3
{3}	NaH ⇒ Na + ½H_2	1.8	No	**No Na**	

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

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

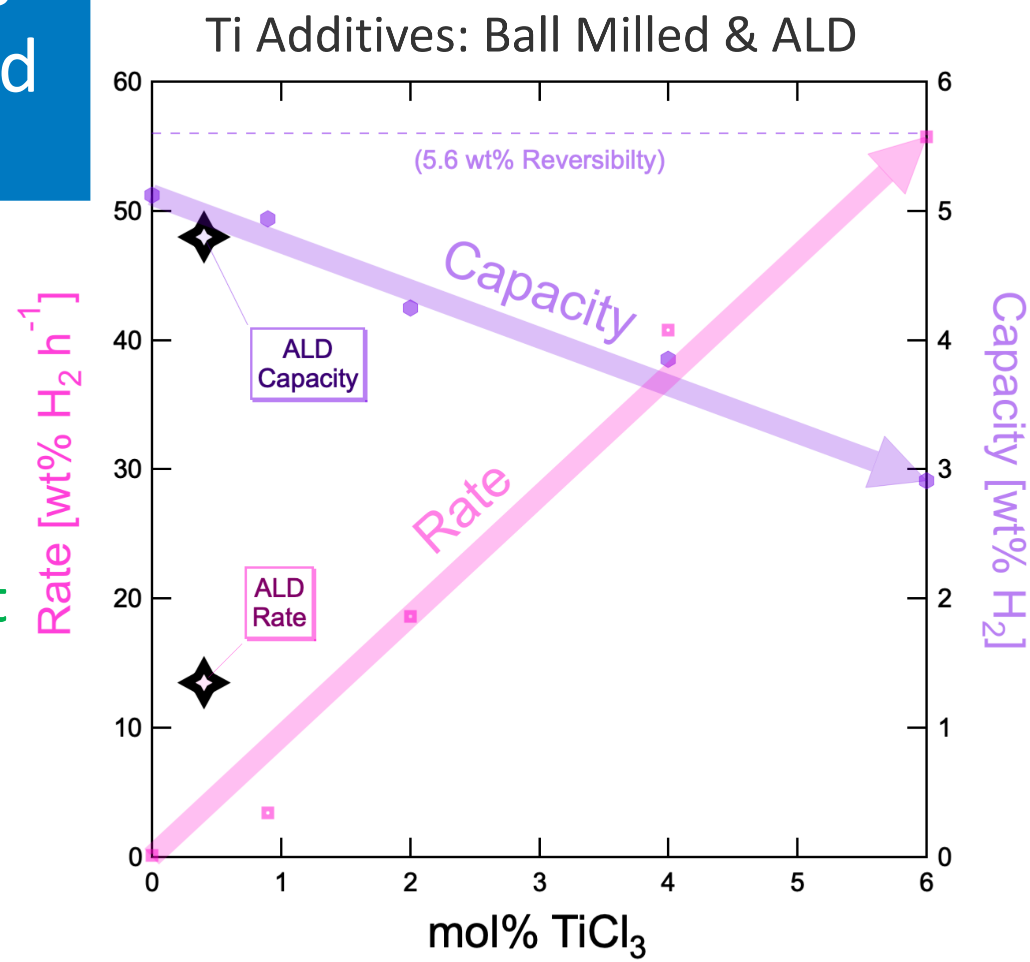
Remaining Challenges and Barriers: How good is ALD-$NaAlH_4$?

Rates:

- ALD-$NaAlH_4$ rate is an excellent start with efficient Ti loading
- A 10x increase from current levels is required for the DOE charging target

Reversible Capacity:

- ALD-$NaAlH_4$ Reversibility Capacity is exceptional
- $\geq$5 wt% H_2 is needed for a pathway to technology



