Atomic Layer Deposition for Materials-Based H_2 Storage: Opportunities and Limitations

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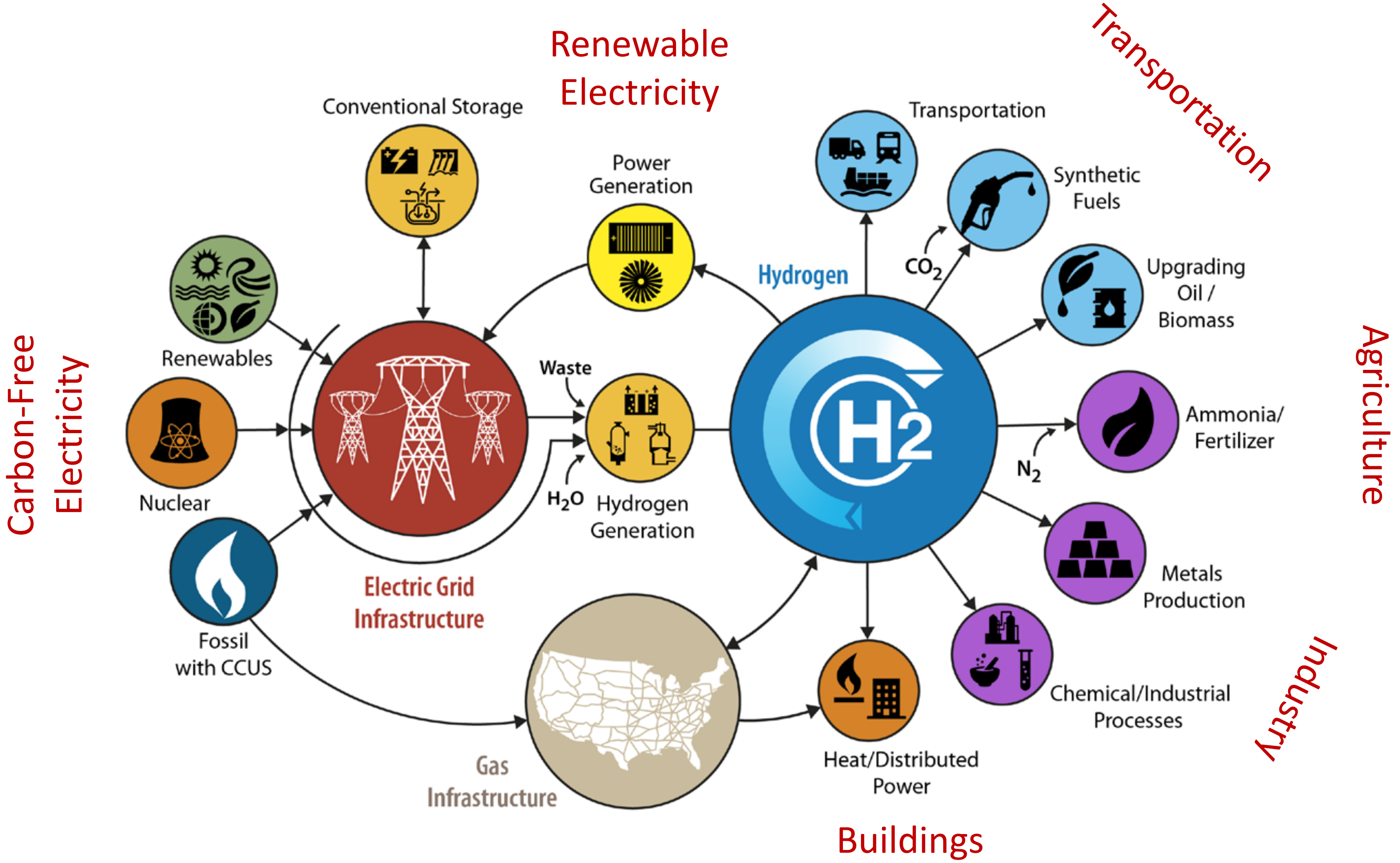
240th ECS Fall Meeting: October 10th-14th, 2021

a: National Renewable Energy Laboratory; Golden, CO
b: Colorado School of Mines; Golden, CO

c: SLAC Accelerator Laboratory; Menlo Park, CA

A future built on renewable energies relies on hydrogen storage



Credit: National Renewable Energy Laboratory

Hydrogen storage technologies

Physical-based | **Material-based**

Compressed Gas | **Cold/Cryo Compressed** | **Liquid H_2**

700 bar, 40 g/L

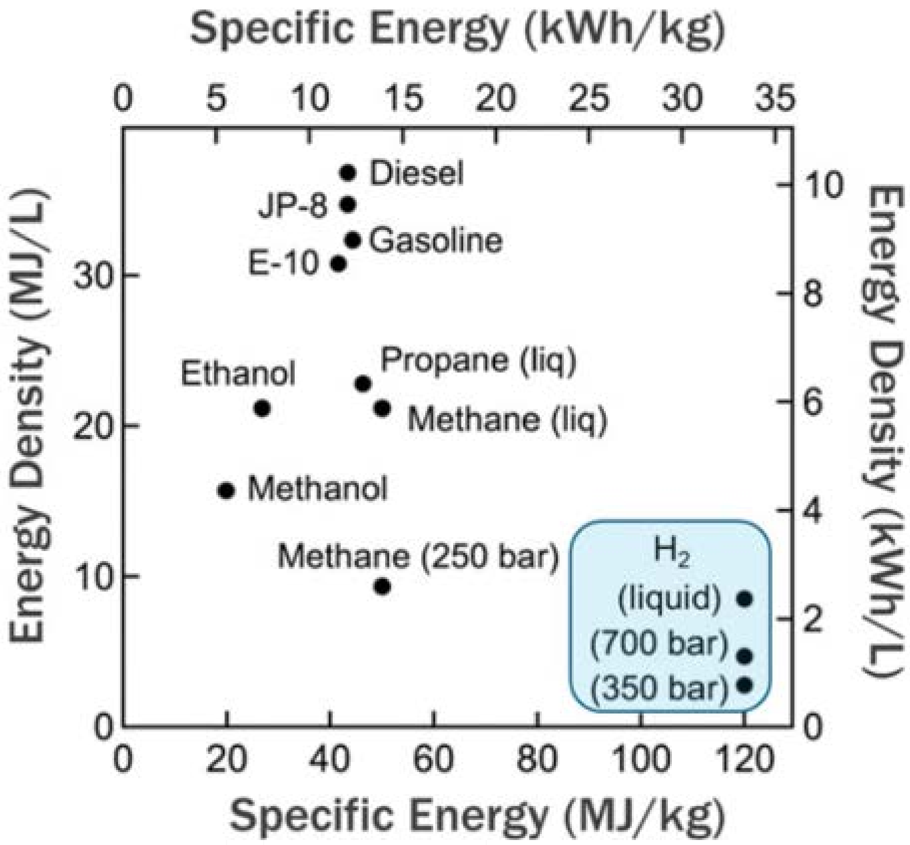
20 K, 71 g/L

Adsorbent | **Liquid organic** | **Interstitial hydride**

Ex. MOF-5

Ex. BN-methyl cyclopentane

Ex. $LaNi_5H_6$



Wieliczko, M., & Stetson, N. (2020). Hydrogen technologies for energy storage: A perspective. *MRS Energy & Sustainability*, *7*, E43

Hydrogen storage technologies

Application requirements:

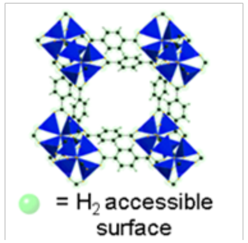
- hydrogen uptake and release
  - thermodynamics rates
    - kinetic rates
      - cyclability
- mass of the carrier

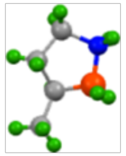
Material-based

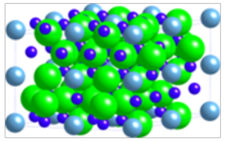
H_2 carriers are materials that:

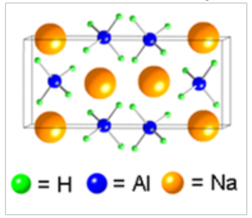
- hydrogen-rich (near ambient conditions)
- liquid- or solid-state
- release H_2 on demand

