Atomic Layer Deposition for Materials-Based H_2 Storage: $Mg(BH_4)_2$ as a case study

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Thomas Gennett,[a,c] Steven T. Christensen[a]

ASE Summit: June 9th-11th, 2021

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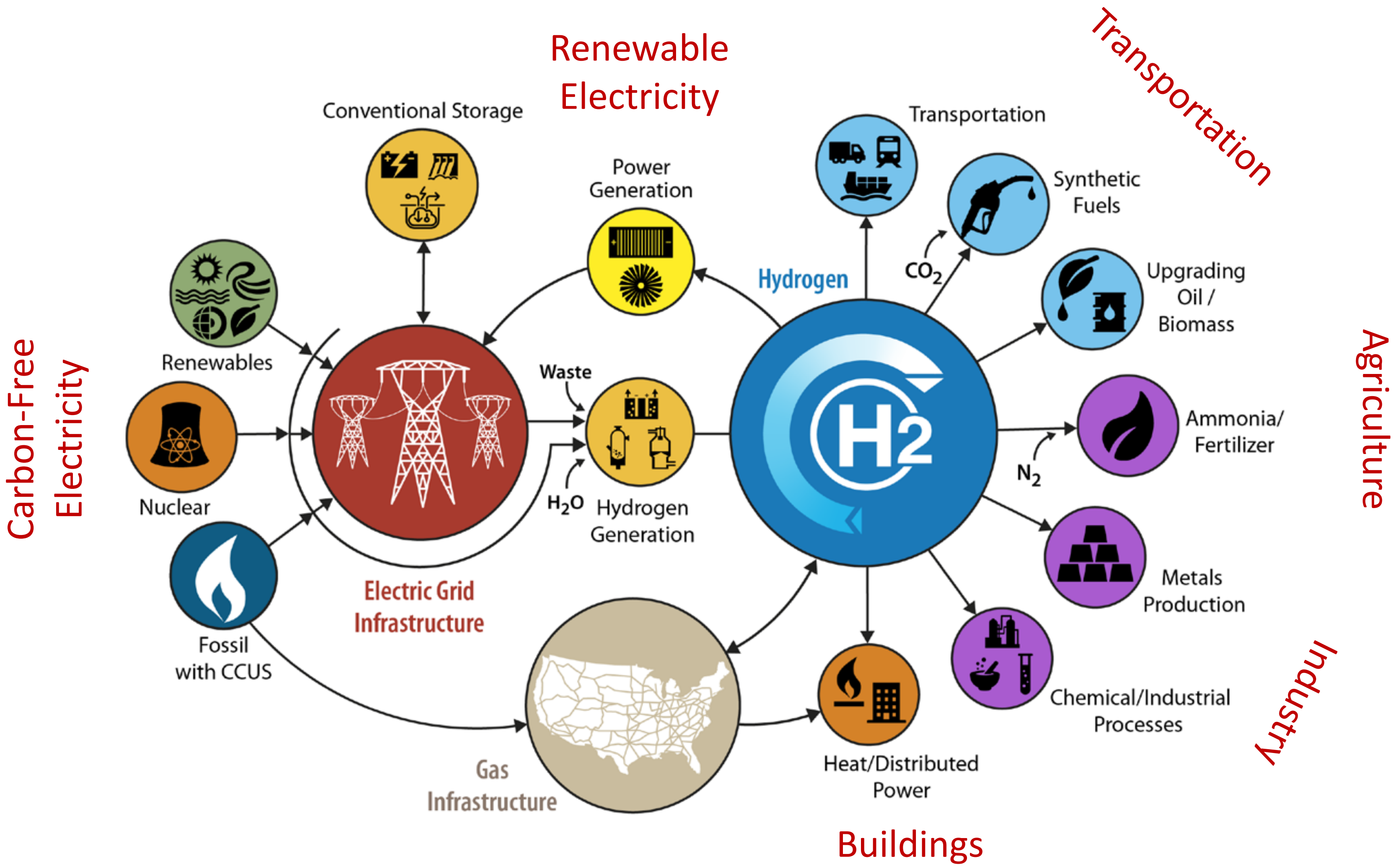
c: Colorado School of Mines; Golden, CO

A future built on renewable energies relies on hydrogen storage



The Hydrogen Materials - Advanced Research Consortium (HyMARC)

Enabling twice the energy density for onboard H_2 storage

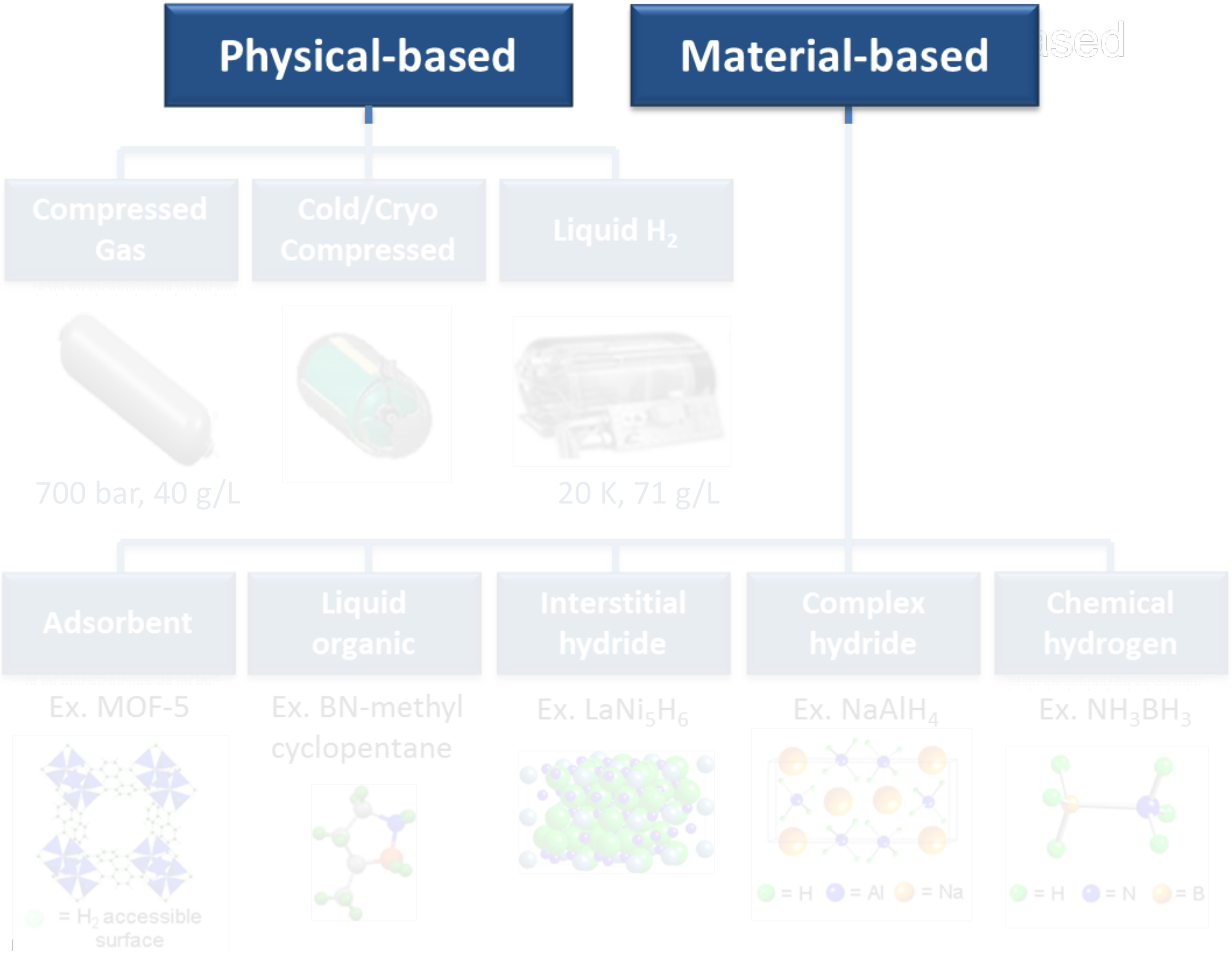
onboard H_2 storage

carriers/long-term storage

A → B (H_2)

Addresses Key Challenges to Hydrogen Storage in
Advanced Materials Through a Multi-Lab Collaboration

Hydrogen storage technologies



Hydrogen storage technologies

Physical-based

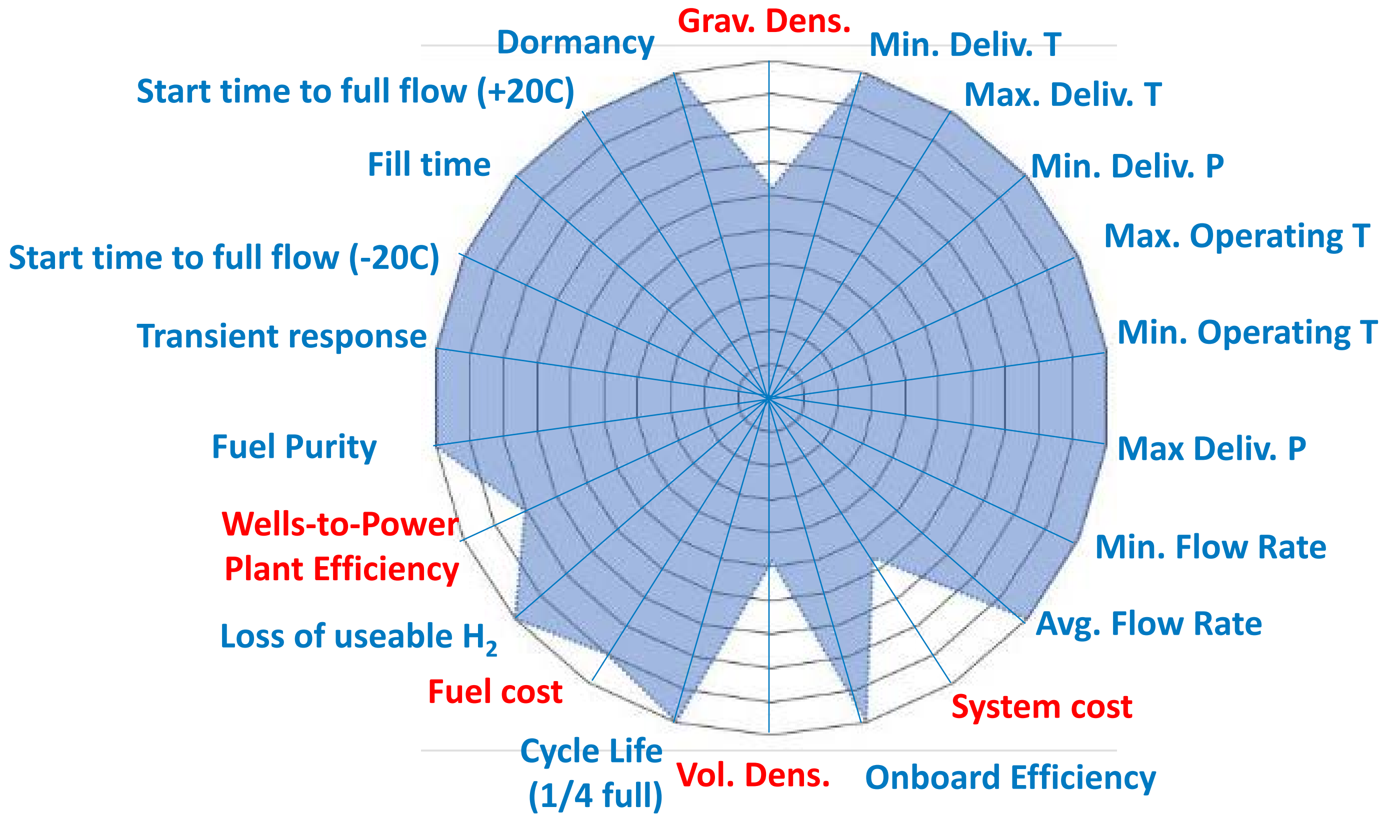
Compressed Gas

700 bar, 40 g/L

Adsorbent

Ex. MOF-5

700 bar compressed gas (2015 record)
vs.
revised ultimate targets



Hydrogen storage technologies

Physical-based

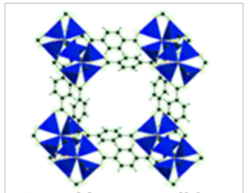
- Compressed Gas
- Cold/Cryo Compressed
- Liquid H_2