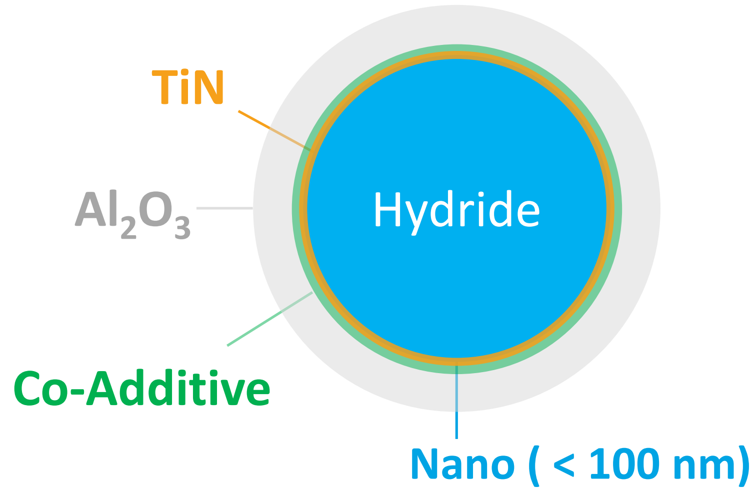
Conventional balled milled Ti additives increase rate at the cost of reversible capacity:

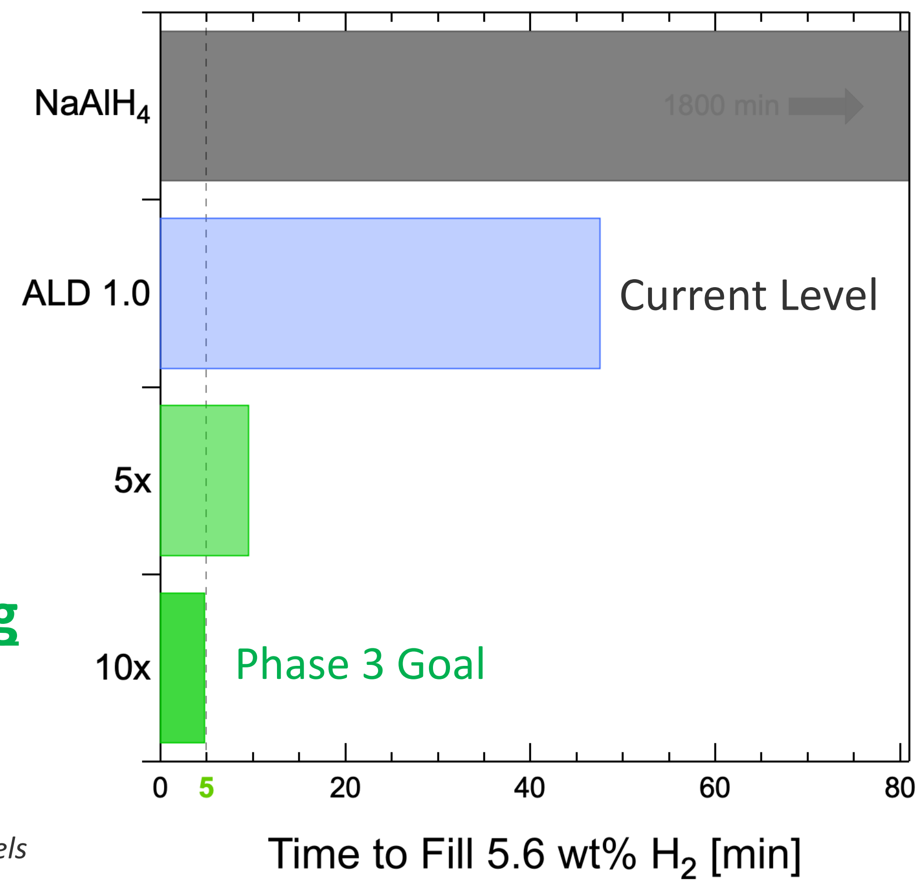
$$NaAlH_4 + TiCl_3 \Rightarrow \underline{NaCl} + Ti + NaAlH_4 \ldots$$

Data in figure adapted from: "Effect of Ti-catalyst content on the reversible hydrogen storage properties of the sodium alanates", G. Sandrock,J Alloys Compd, **339** (2002) 299.