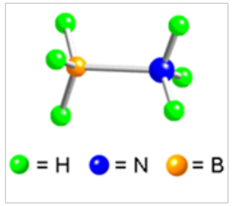
Adsorbent	Liquid organic	Interstitial hydride	Complex hydride	Chemical hydrogen
Ex. MOF-5	Ex. BN-methyl cyclopentane	Ex. $LaNi_5H_6$	Ex. $NaAlH_4$	Ex. NH_3BH_3









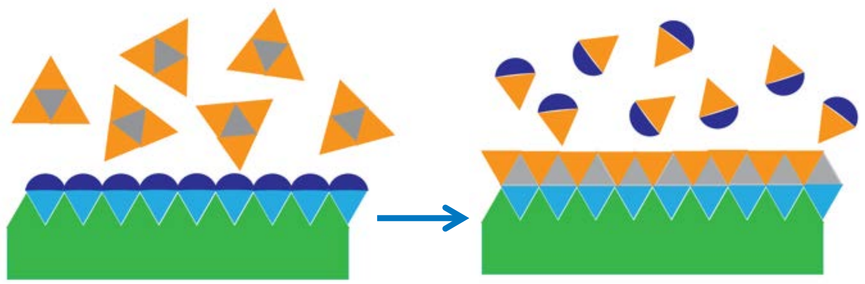


Atomic Layer Deposition (ALD)

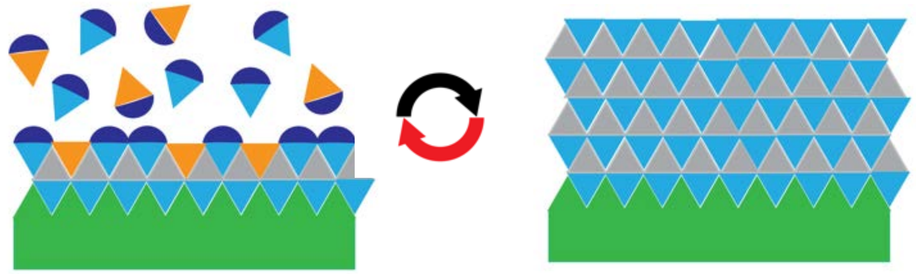
- Coating retains nanostructure: increased mass and heat transfer
- Atomically thin to maintain the gravimetric capacity the carrier
- Manipulation of the thermodynamic pathway
- Catalyst additive to enhance reaction rates

Schematic of ALD

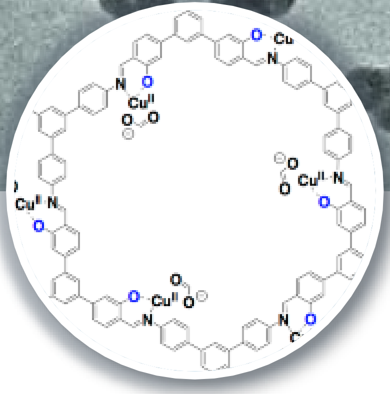
First half-cycle: metal-precursor



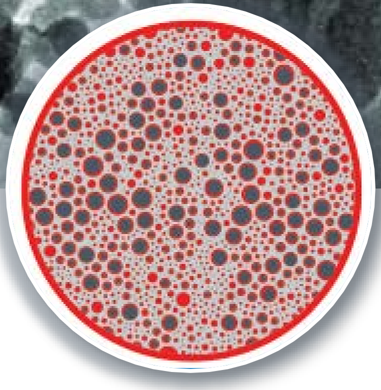
Second half-cycle: reactive-precursor



Examples of how ALD can benefit H_2 storage materials



Cu(I) sites
into a 2D COF



Encapsulation of
$Mg(BH_4)_2$

Catalysis for
de-/rehydrogenation
of LOHCs

Covalent organic frameworks for H_2 storage

Physical-based

- Compressed Gas

700 bar, 40 g/L

- Cold/Cryo Compressed

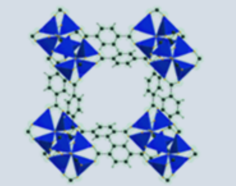
- Liquid H_2

20 K, 71 g/L

Material-based

- **Adsorbent**

Ex. MOF-5



- Liquid organic

Ex. BN-methyl cyclopentane

- Interstitial hydride

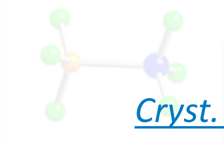
Ex. $LaNi_5H_6$

- Complex hydride

Ex. $NaAlH_4$

- Chemical hydrogen

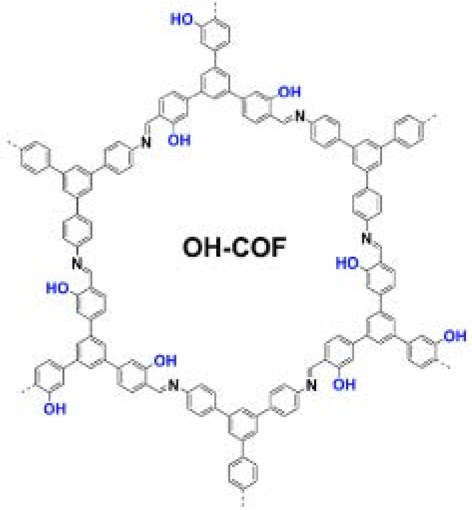
Ex. NH_3BH_3



➢ High surface area: ~1 H_2 wt%/ 500 $m^2.g^{-1}$

➢ H_2 adsorption enthalpy: 15-25 kJ/mol

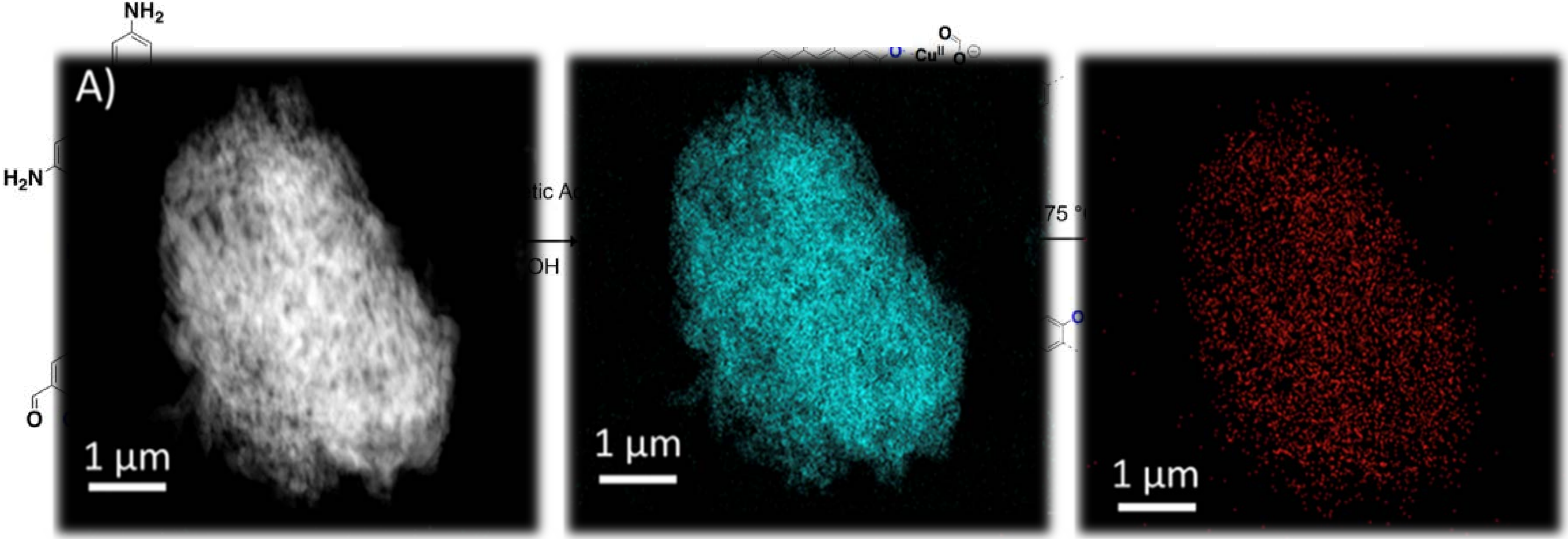
<u>Material used in this work:</u>
2D imine-based
covalent organic framework (COF)
for simultaneous tuning of
surface area and H_2 binding