700 bar, 40 g/L

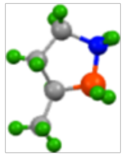
20 K, 71 g/L

Material-based

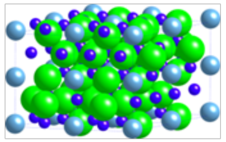
- **Adsorbent** — Ex. MOF-5



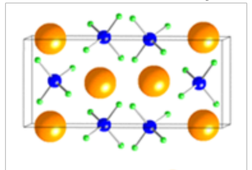
- **Liquid organic** — Ex. BN-methyl cyclopentane



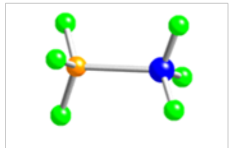
- **Interstitial hydride** — Ex. $LaNi_5H_6$



- **Complex hydride** — Ex. $NaAlH_4$



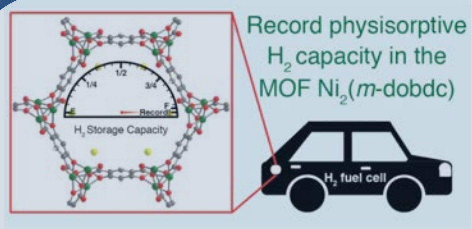
- **Chemical hydrogen** — Ex. NH_3BH_3



Materials have the potential to reach DOE targets for light-duty vehicles:

- 4.5 H_2 wt%
- $p < 100$ bar
- $-40^\circ C < T < 40^\circ C$

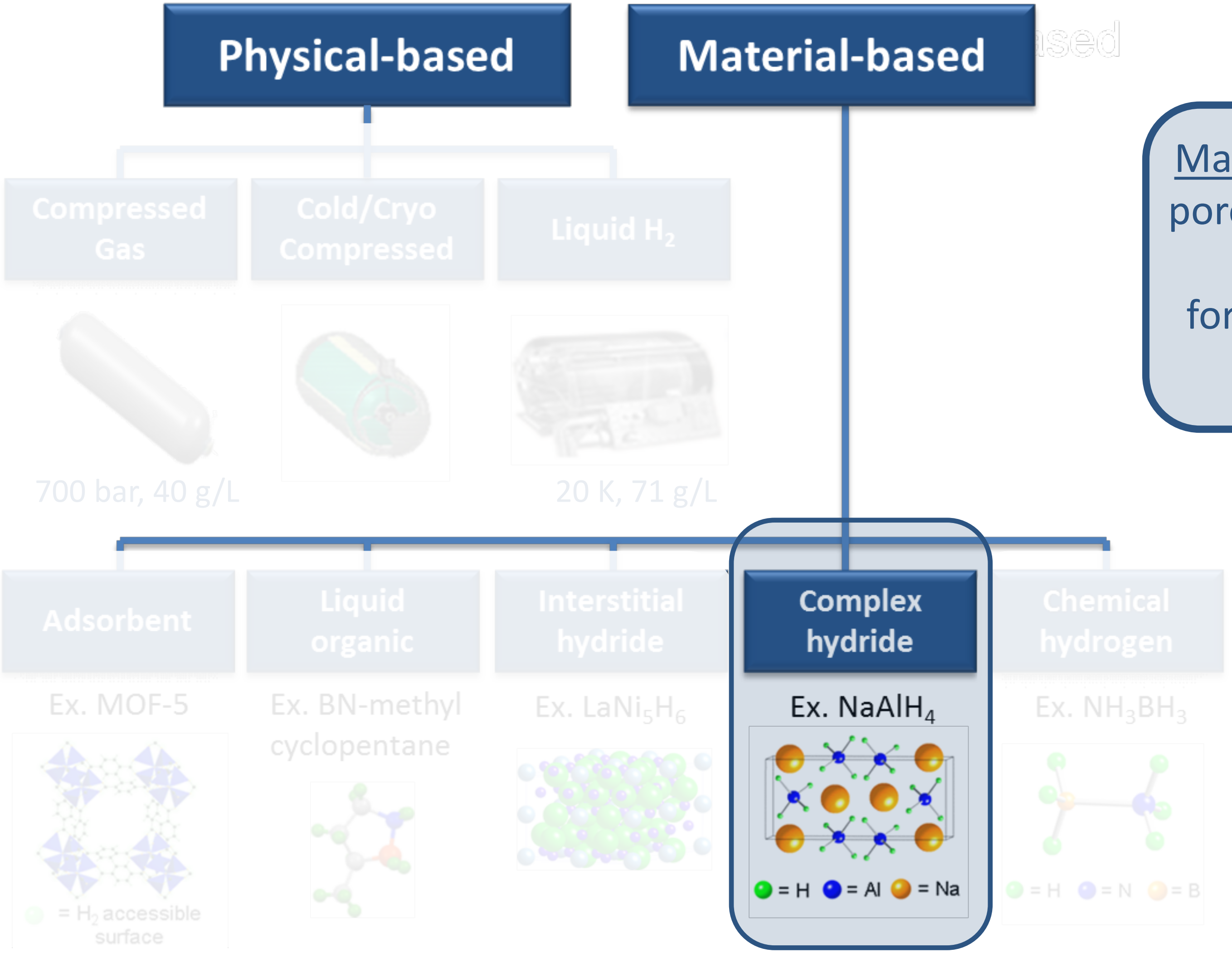
at lower system costs than the 700 bar technology.



HyMARC has the world record room temperature sorbent (11g/L)

Kapelewski et al., *Chem. Mater.* 2018, 30, 22, 8179–8189

Complex hydride: $Mg(BH_4)_2$



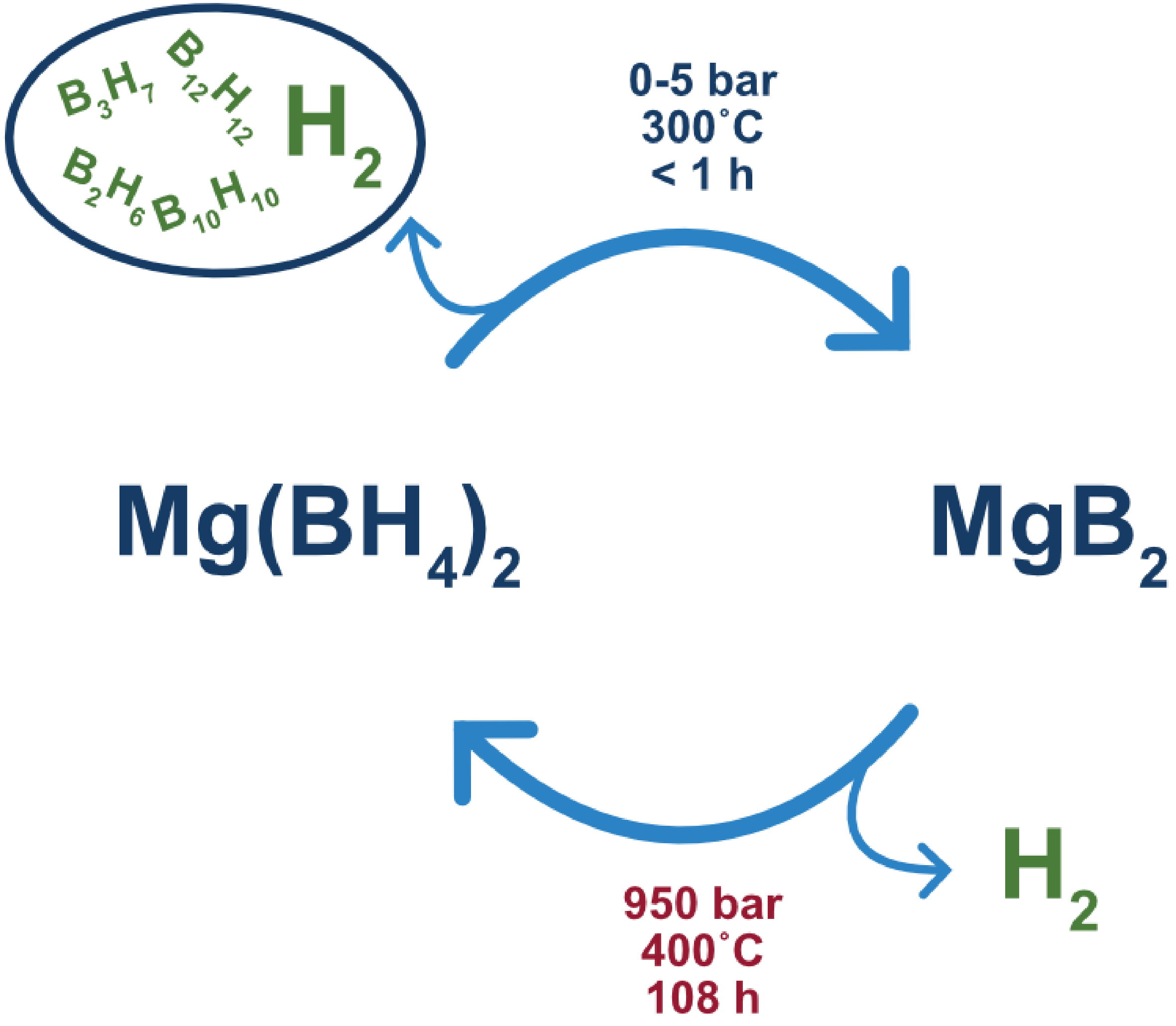
<u>Material used in this work:</u>
porous and nanostructured
γ-$Mg(BH_4)_2$
for increased H_2 diffusion
and reaction rates

$Mg(BH_4)_2$ vs. DOE targets

- Exceeds DOE targets:
  - Volumetric H_2 capacity (82 g/L)
  - Gravimetric H_2 capacity (14.9 wt%)

Y. Filinchuk et al., Angew. Chem. Int. Ed. (2011), 50, 11162 –11166

- Requires improvements:
  - Kinetics
  - Reversibility:
    - Suppression of B_2H_6 liberation: fuel cell damage and material loss
    - Suppression of $B_{12}H_{12}$ formation: thermodynamic energy well
  - Desorption temperature: 300˚C for neat material

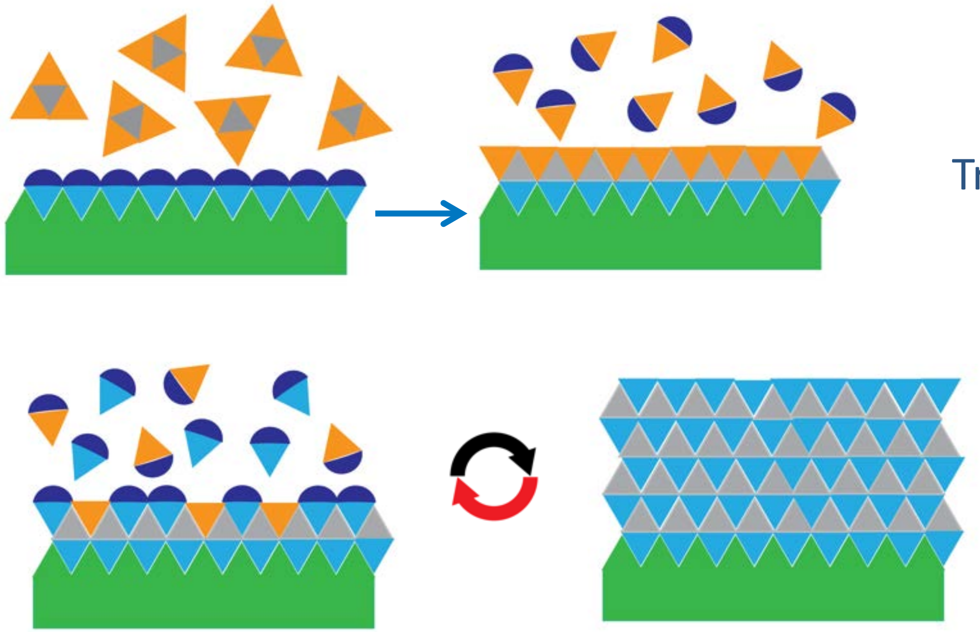


N. Leick et al., *ACS Appl. Energy Mater.* 2021, 4, 2, 1150–1162
G. Severa et al., *Chem. Commun.*, 2010, 46, 421-423

Approach: Additives through atomic layer deposition (ALD)