Proposed Future Work: Increase Rates / Capacity

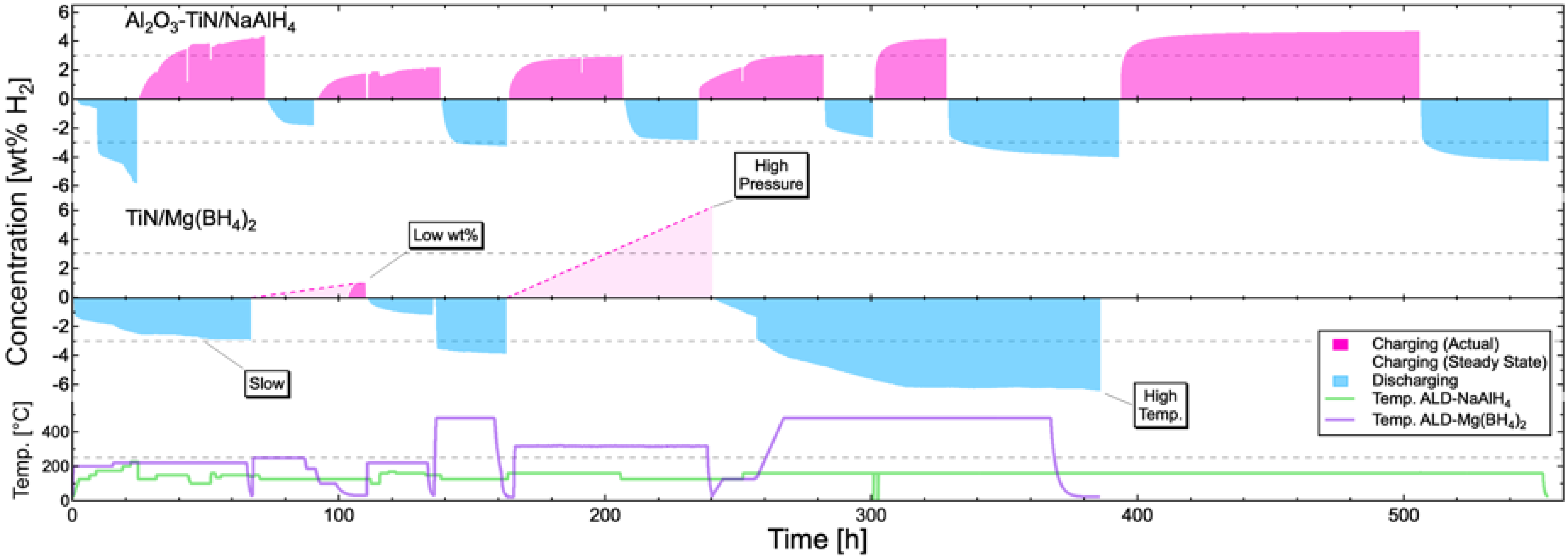
- Co-Additives: Ti + Fe*
  - **<u>Increase Rate > 2x</u>**
  - Decrease Temperatures
  - *Fe, Ni, Ce, Zr, Pd…
- Nano-size Hydride
  - **<u>Increase Rate > 5x+</u>**
  - Increase reversible capacity by control of reaction pathways
- Al_2O_3 Coating
  - **<u>Improve Cycling, Handling</u>**
  - ALD Al_2O_3 passivates w/o loss in capacity