W. Braunecker et al., *Cryst. Growth Des.* 2018, 18, 7, 4160–4166

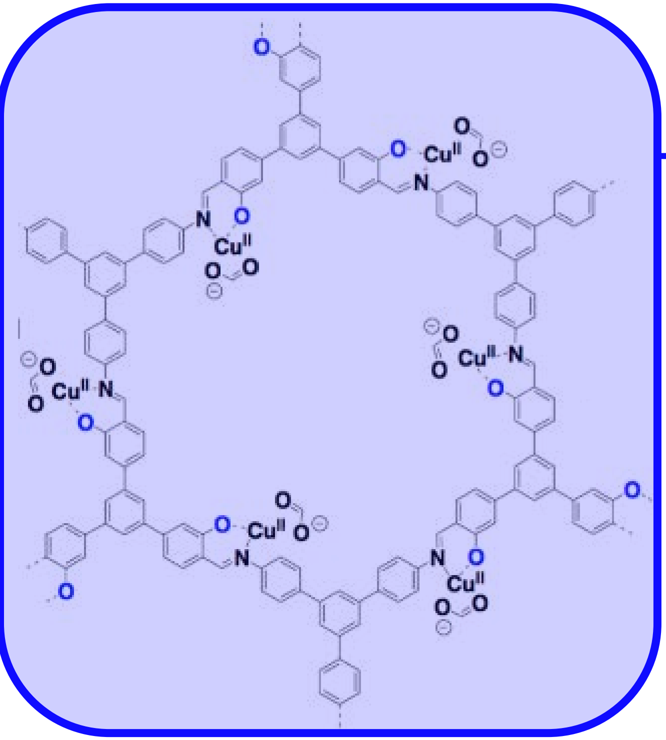
Covalent organic frameworks for H_2 storage: wet-chemical approach

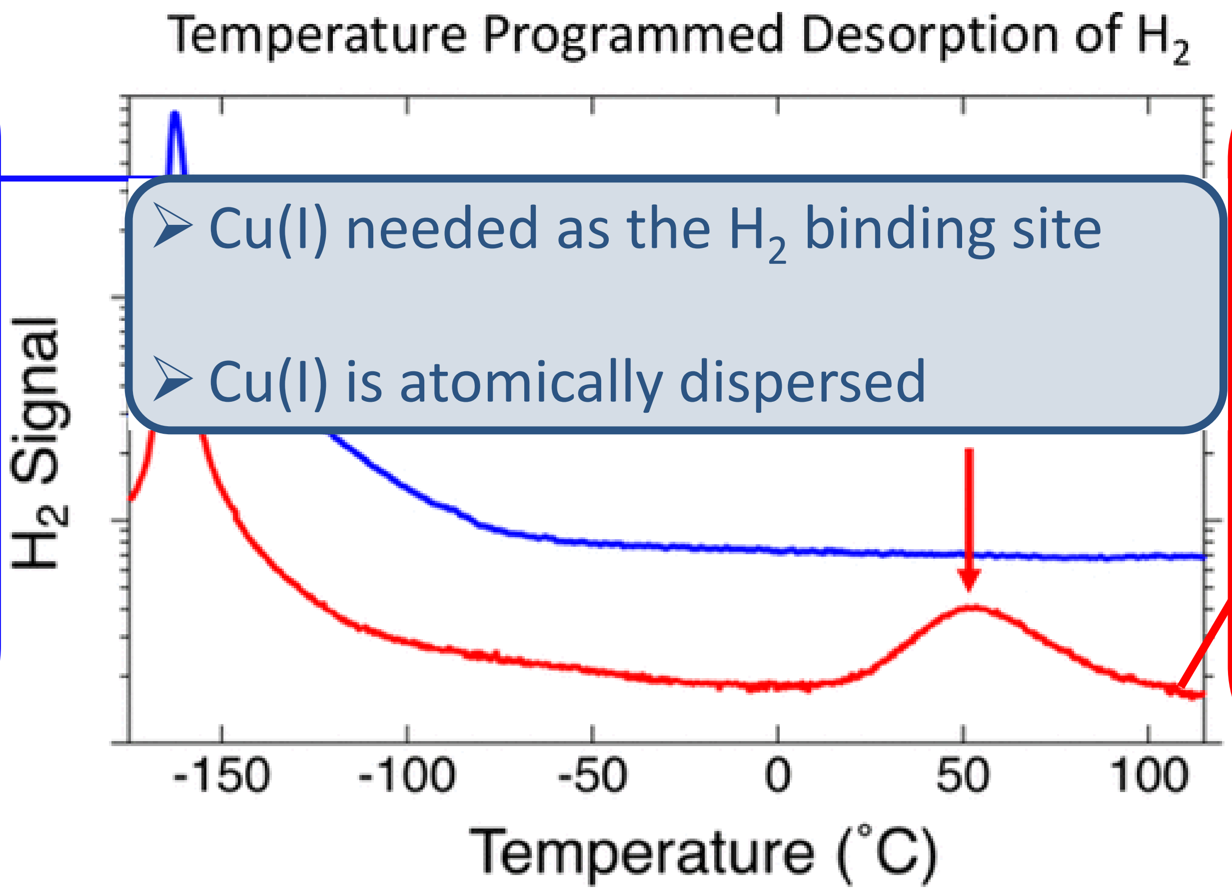
HAADF carbon copper



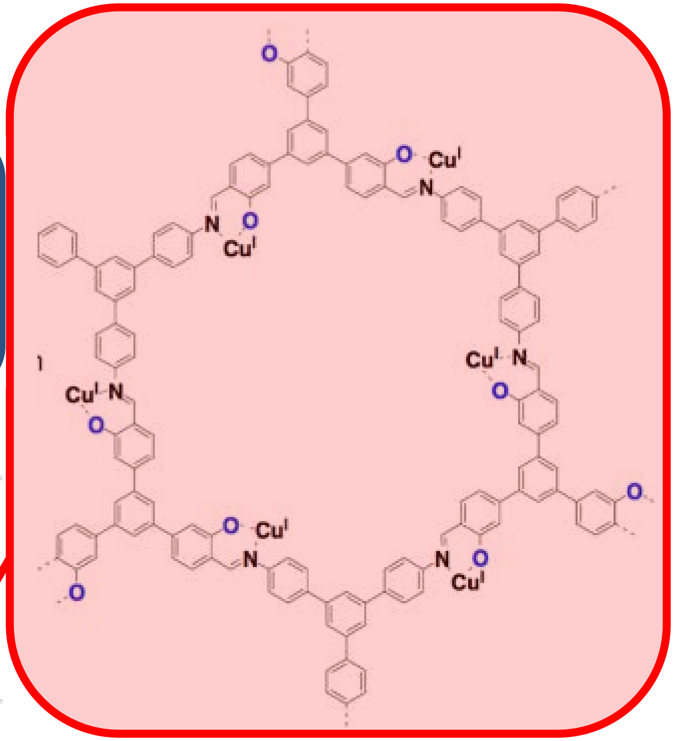
W. Braunecker et al., [ACS Materials Lett. 2020, 2, 3, 227–232]