- Coating retains the $Mg(BH_4)_2$ nanostructure for cyclability
- Atomically thin to maintain the gravimetric capacity of $Mg(BH_4)_2$
- Manipulation of the thermodynamic pathway for H_2 release
- Mitigate material loss
- Catalyst additive to enhance reaction rates

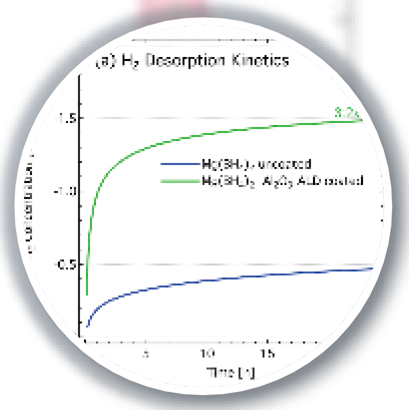
Room temperature ALD
to prevent phase change and H_2 release of γ- $Mg(BH_4)_2$



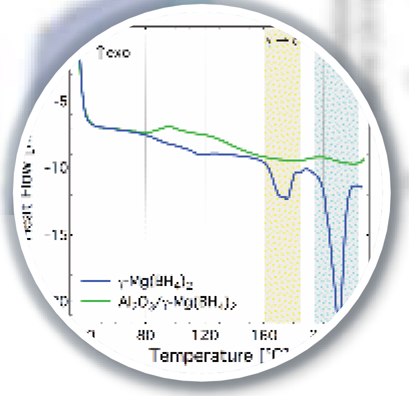
Al-precursor:
8 s
Trimethylaluminum
(TMA, $Al(CH_3)_3$)

O-Precursor:
8 s
Water (H_2O)

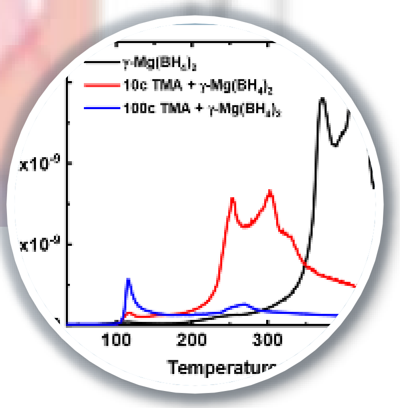
Approach to improve the performance of $Mg(BH_4)_2$