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

Summary



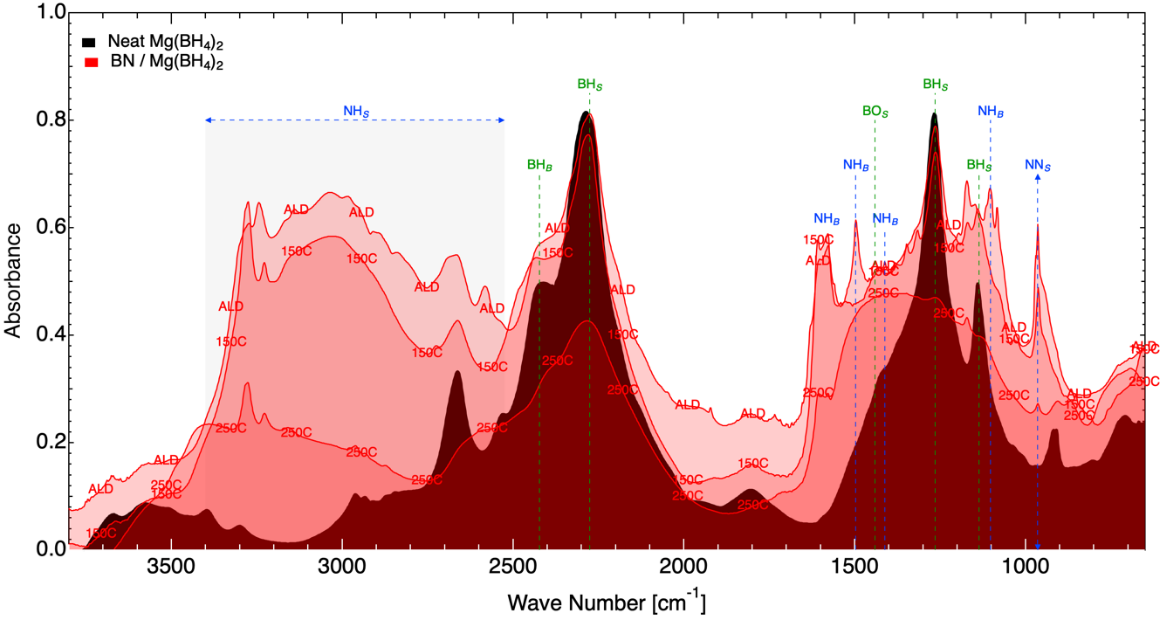
The best performers for Phase 1 and 2: **TiN**/$Mg(BH_4)_2$; Al_2O_3-**TiN**/$NaAlH_4$.
ALD **TiN** significantly improved rates, cycling ***and*** reversible capacity.

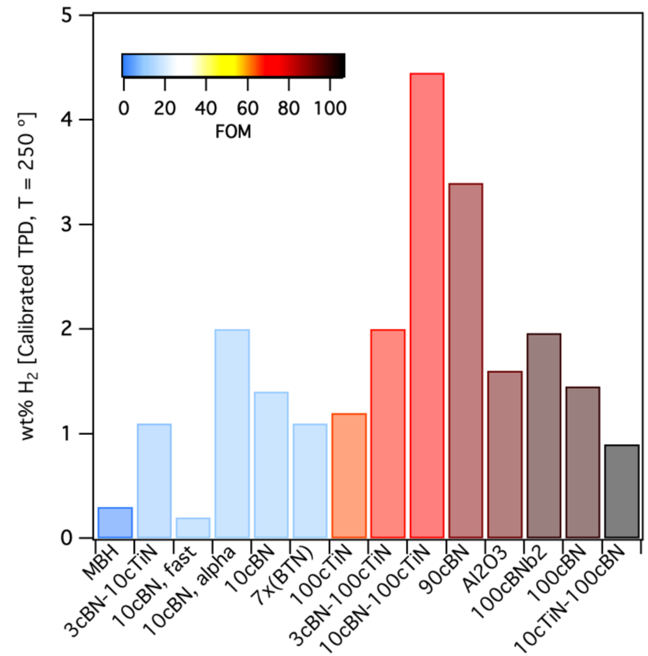
Go/No-Go Phase 2

- ±3 wt% H_2 reversible capacity, 3 cycles ✓ Surpassed
- 5-fold (5x) improvement of the absorption kinetics. ✓ Surpassed
- Operability: **≤ 250 °C**, ≤ **120 bar H_2** ✓ Met
- **STRETCH** 5 cycles, ± 3 wt% reversibility. ✓ Surpassed

A&P: Responses to Previous Year Reviewers' Comments

- Previous year AMR reviews emphasized the need to understand the ALD 'BN' / $Mg(BH_4)_2$ discharging mechanism and pointed to:
  - Potential reactions with $Mg(BH_4)_2$ and ALD precursors
  - Spectroscopy to probe species like N-H, B-H
  - Systematic studies of ALD coatings on $Mg(BH_4)_2$
- In response, over twenty new materials were synthesized and characterized with NMR, IR, XRD, TPD, and microscopy which resulted in the 'desorption mechanism' summarized in slide 5. Some highlights are given below.