Covalent organic frameworks for H_2 storage: wet-chemical approach





- Cu(I) needed as the H_2 binding site
- Cu(I) is atomically dispersed

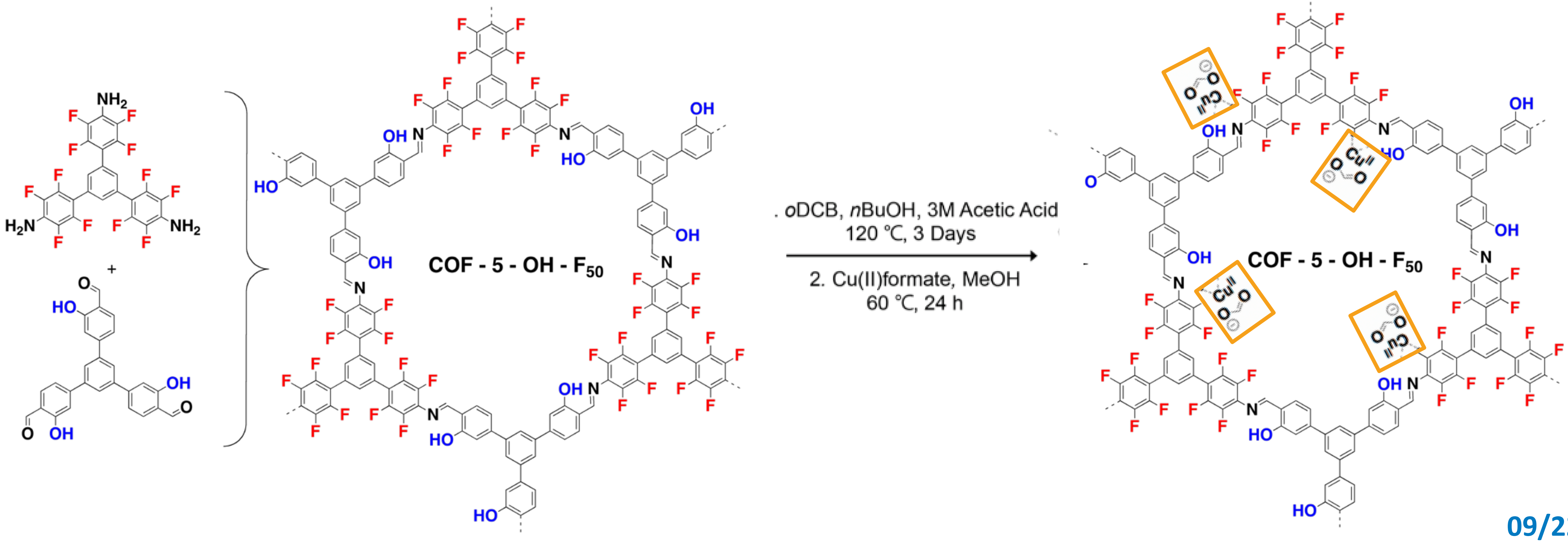


W. Braunecker et al., *ACS Materials Lett. 2020, 2, 3, 227–232*

Covalent organic frameworks for H_2 storage: wet-chemical approach

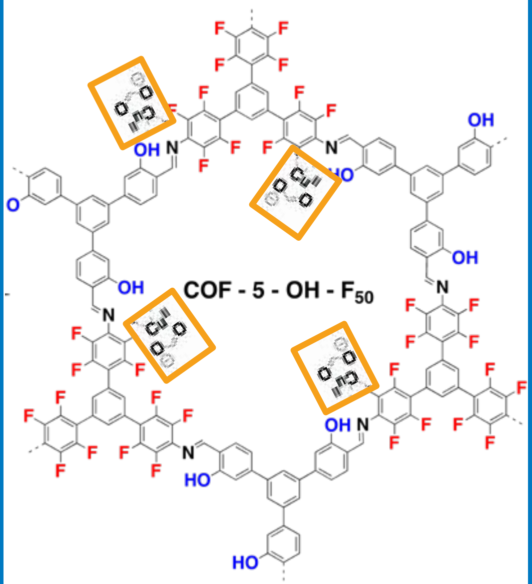
1. Partial fluorination of COFs stabilizes the structure

2. Fluorination to increase isosteric heat of adsorbtion with H_2



Opportunity for ALD to simultaneously…

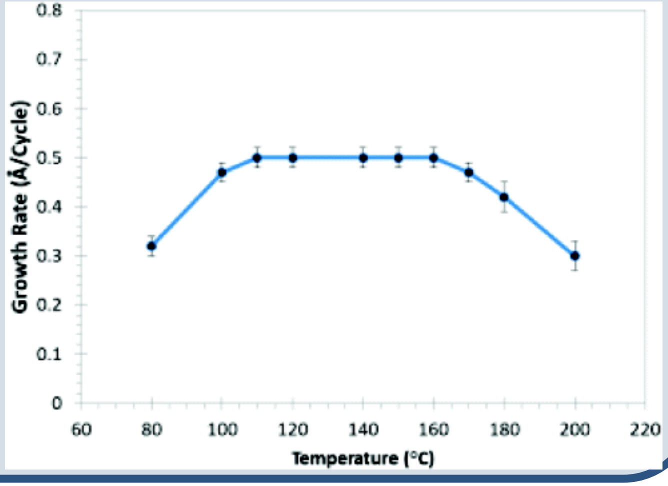
- …target specific binding sites for Cu-precursors, and …
- …deposit atomically dispersed copper
- …in a non-reduced state, e.g.
  -Cu(II) formate,
  -Cu(I)



3-step Cu(0) ALD:

Prec. A: Cu-$(OCHMeCH_2NMe_2)_2$
Prec. B: formic acid
} Cu(II) formate

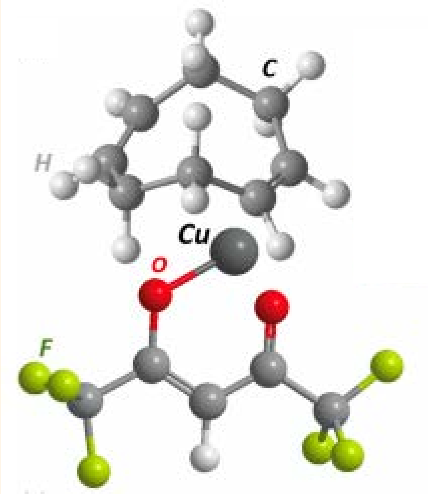
Prec. C: hydrazine →



T. Knisley et al.,
Chem. Mater. 2011, 23, 20, 4417–4419

Cu_2O ALD:

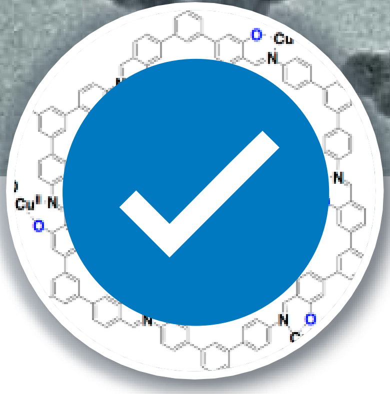
Prec. A: copper(I) hexafluoro-2,4-pentanedionate cyclooctadiene
aka: Cu(hfac)(cod)
Prec. B: H_2O



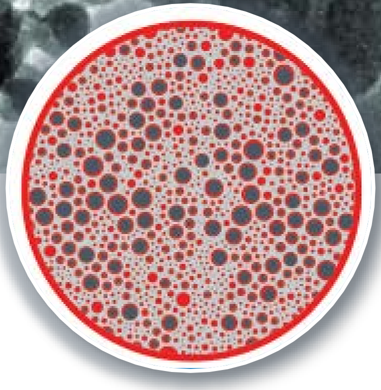
LMGP

Sekkat et al.,
Commun Mater 2, 78 (2021)

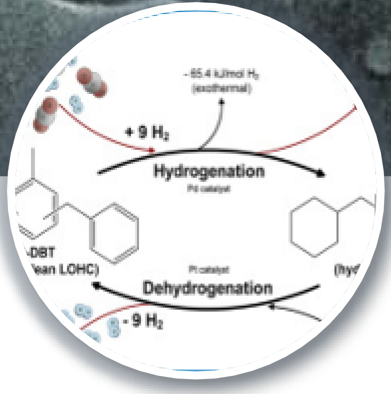
Examples of how ALD can benefit H_2 storage materials