ALD of Al_2O_3:
TMA + H_2O



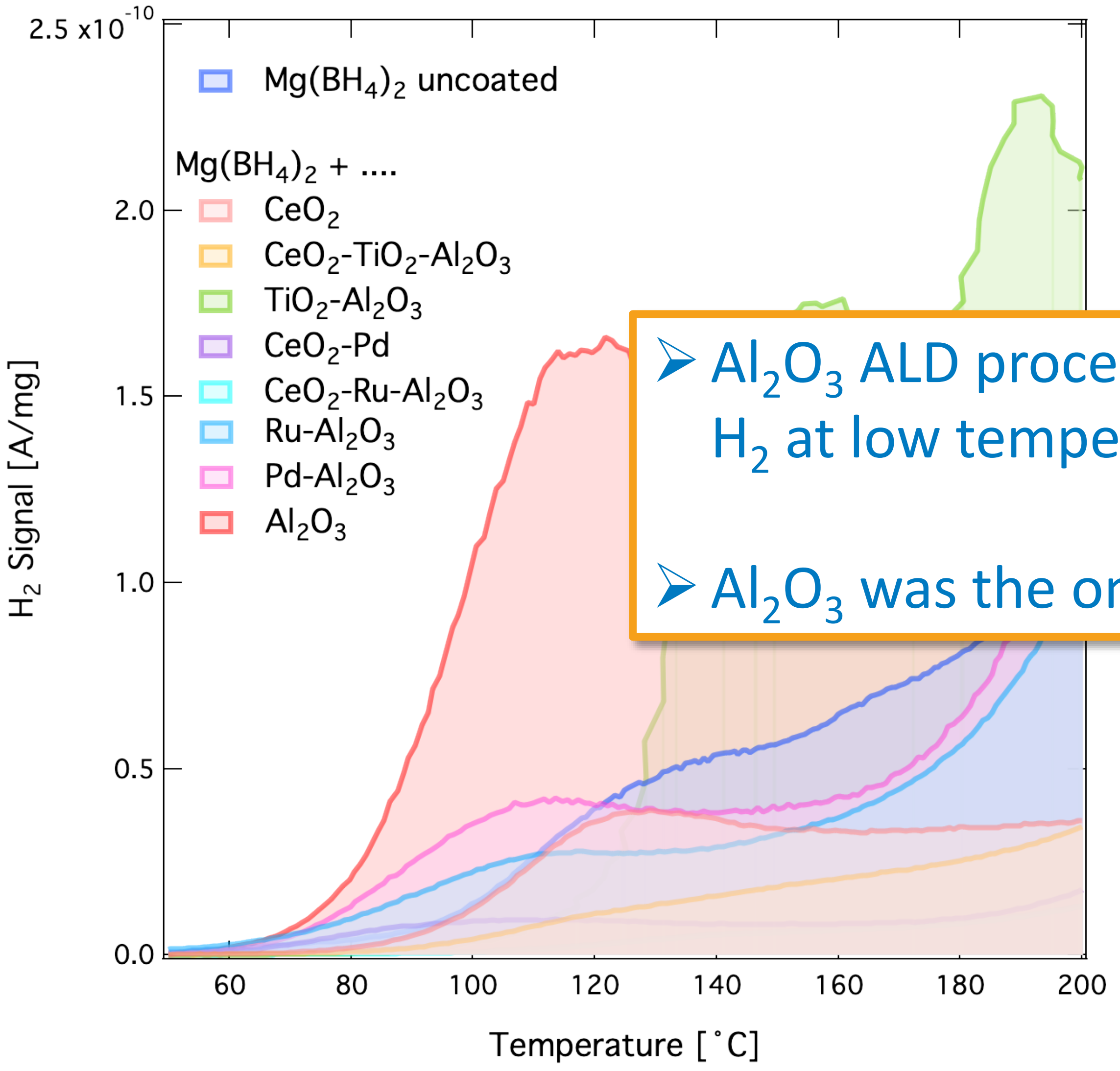
H_2O pulsing only

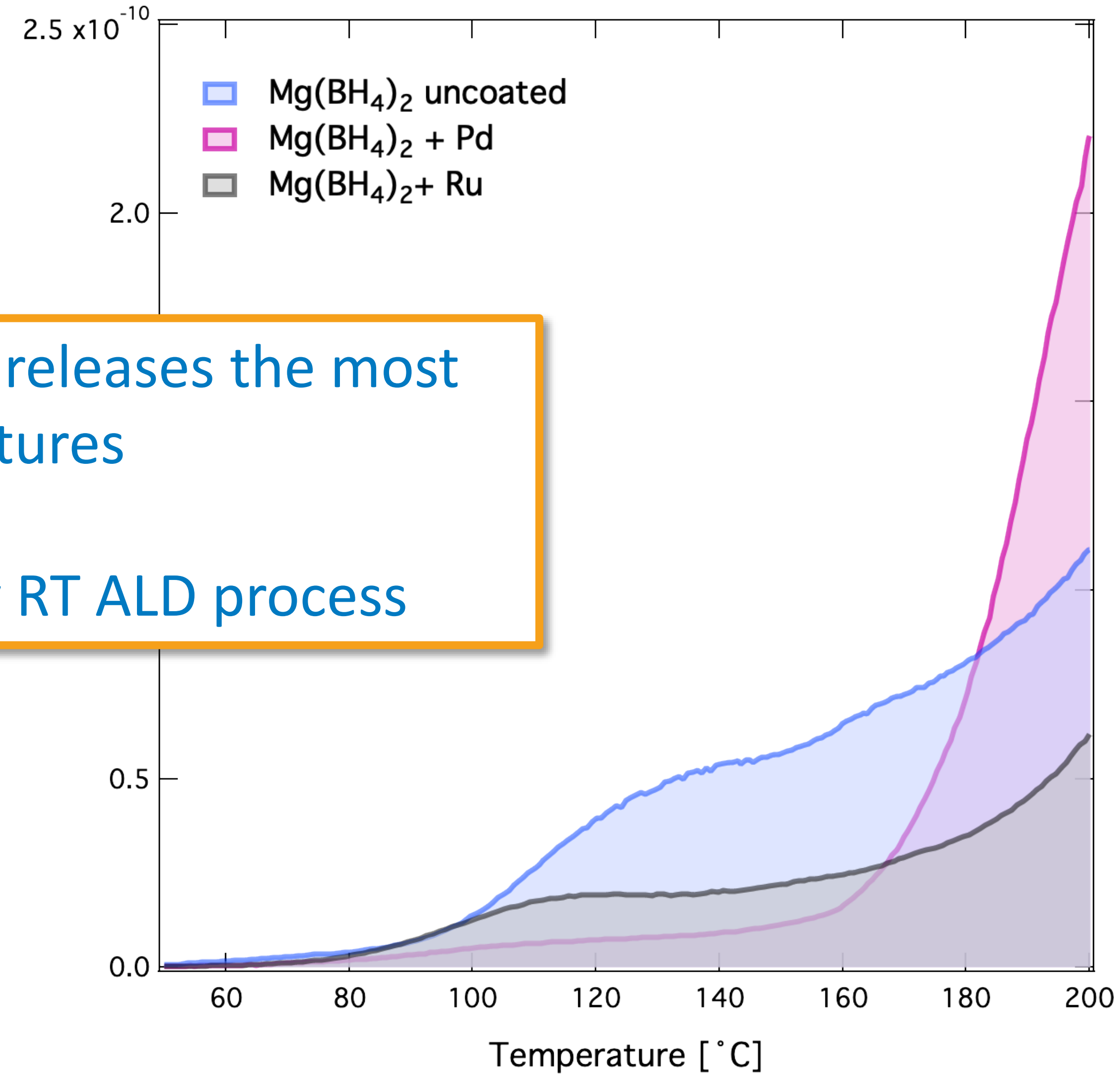


TMA pulsing only

$Mg(BH_4)_2$ + ALD

Temperature Programmed Desorption

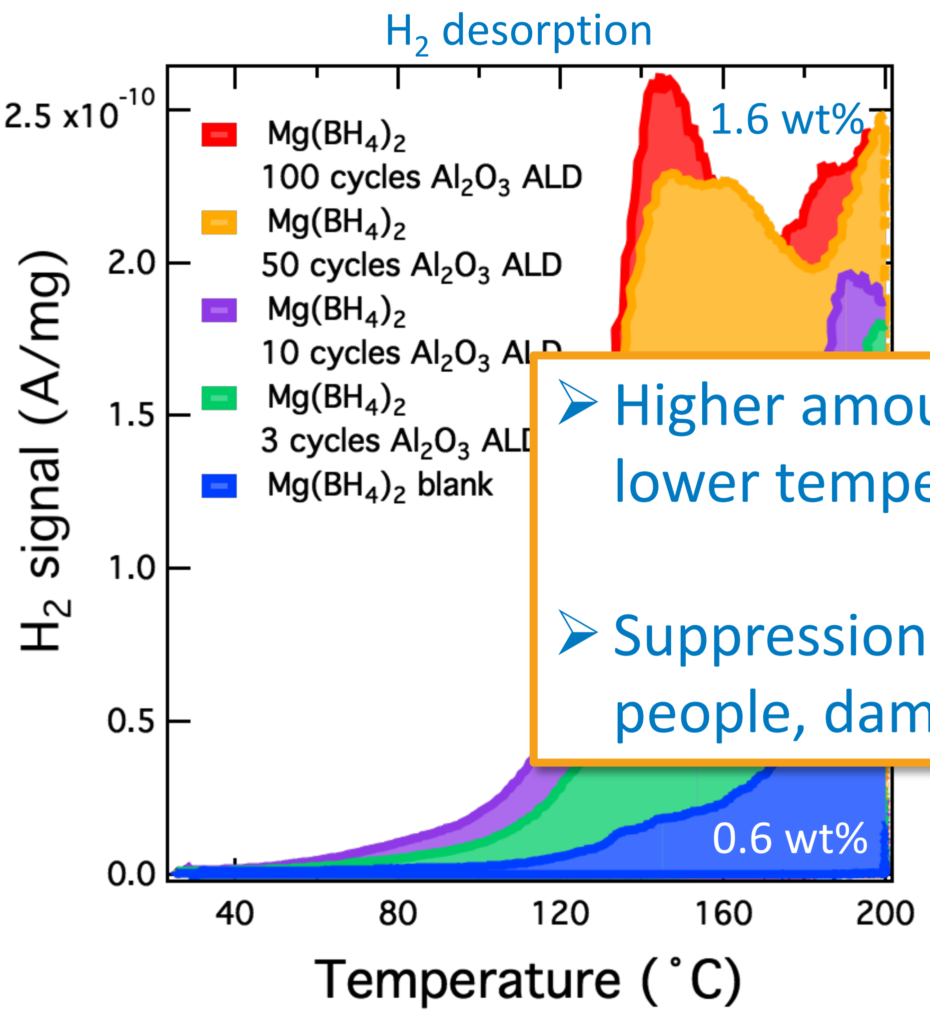


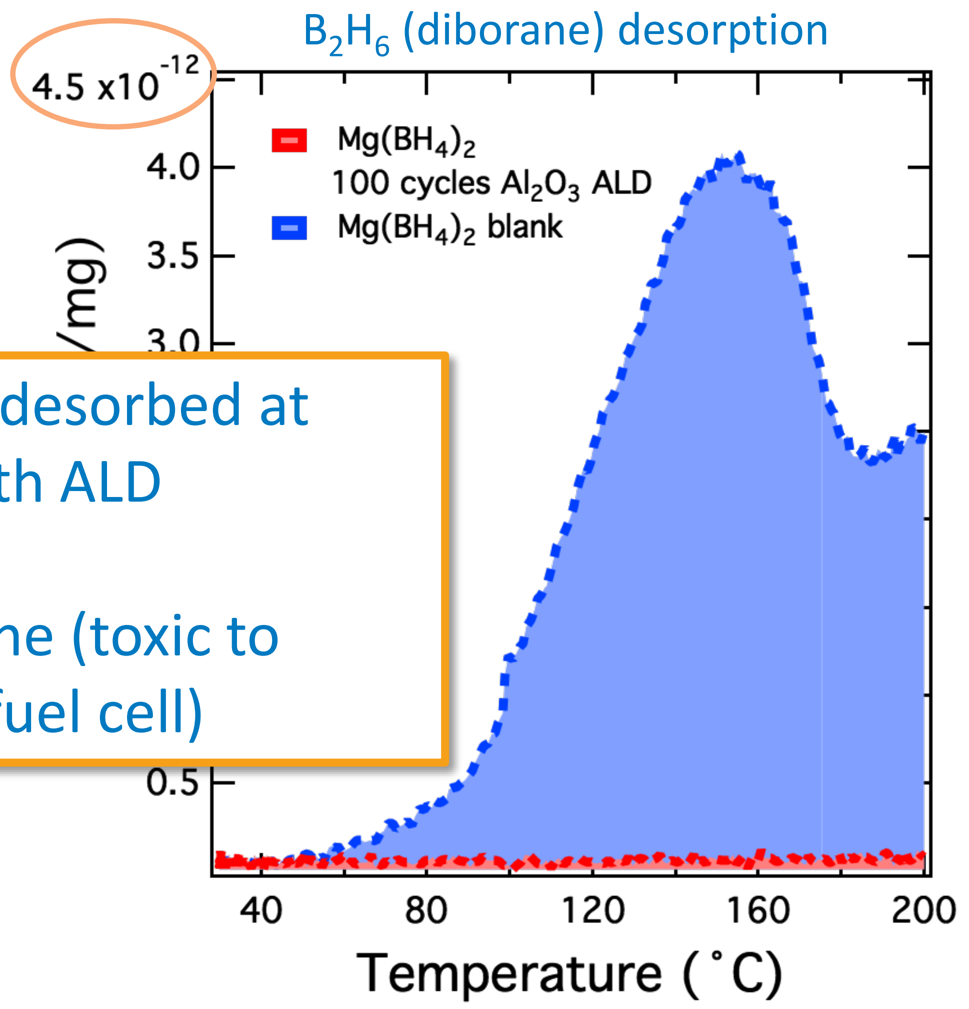


- Al_2O_3 ALD process releases the most H_2 at low temperatures
- Al_2O_3 was the only RT ALD process

$Mg(BH_4)_2$ + ALD of Al_2O_3

Temperature Programmed Desorption

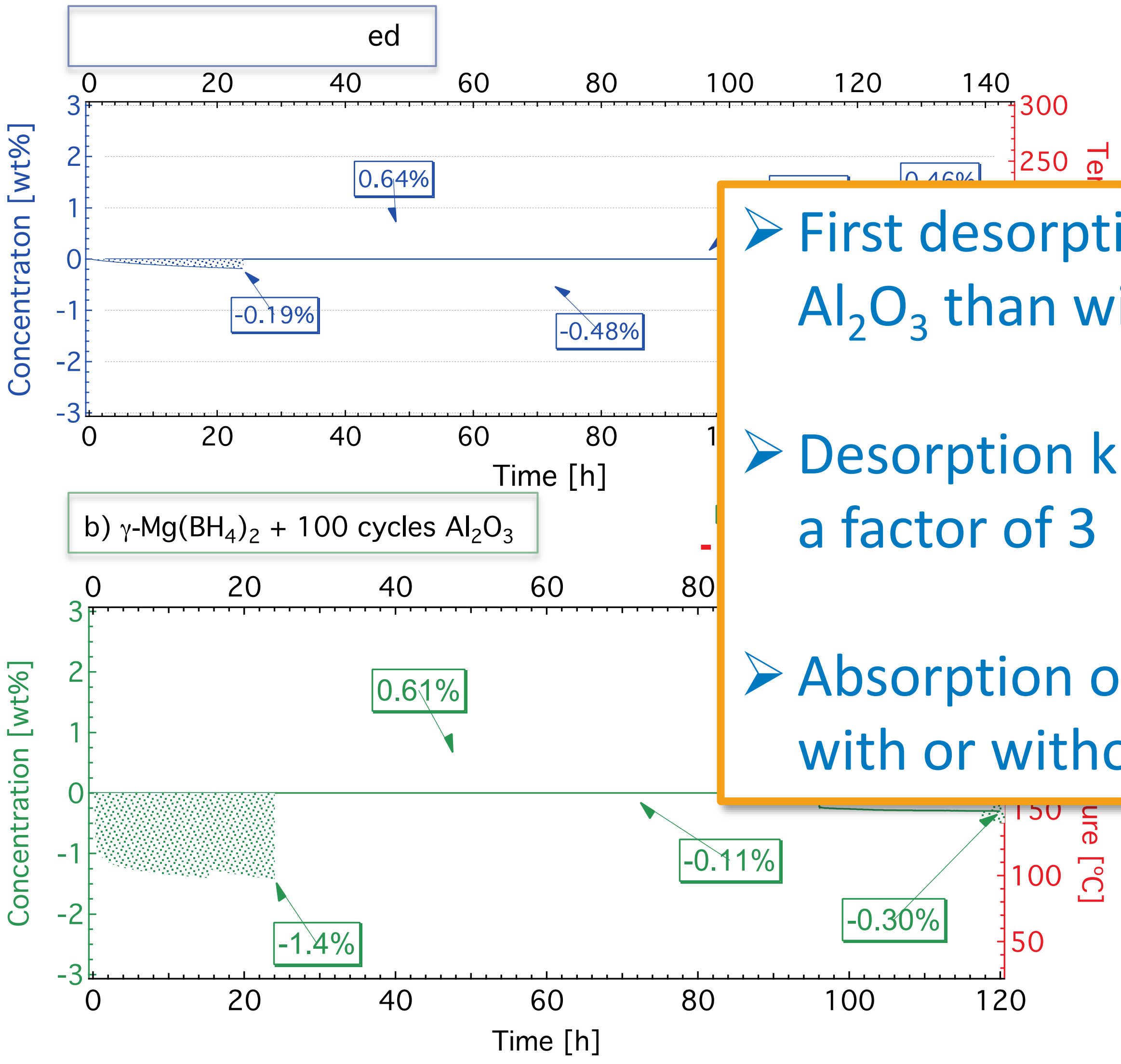


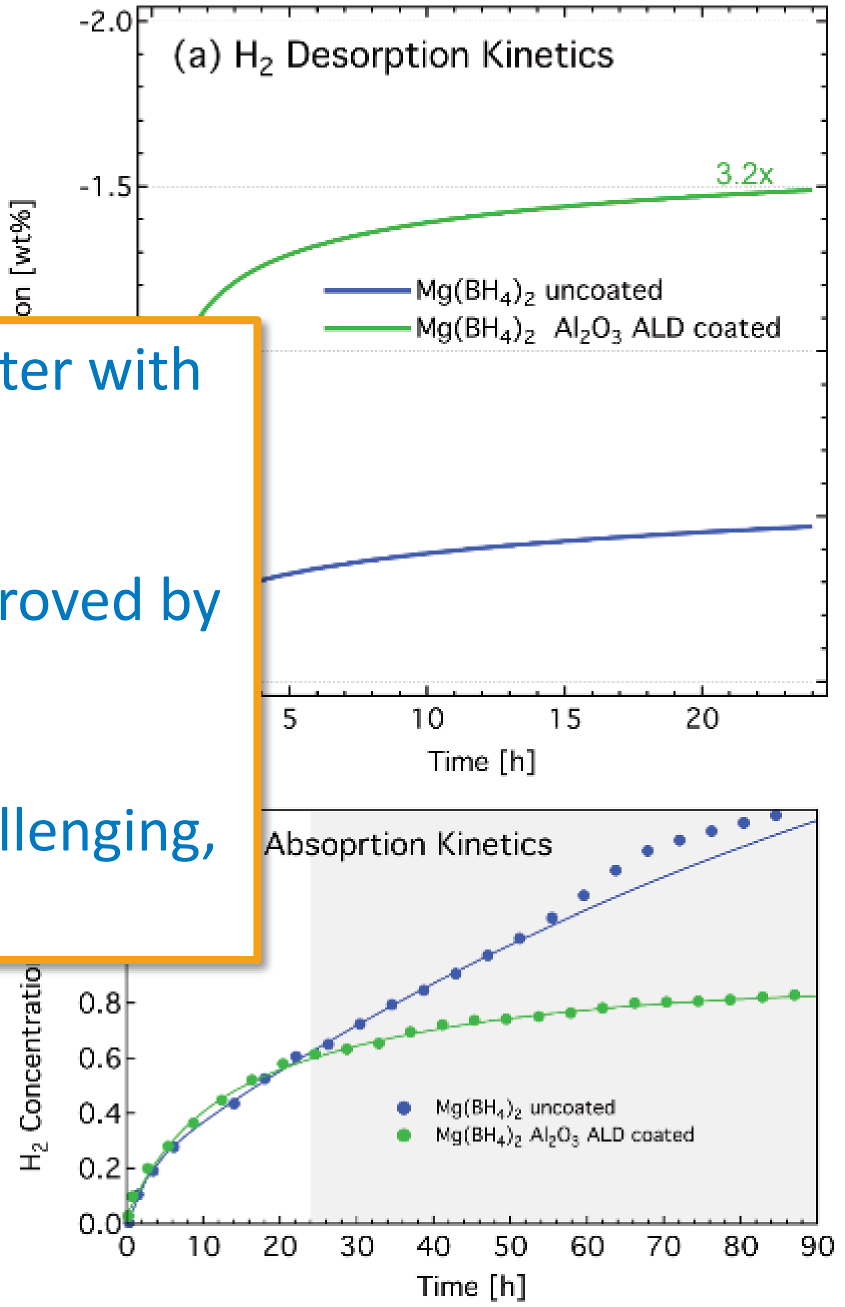


- Higher amounts of H_2 desorbed at lower temperature with ALD
- Suppression of diborane (toxic to people, damages the fuel cell)