Left: FTIR of changes to ALD BN/$Mg(BH_4)_2$ after ALD, 150 °C, 250 °C where N-H and B-H reduce which points to the $H^{\delta-}$+ $H^{\delta+}$ reaction. ***Right***: Figure of Merit (FOM) ranking potential of gravimetric penalties of ALD coatings to wt% H_2 release. FOM does not show a dependence film thickness (BN, TiN cycles) which supports the $H^{\delta-}$+ $H^{\delta+}$ reaction.

$$FOM = (BNcycles) + \frac{\rho_{TiN} GPC_{TiN}}{\rho_{BN} GPC_{BN}} (TiNcycles)$$

Gravimetric density (ρ); Growth-per-cycle (GPC); Cycles (c)

Thank You

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Publication Number

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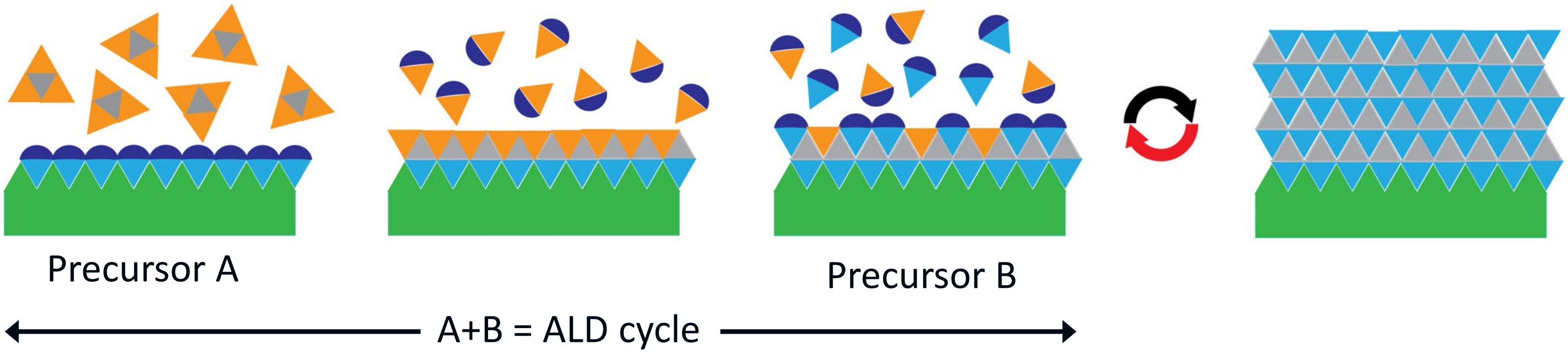
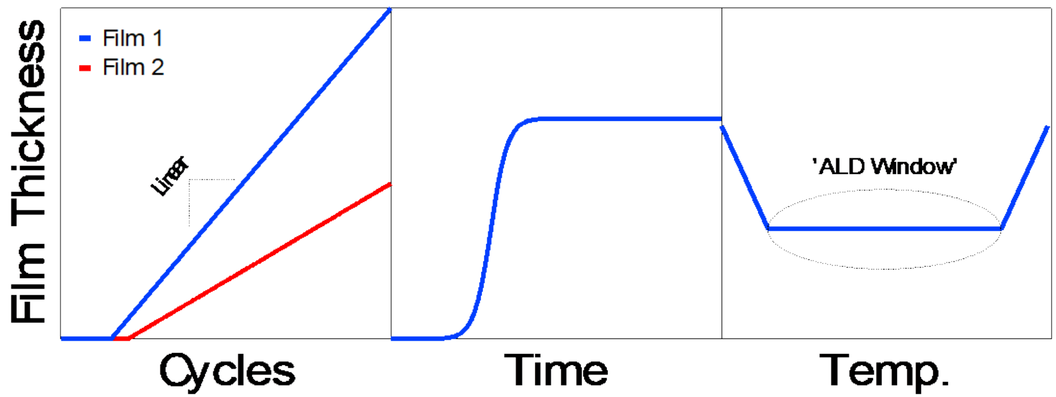
Technical Back-Up Slides

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