ALD is a promising technique to engineer open metal sites in COFs

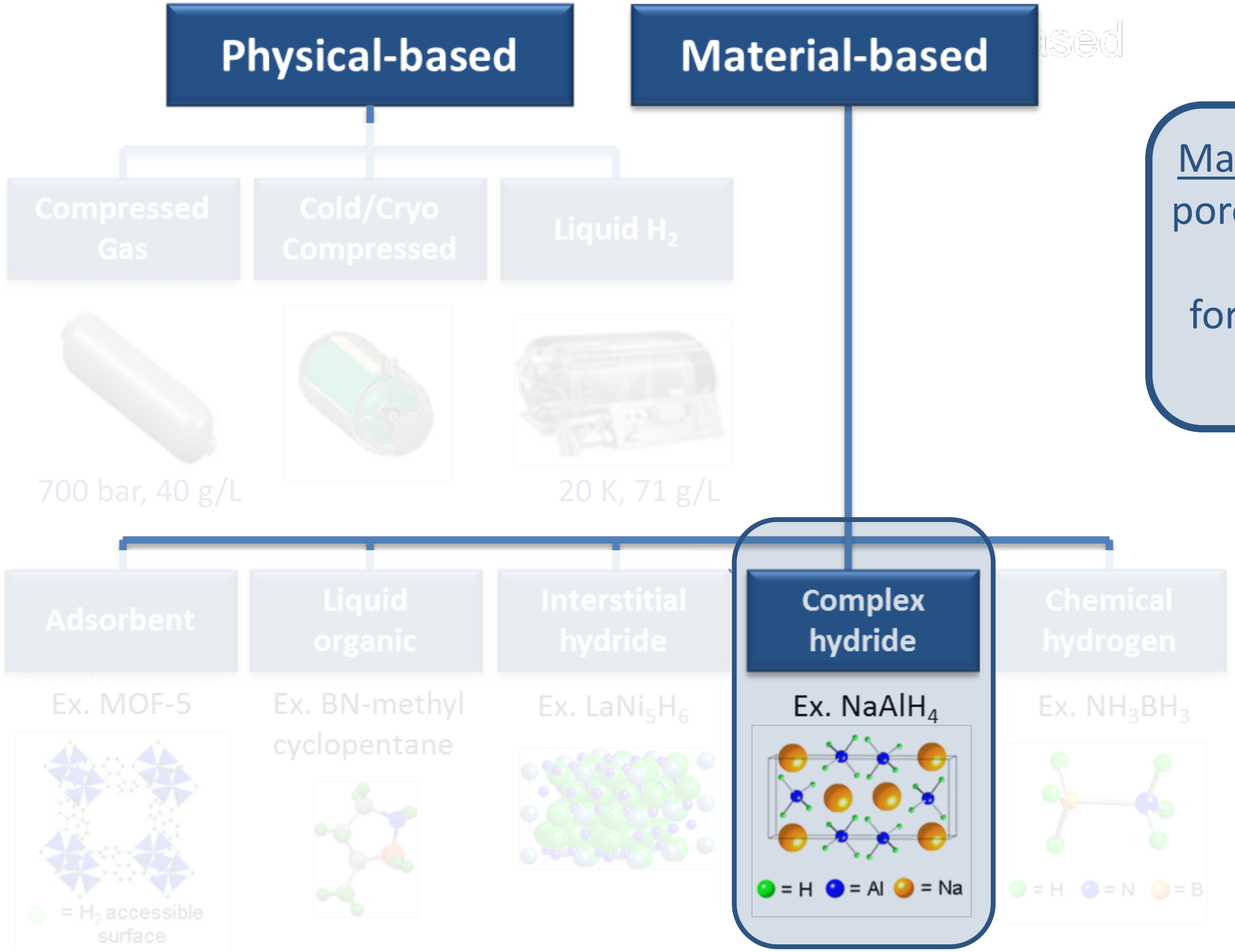


Encapsulation of $Mg(BH_4)_2$



Catalysis for de-/rehydrogenation of LOHCs

Complex hydride: $Mg(BH_4)_2$



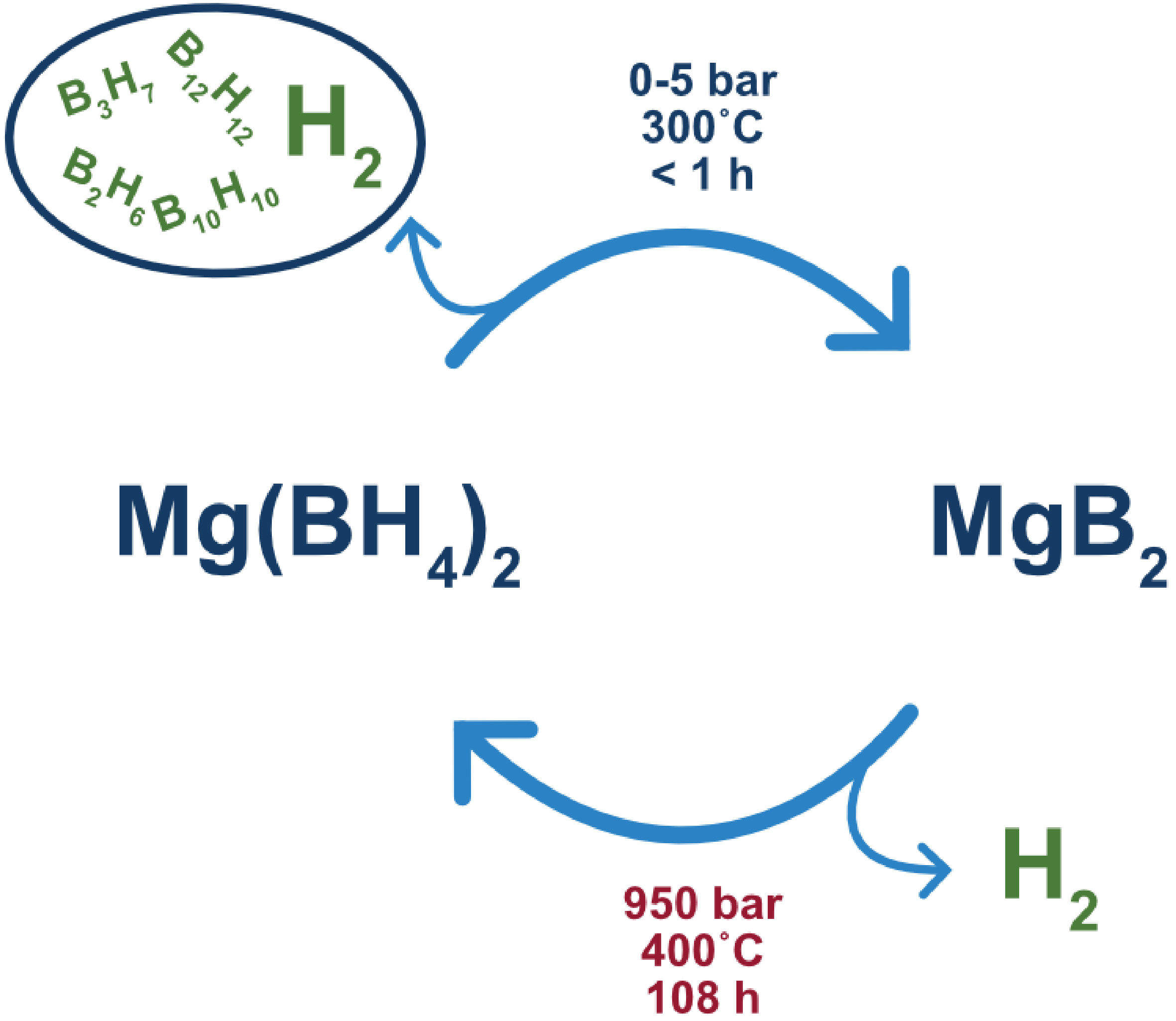
<u>Material used in this work:</u>
porous and nanostructured
γ-$Mg(BH_4)_2$
for increased H_2 diffusion
and reaction rates

$Mg(BH_4)_2$ 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

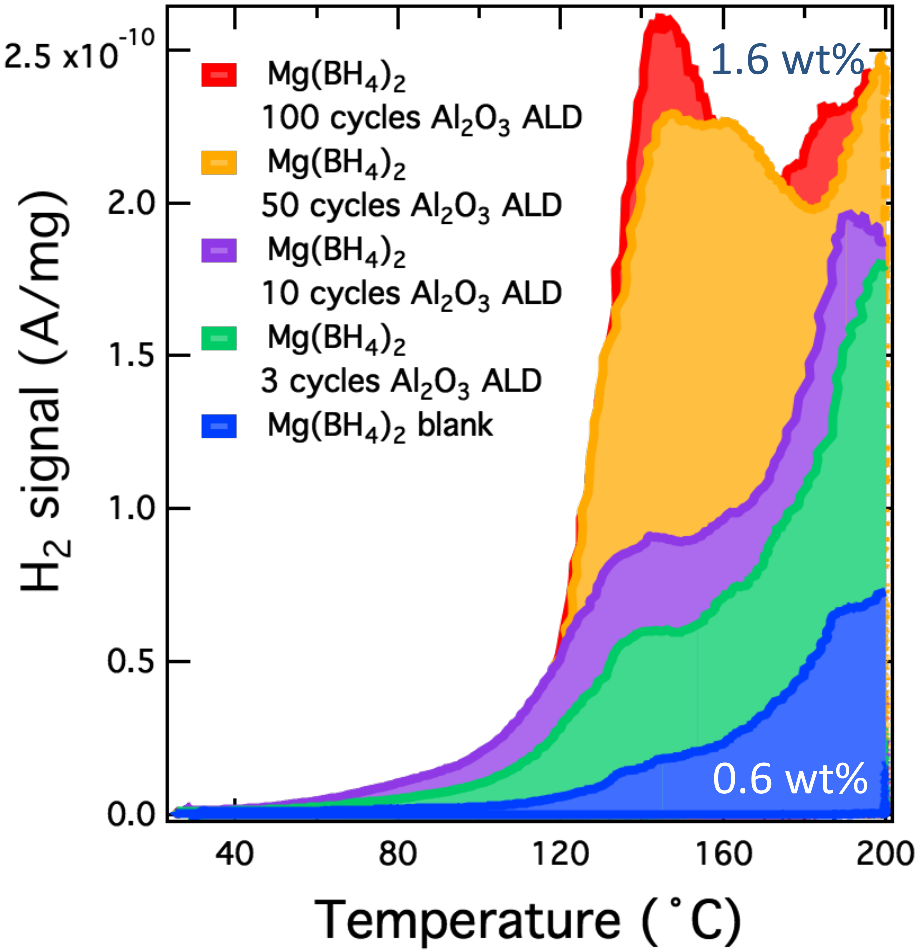
- Requires improvements:
  - Kinetics
  - Reversibility:
    - Suppression of B_2H_6 liberation: fuel cell damage and material loss
    - Suppression of $B_{12}H_{12}$ formation: thermodynamic energy well
  - Desorption temperature: 300˚C for neat material