N. Leick et al., *ACS Appl. Energy Mater.* 2021, 4, 2, 1150–1162

$Mg(BH_4)_2$ + ALD of Al_2O_3



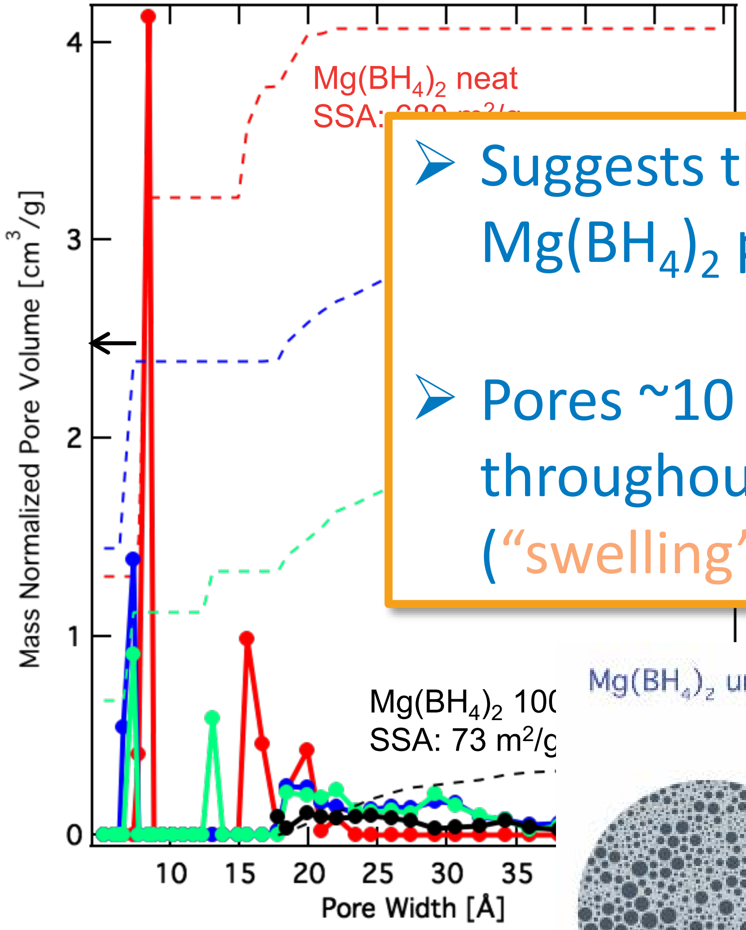


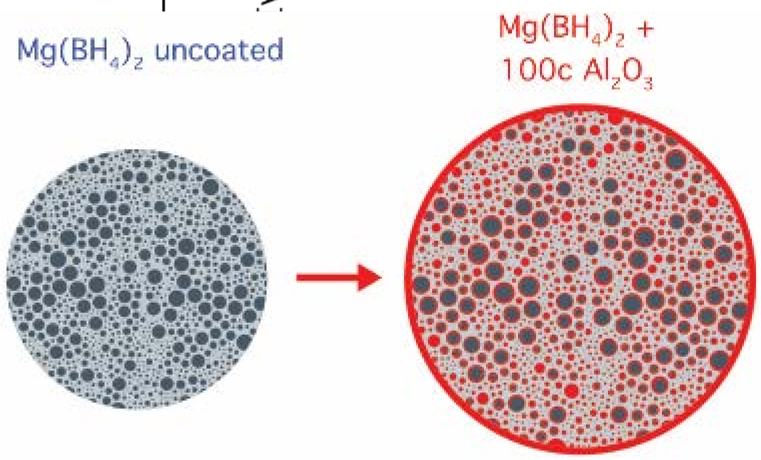
- First desorption performs better with Al_2O_3 than without it
- Desorption kinetics were improved by a factor of 3
- Absorption of H_2 remains challenging, with or without Al_2O_3 ALD

N. Leick et al., *ACS Appl. Energy Mater.* 2021, 4, 2, 1150–1162

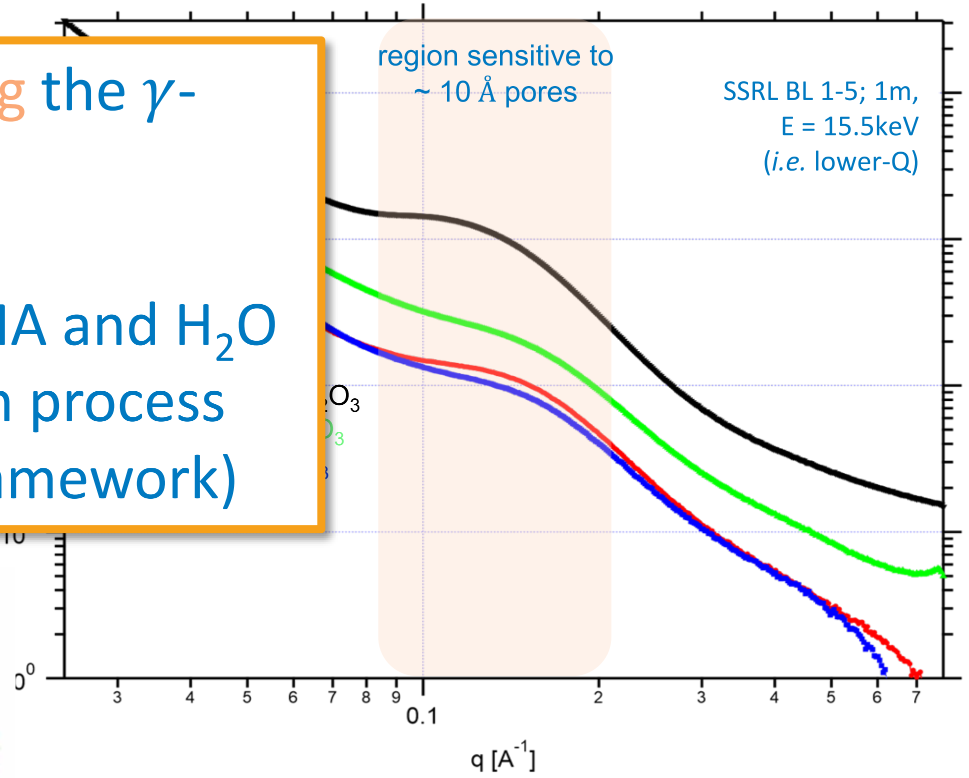
$Mg(BH_4)_2$ + ALD of Al_2O_3

Porosimetry based on N_2 physisorbtion





Small angle X-ray spectroscopy on Al_2O_3 ALD-coated γ-$Mg(BH_4)_2$

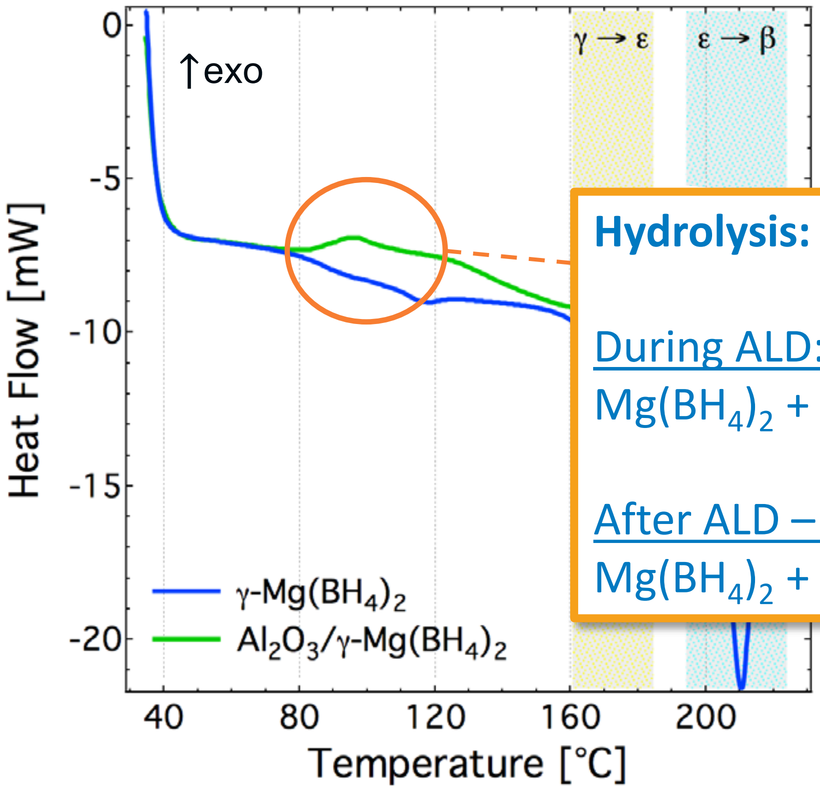


- Suggests the coating is infiltrating the γ-$Mg(BH_4)_2$ pore structure
- Pores ~10 Å are accessible to TMA and H_2O throughout the entire deposition process ("swelling" of the γ-$Mg(BH_4)_2$ framework)

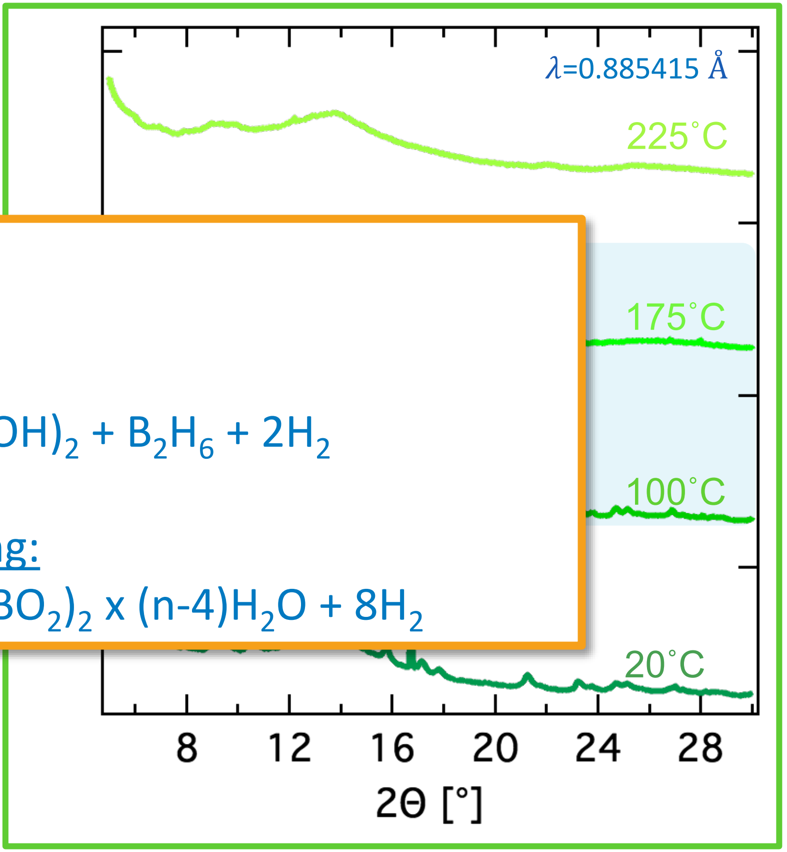
N. Leick et al., *ACS Appl. Energy Mater.* 2021, 4, 2, 1150–1162

$Mg(BH_4)_2$ + ALD of Al_2O_3

Differential Scanning Calorimetry



X-Ray Diffraction - *in situ* heating



Hydrolysis:

<u>During ALD:</u>

$Mg(BH_4)_2 + 2H_2O \rightarrow Mg(OH)_2 + B_2H_6 + 2H_2$

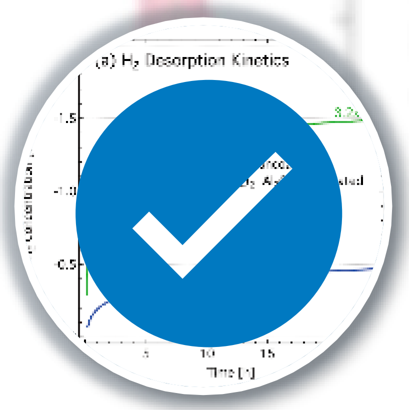
<u>After ALD – during heating:</u>

$Mg(BH_4)_2 + nH_2O \rightarrow Mg(BO_2)_2 \text{ x } (n\text{-}4)H_2O + 8H_2$

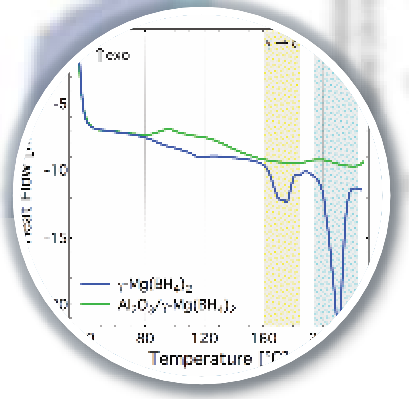
loss of crystalline structure

N. Leick et al., *ACS Appl. Energy Mater.* 2021, 4, 2, 1150–1162

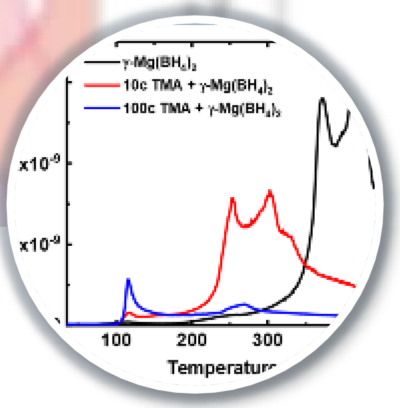
Approach to improve the performance of $Mg(BH_4)_2$



ALD of Al_2O_3:
TMA + H_2O

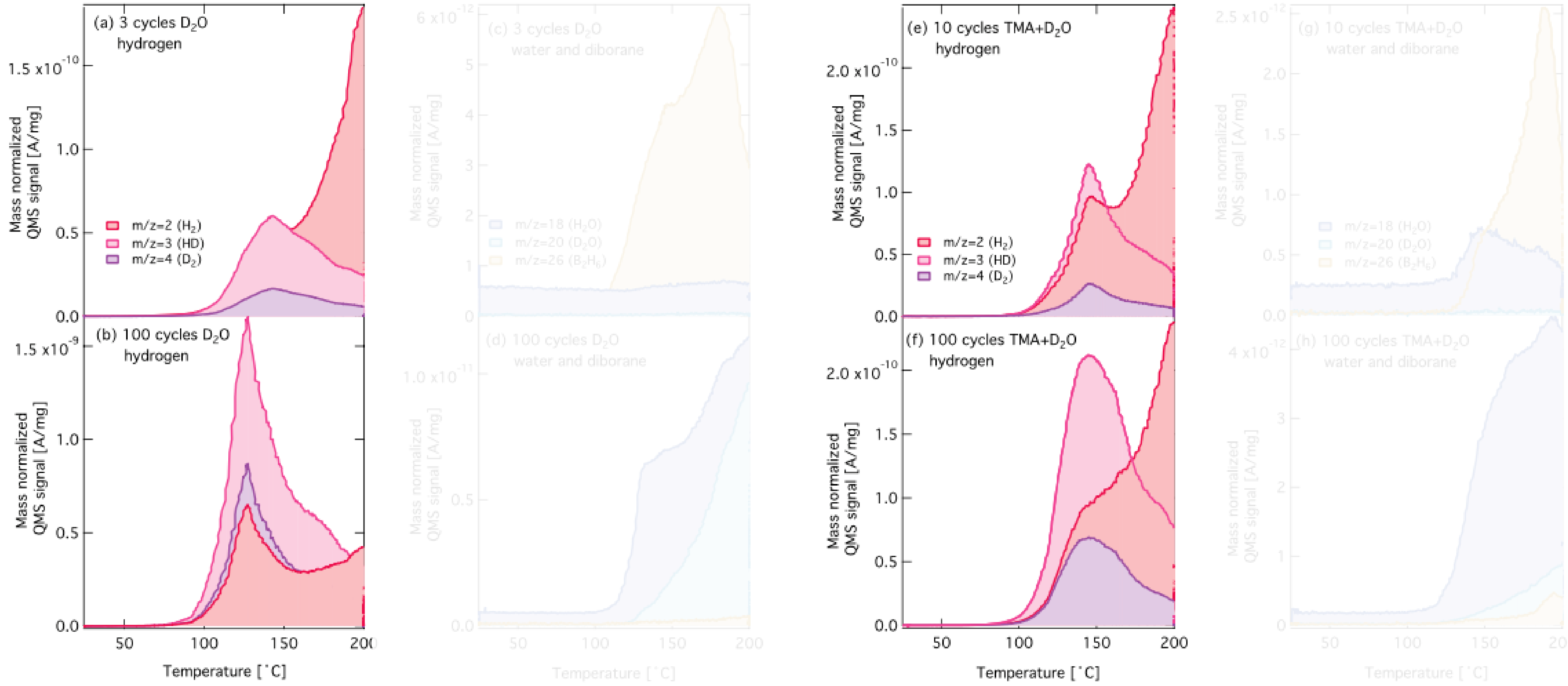


H_2O pulsing only



TMA pulsing only

$Mg(BH_4)_2$: hydrolysis from TPD



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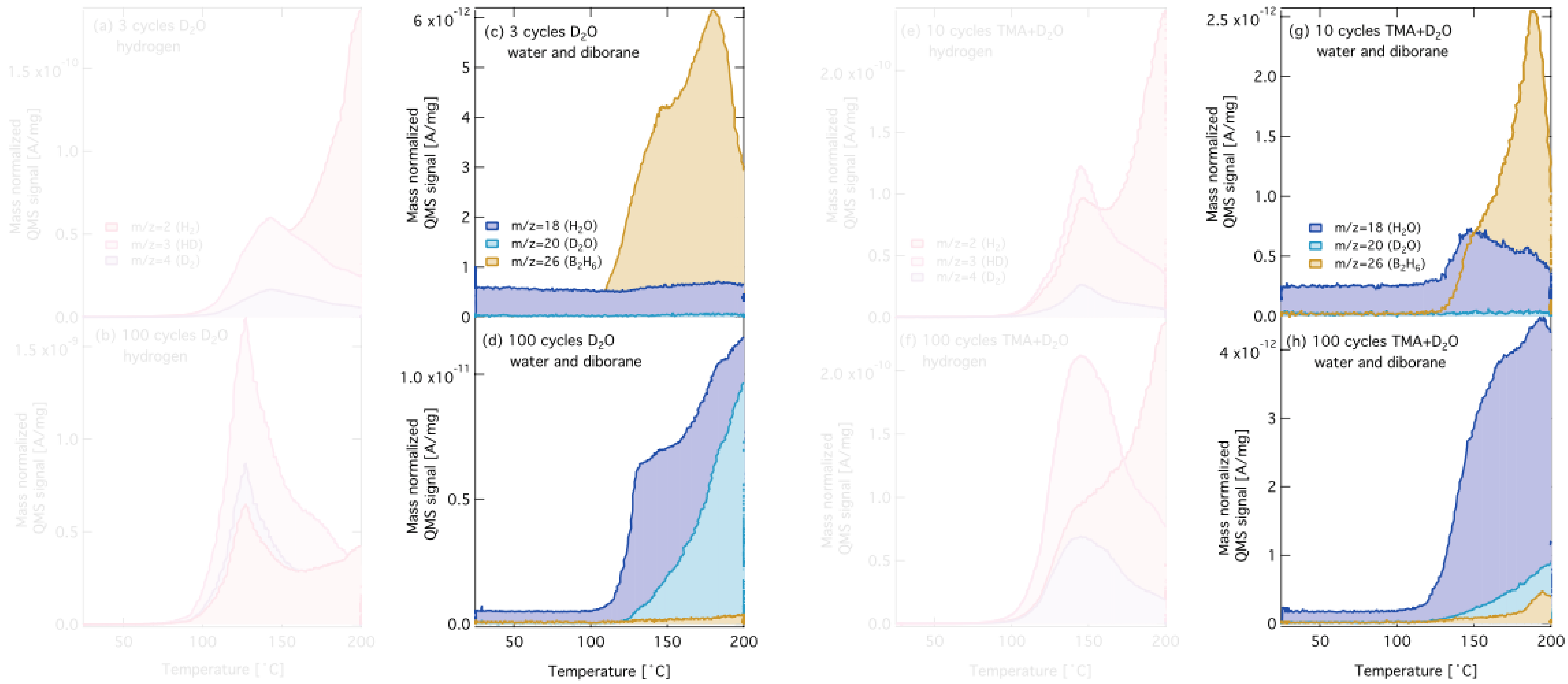

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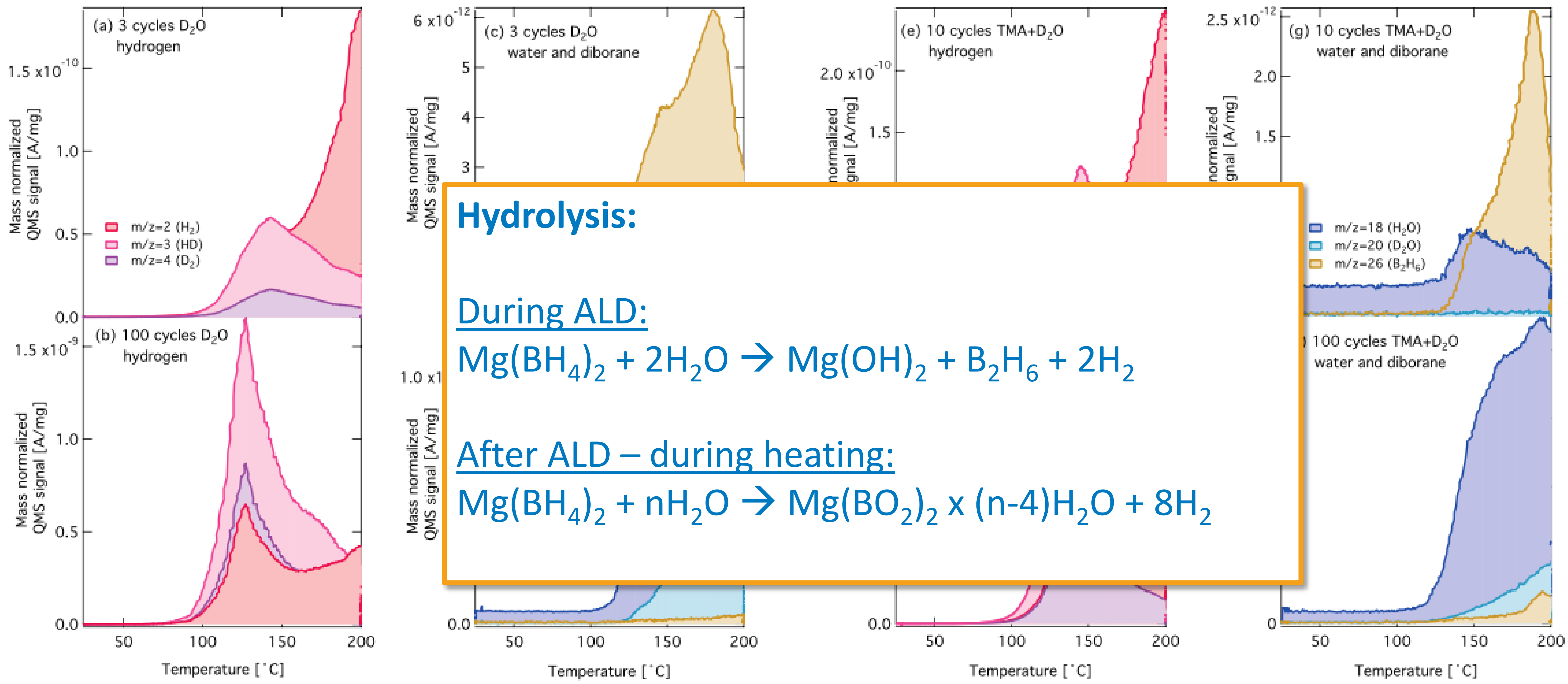
$Mg(BH_4)_2$: hydrolysis from TPD