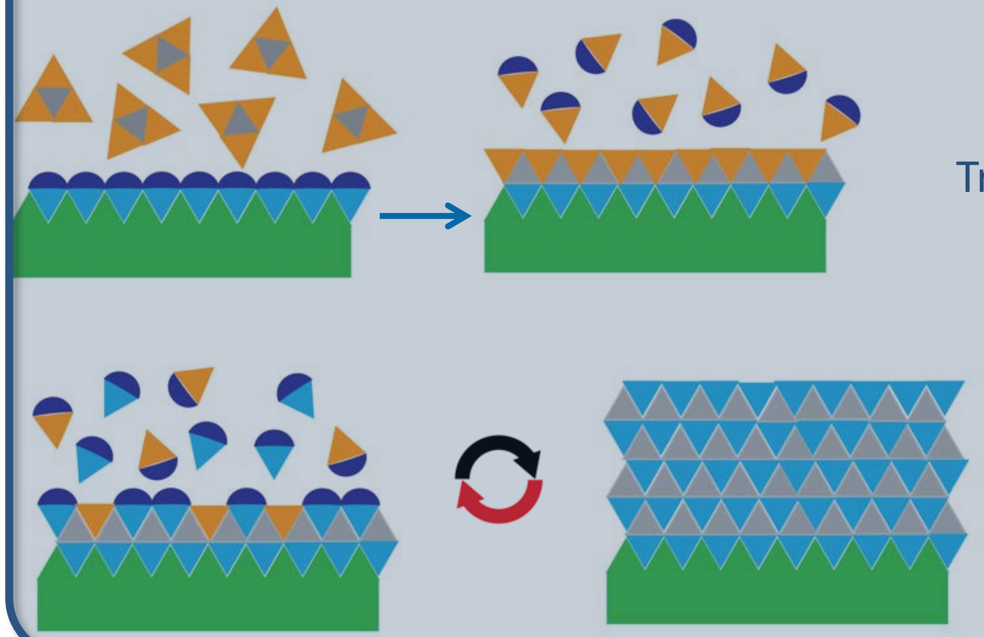
N. Leick et al., *ACS Appl. Energy Mater.* 2021, 4, 2, 1150–1162
G. Severa et al., *Chem. Commun.*, 2010, 46, 421-423

$Mg(BH_4)_2$ + ALD of Al_2O_3

Temperature Programmed Desorption



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



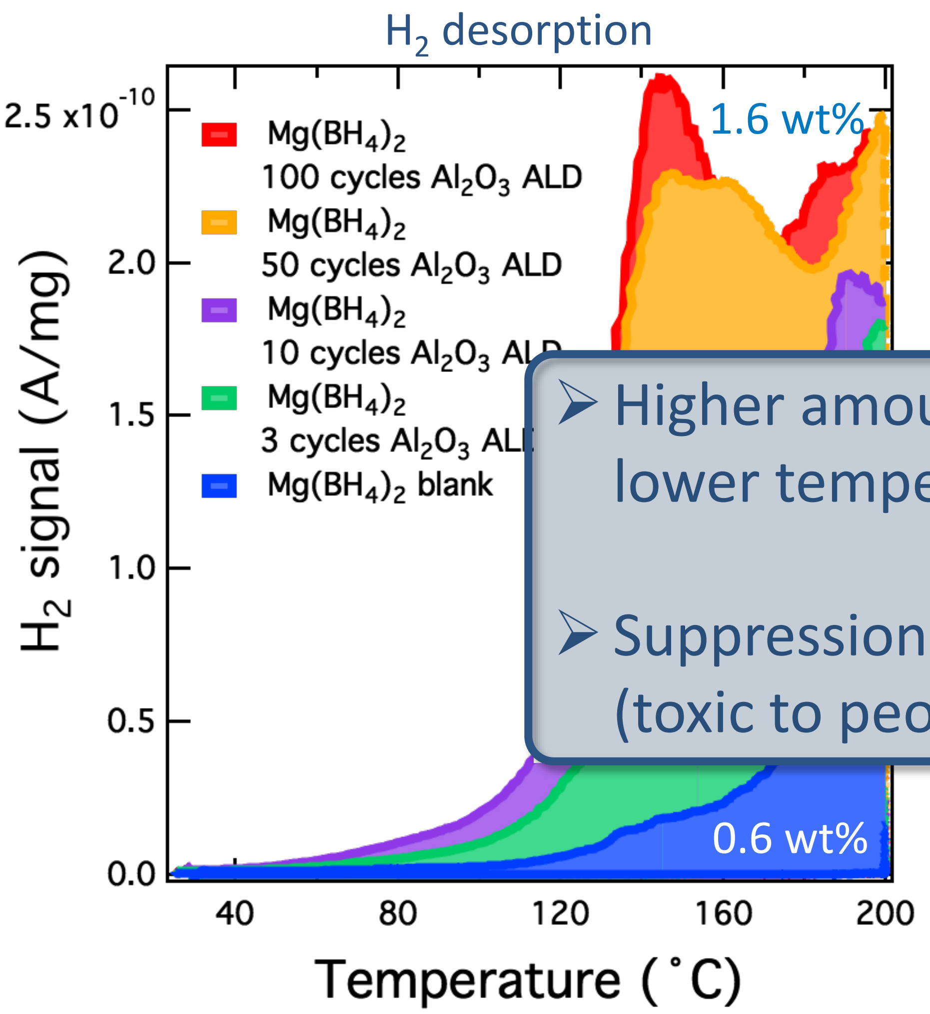
Al-precursor:
8 s
Trimethylaluminum
(TMA, $Al(CH_3)_3$)

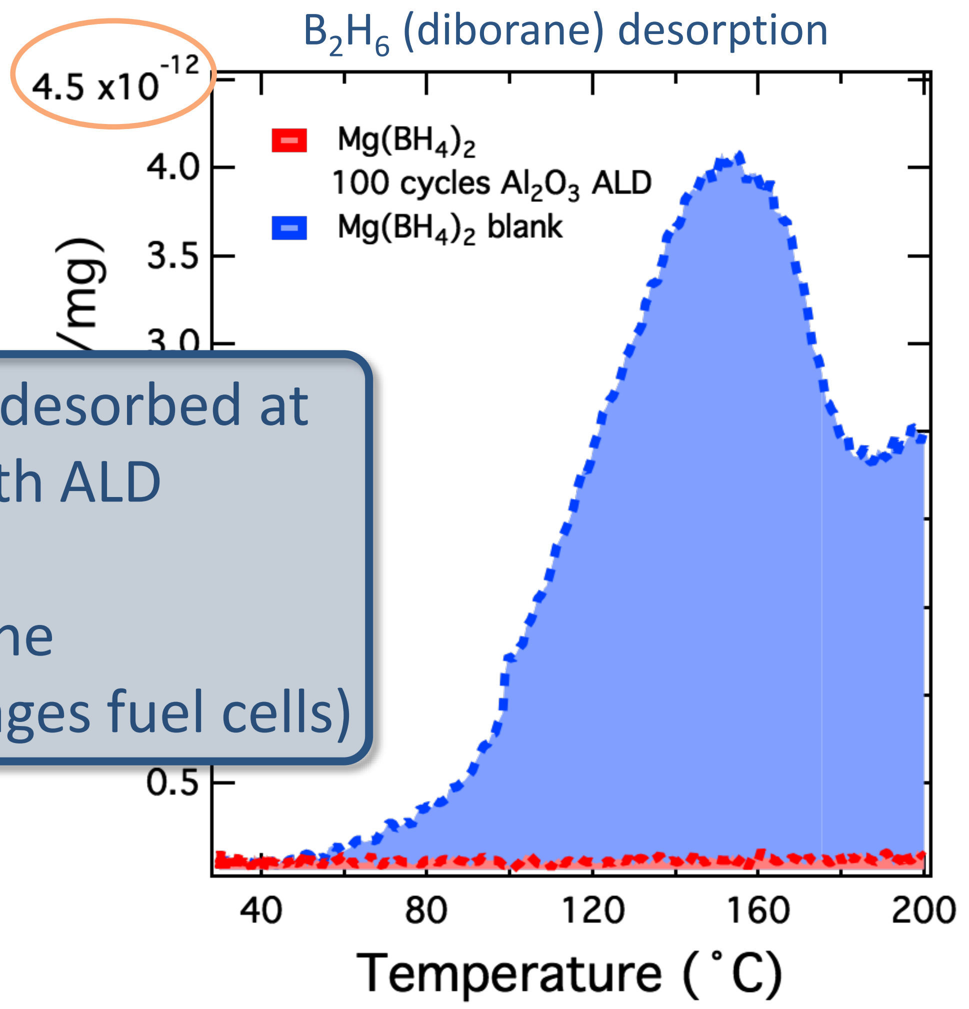
O-Precursor:
8 s
Water (H_2O)

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

$Mg(BH_4)_2$ + ALD of Al_2O_3

Temperature Programmed Desorption



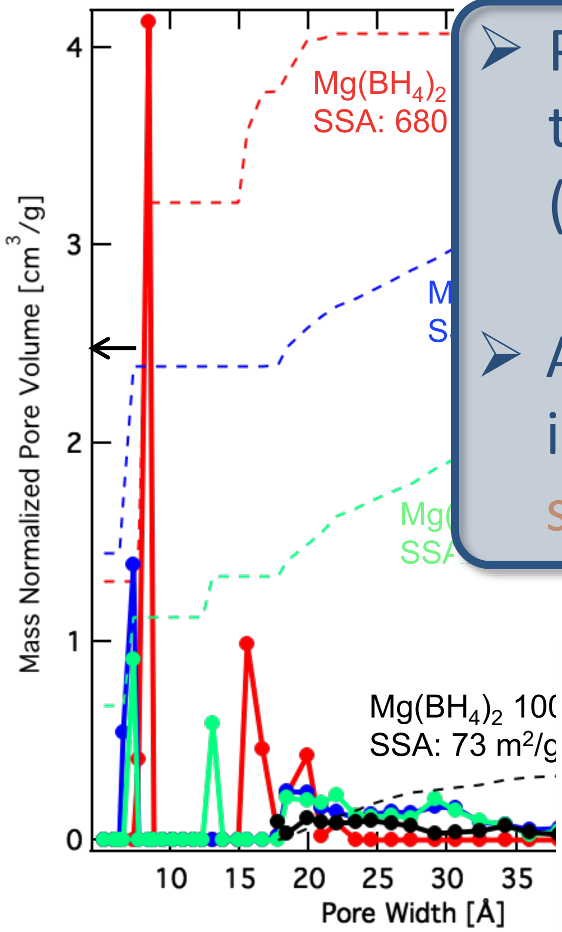


- Higher amounts of H_2 desorbed at lower temperature with ALD
- Suppression of diborane (toxic to people, damages fuel cells)