Hydrolysis:

<u>During ALD:</u>

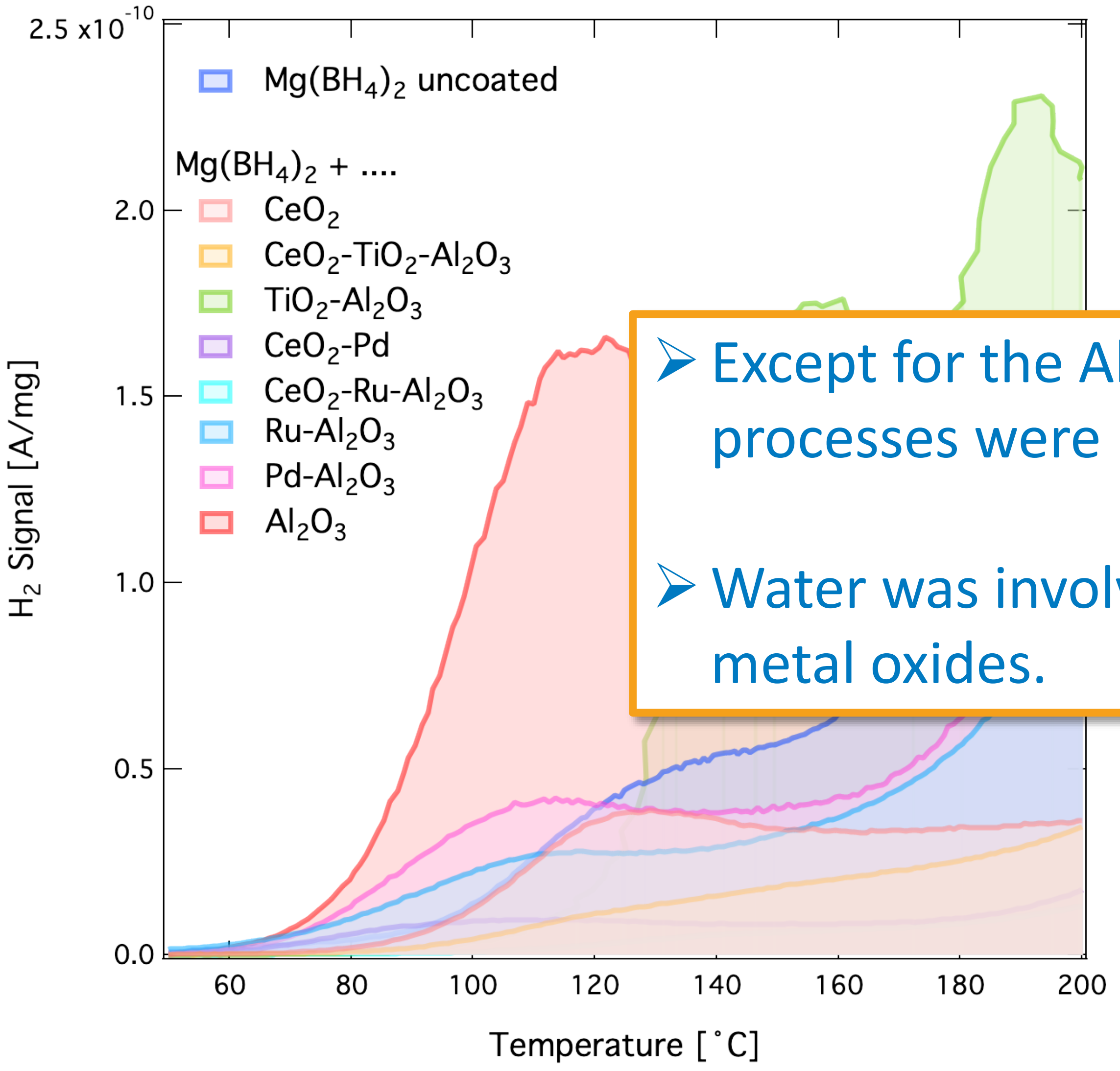
$Mg(BH_4)_2 + 2H_2O \rightarrow Mg(OH)_2 + B_2H_6 + 2H_2$

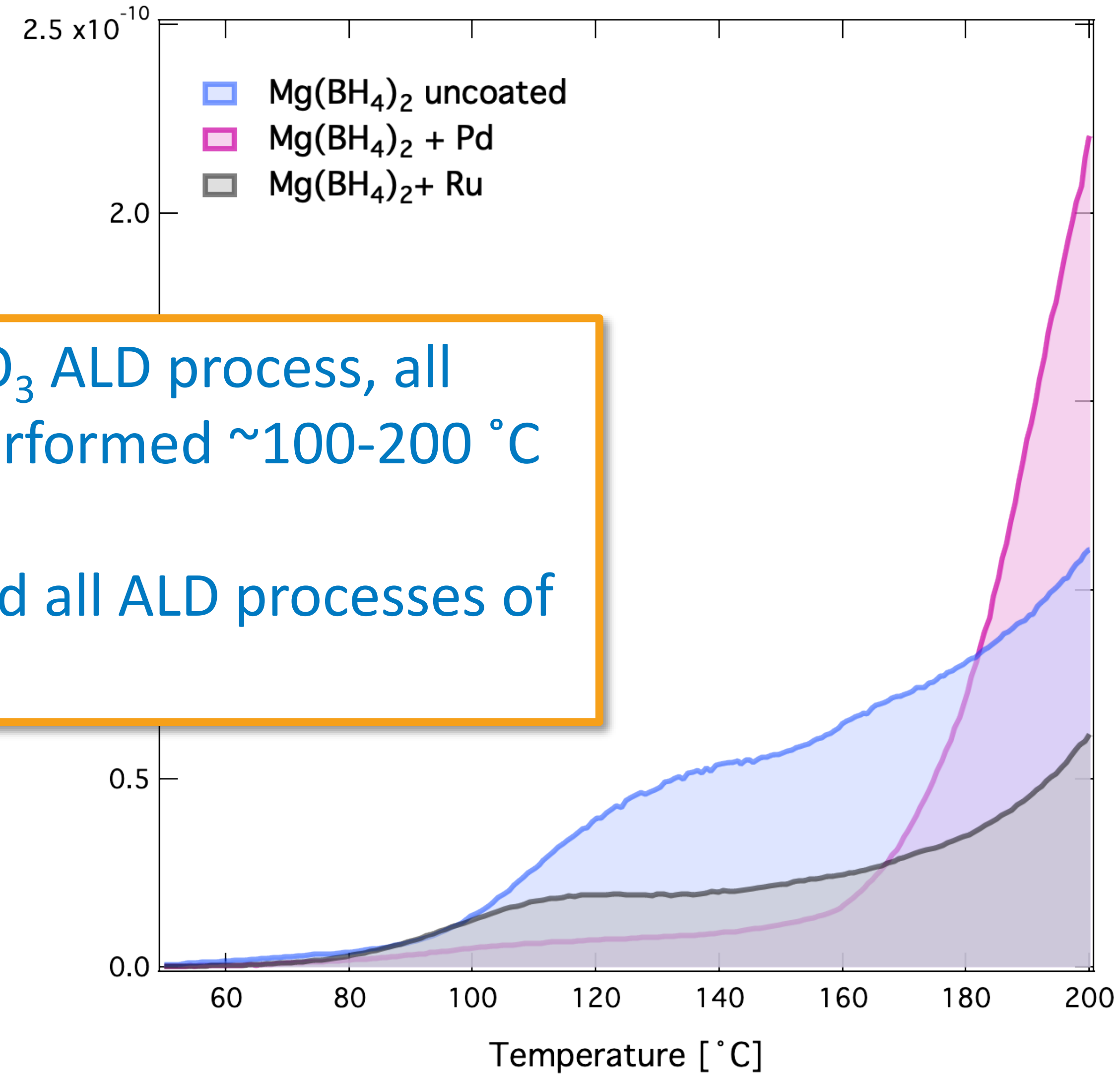
<u>After ALD – during heating:</u>

$Mg(BH_4)_2 + nH_2O \rightarrow Mg(BO_2)_2 \times (n-4)H_2O + 8H_2$

N. Leick et al., *ACS Appl. Energy Mater.* 2021, 4, 2, 1150–1162

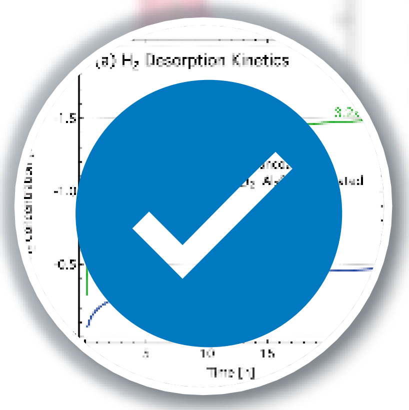
$Mg(BH_4)_2$ + ALD





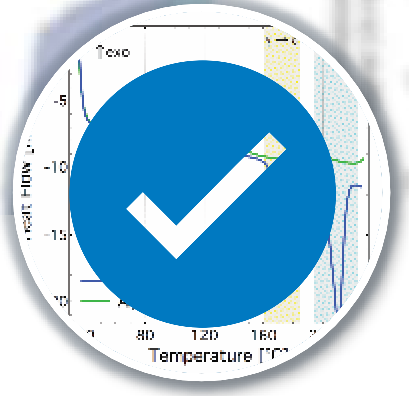
- Except for the Al_2O_3 ALD process, all processes were performed ~100-200 ˚C
- Water was involved all ALD processes of metal oxides.

Approach to improve the performance of $Mg(BH_4)_2$

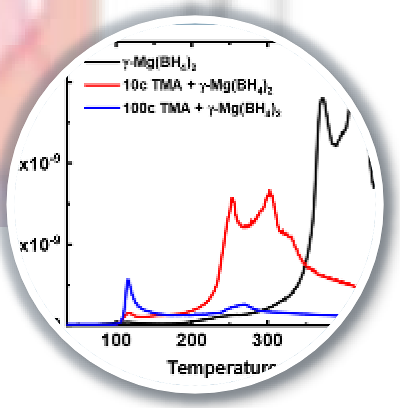


ALD of Al_2O_3:

TMA + H_2O

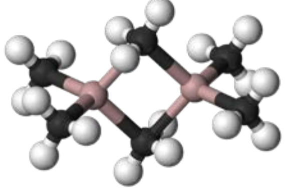


H_2O pulsing only

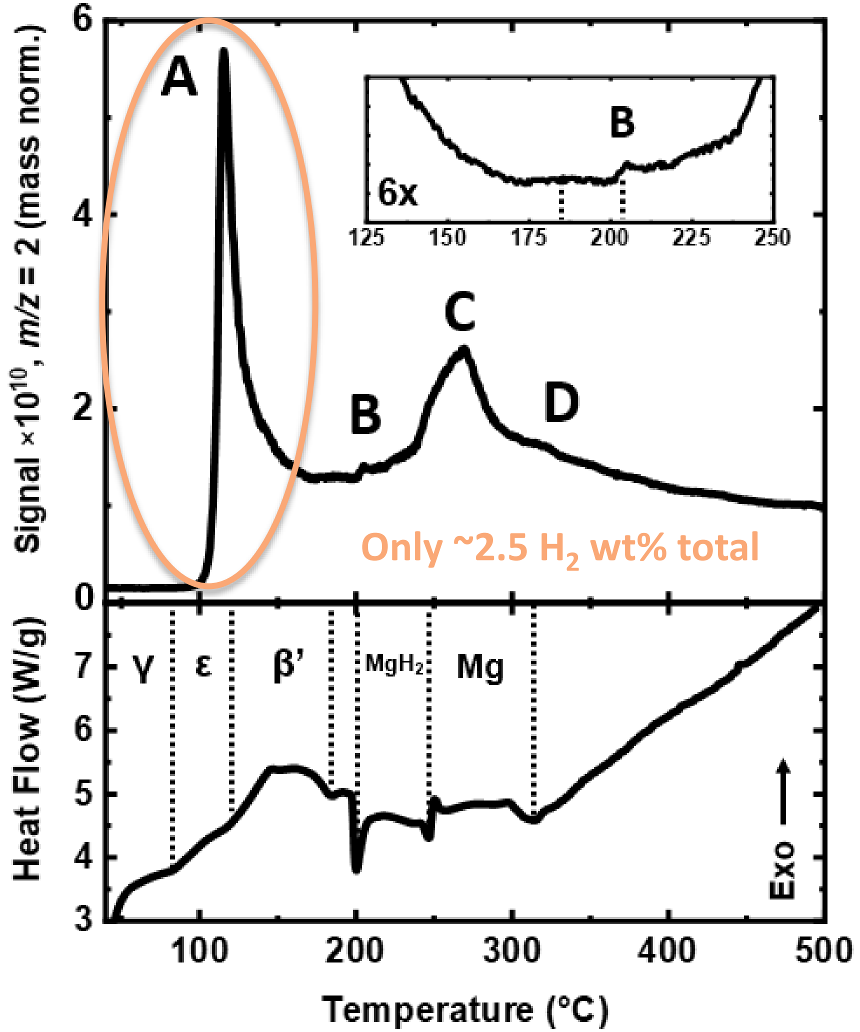


TMA pulsing only

100c TMA + γ-$Mg(BH_4)_2$



TPD/DSC with identical heating rates



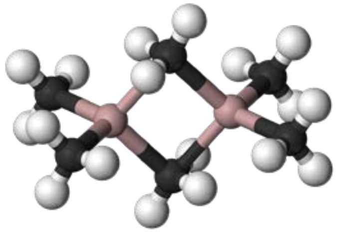
Event A (~90 °C)
- releases H_2 in the γ → ε structural phase transformation region
- releases H_2 rapidly

Event C coincides with MgH_2 → Mg transition
- begins at 240 °C, a reduction of over 125 °C compared to uncoated $Mg(BH_4)_2$

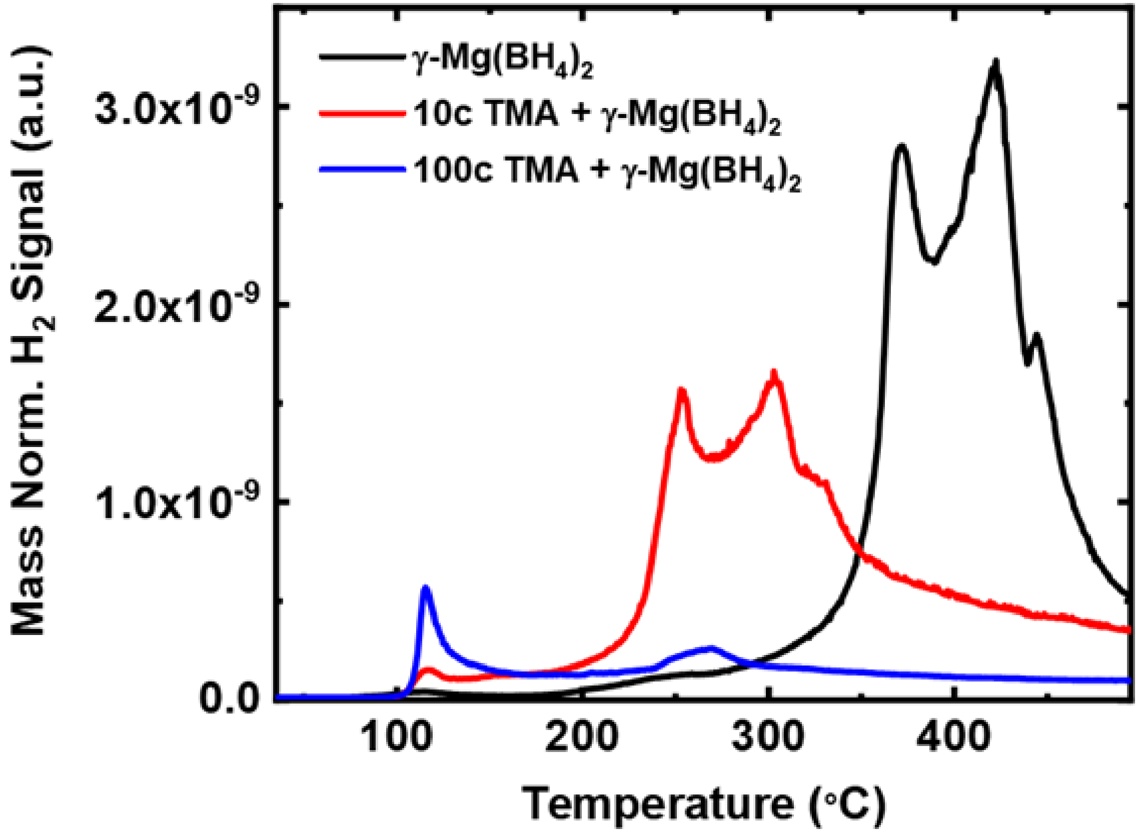
Low H_2 capacity
- ~0.6 H_2 wt% released below 175 °C
- ~2.5 H_2 wt% from 20 – 500 °C

N. Strange, N. Leick, S. Shulda, A. Schneemann, V. Stavila, A. Lipton, M. Toney, T. Gennett, S. Christensen - Reactive Vapor-Phase Additives towards Destabilizing γ-$Mg(BH_4)_2$ for Improved Hydrogen Release (submitted)

Volatile reaction products causing loss of H_2 capacity?



Temperature Programmed Desorption



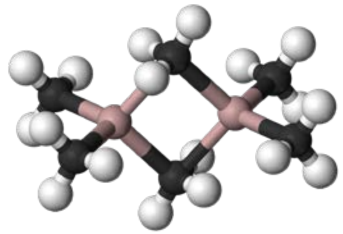
H_2 wt% from Integrated TPD Signal

	20-175 °C	20-250 °C	20-500 °C
γ-$Mg(BH_4)_2$	0.16	0.37	13.7
10c TMA	0.33	1.54	14.5
100c TMA	0.58	1.05	2.52

- 10c TMA sample exhibits full retention of native H_2 capacity between room temperature and 500 °C.
- H_2 desorption temperature is lowered by <100 °C.

N. Strange, N. Leick, S. Shulda, A. Schneemann, V. Stavila, A. Lipton, M. Toney, T. Gennett, S. Christensen - Reactive Vapor-Phase Additives towards Destabilizing γ-$Mg(BH_4)_2$ for Improved Hydrogen Release (submitted)

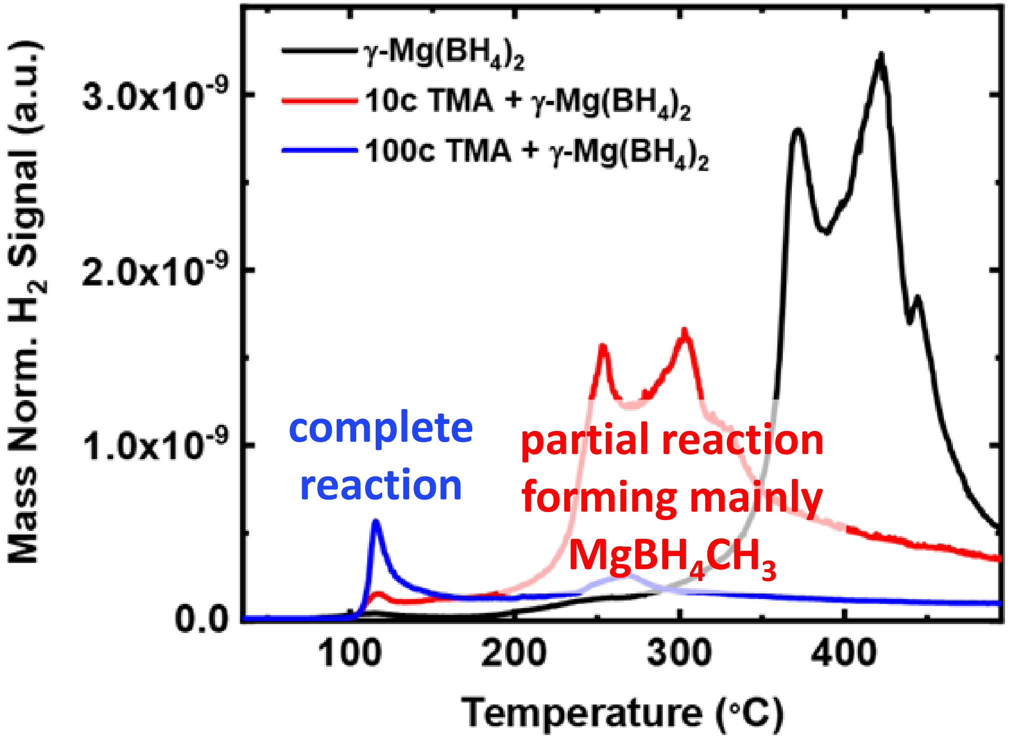
What Mechanism is Responsible for Improvement in H_2 Release?



vdW radius

BH_4^- = 2.05 Å

$-CH_3$ = 2.0 Å



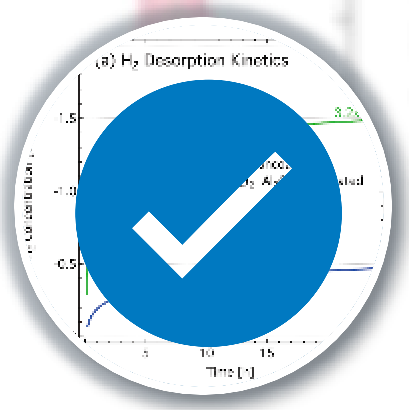
From [11]B, [27]Al NMR, DRIFTS, TPD:

- No reaction with B – pure exchange of BH_4^- and CH_3
- No incorporation if Al-containing species

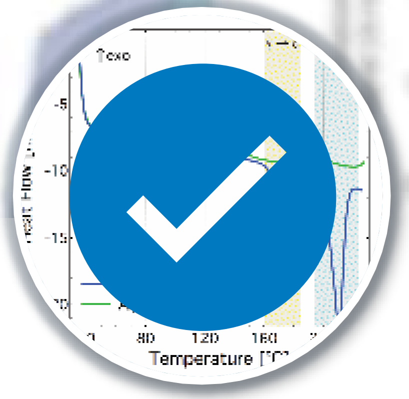
$$Al_2(CH_3)_6 + 3\ Mg(BH_4)_2 \rightarrow 2\ Al(BH_4)_3 + 3\ Mg(CH_3)_2$$

N. Strange, N. Leick, S. Shulda, A. Schneemann, V. Stavila, A. Lipton, M. Toney, T. Gennett, S. Christensen - Reactive Vapor-Phase Additives towards Destabilizing γ-$Mg(BH_4)_2$ for Improved Hydrogen Release (submitted)

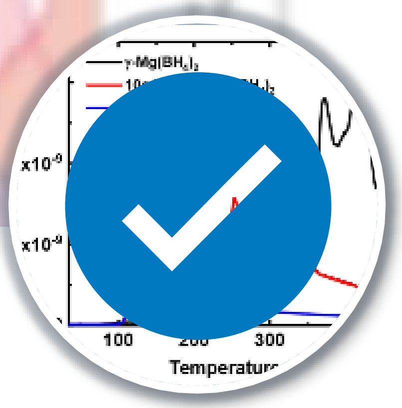
Approach to improve the performance of $Mg(BH_4)_2$



ALD of Al_2O_3:
TMA + H_2O



H_2O pulsing only



TMA pulsing only

Opportunities and Limitations for ALD on complex hydrides for H_2 storage

Short exposure to precursors

Exposure to 1 precursor can be sufficient

VdW radii of functional groups

Control of infiltration vs. coating

Room-temperature ALD processes

Need for more chemistries

Avoid the use of H_2O, oxygen precursors

Acknowledgements

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NREL/PR-5900-80932

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