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

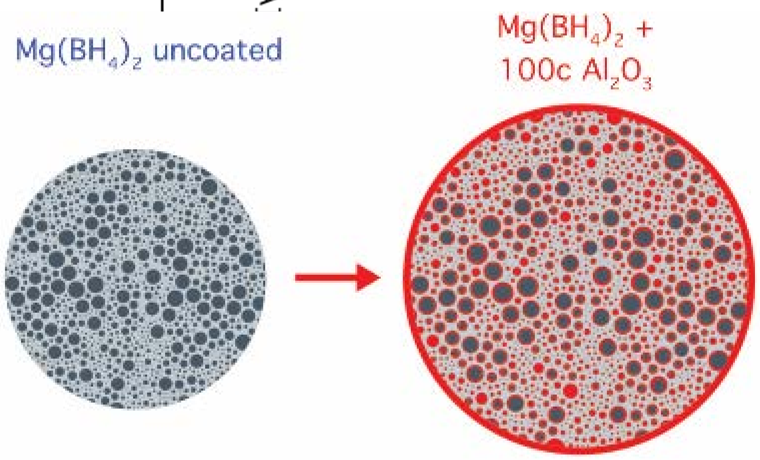
$Mg(BH_4)_2$ + ALD of Al_2O_3

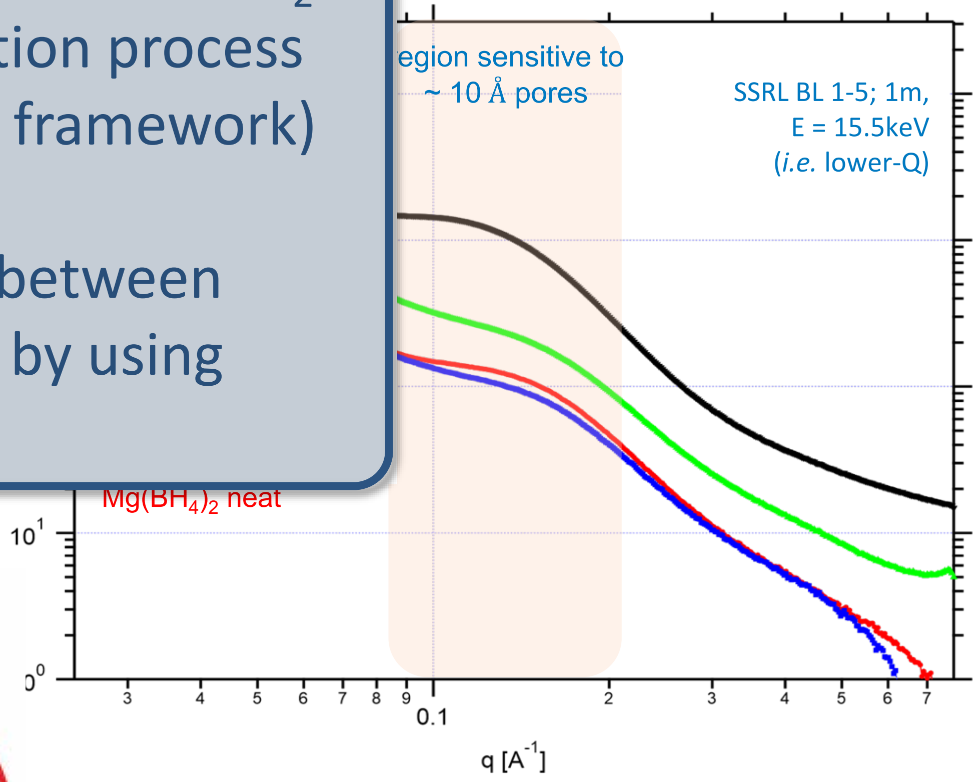
Porosimetry based on N_2 physisorbtion



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

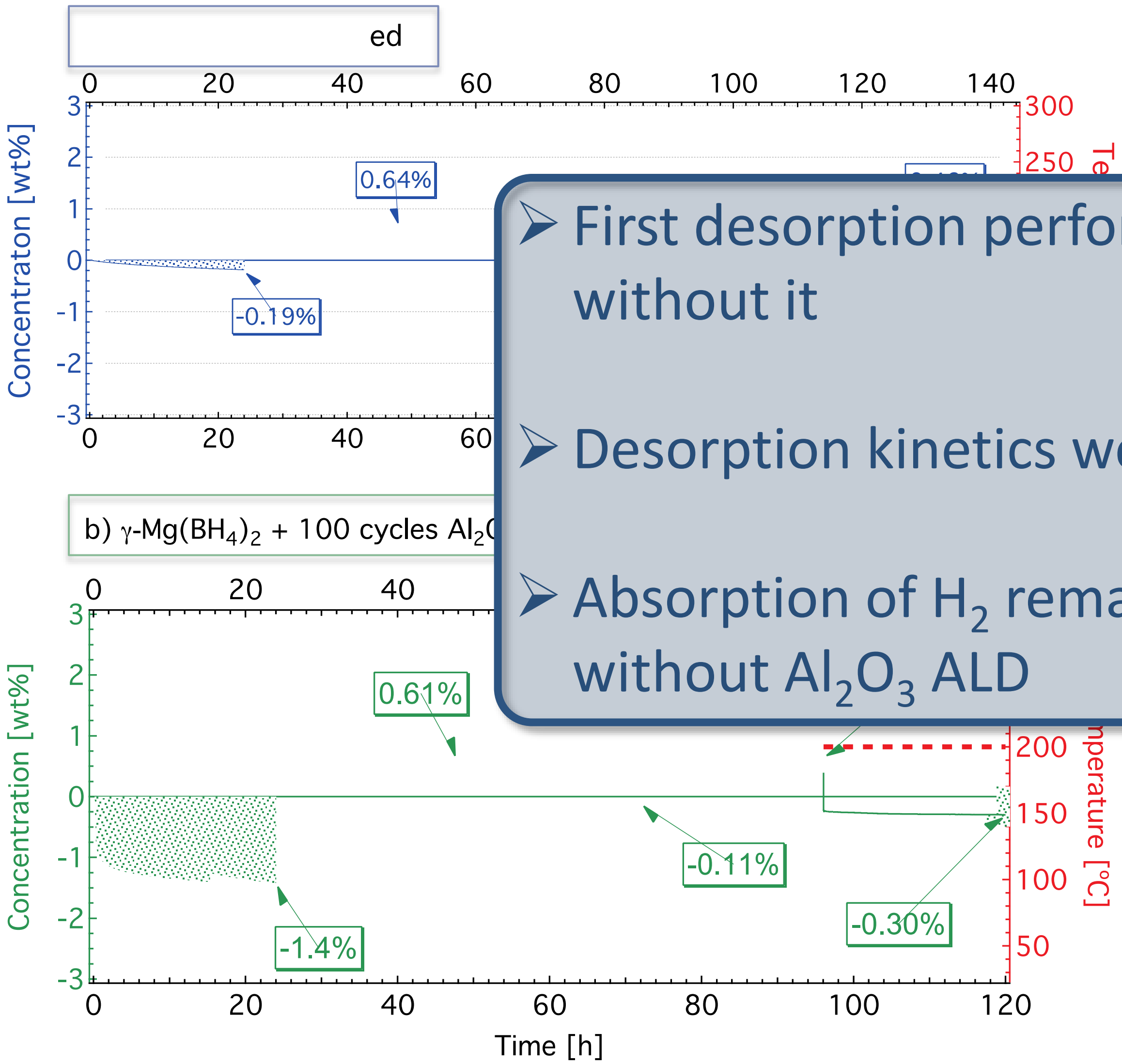
- Pores ~10 Å are accessible to TMA and H_2O throughout the entire deposition process ("swelling" of the γ-$Mg(BH_4)_2$ framework)
- ALD allows for the selectivity between infiltration and encapsulation by using size-exclusive ALD precursors.

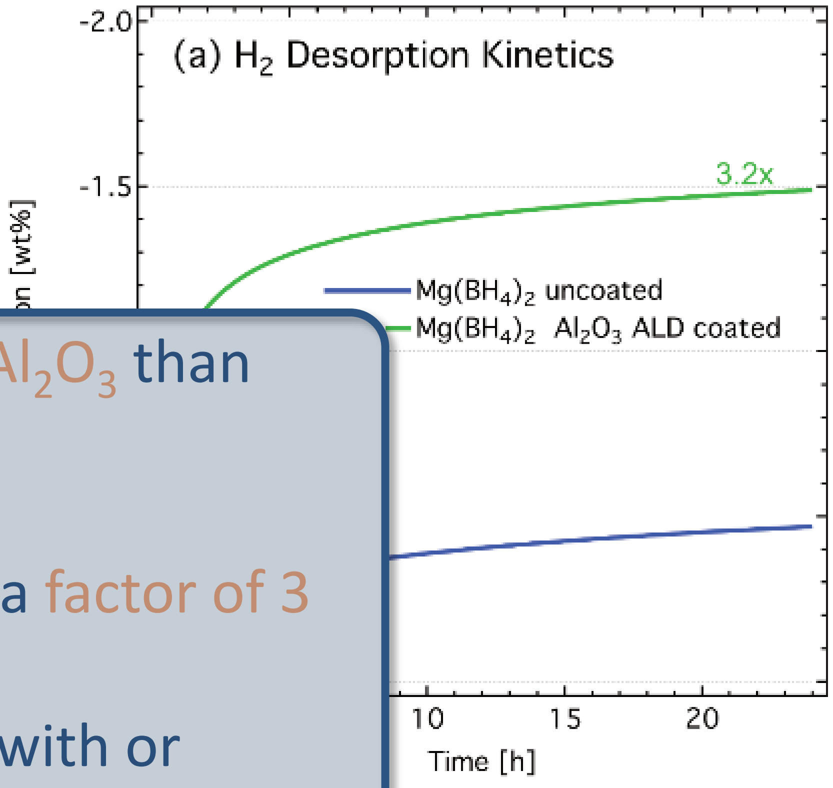


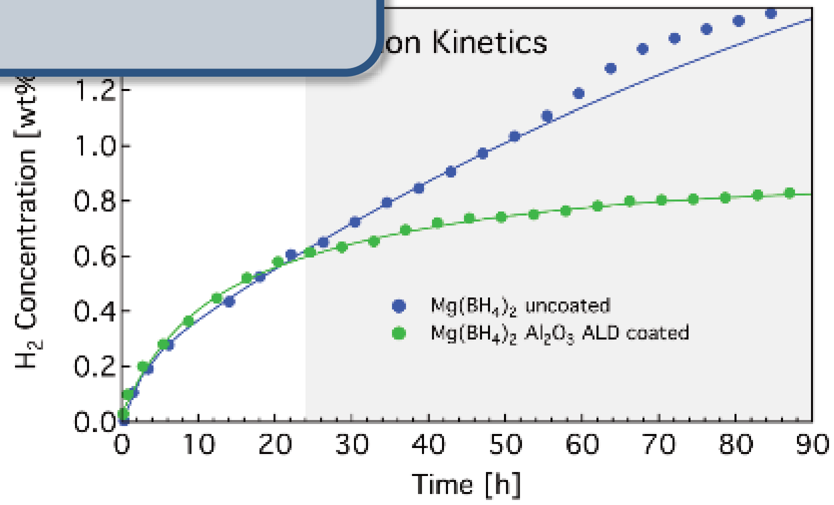


N. Leick et al., *ACS Appl. Energy Mater.* 2021, 4, 2, 1150–1162

$Mg(BH_4)_2$ + ALD of Al_2O_3





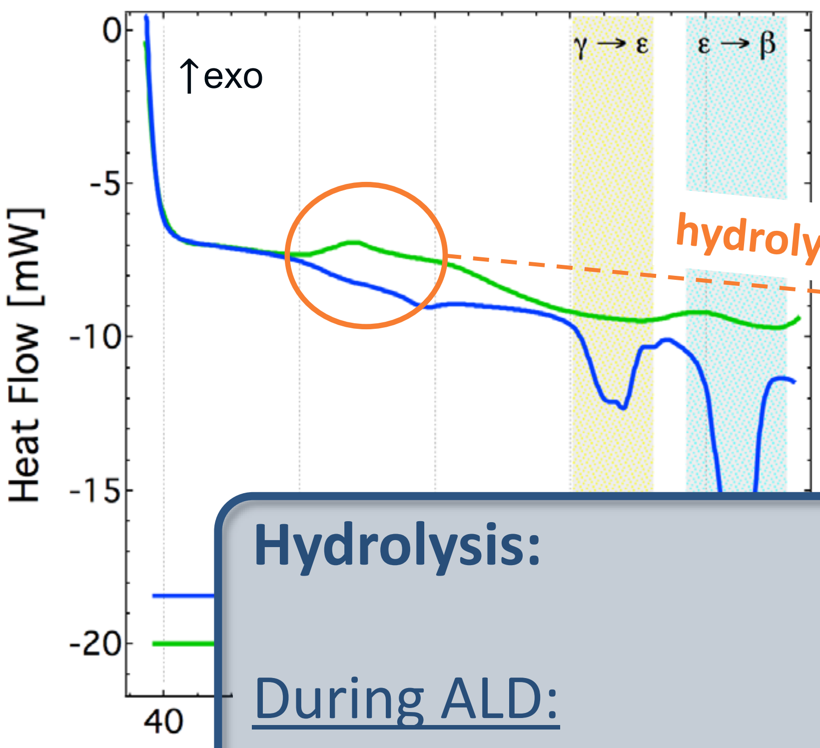


- First desorption performs better with Al_2O_3 than without it
- Desorption kinetics were improved by a factor of 3
- Absorption of H_2 remains challenging, with or without Al_2O_3 ALD

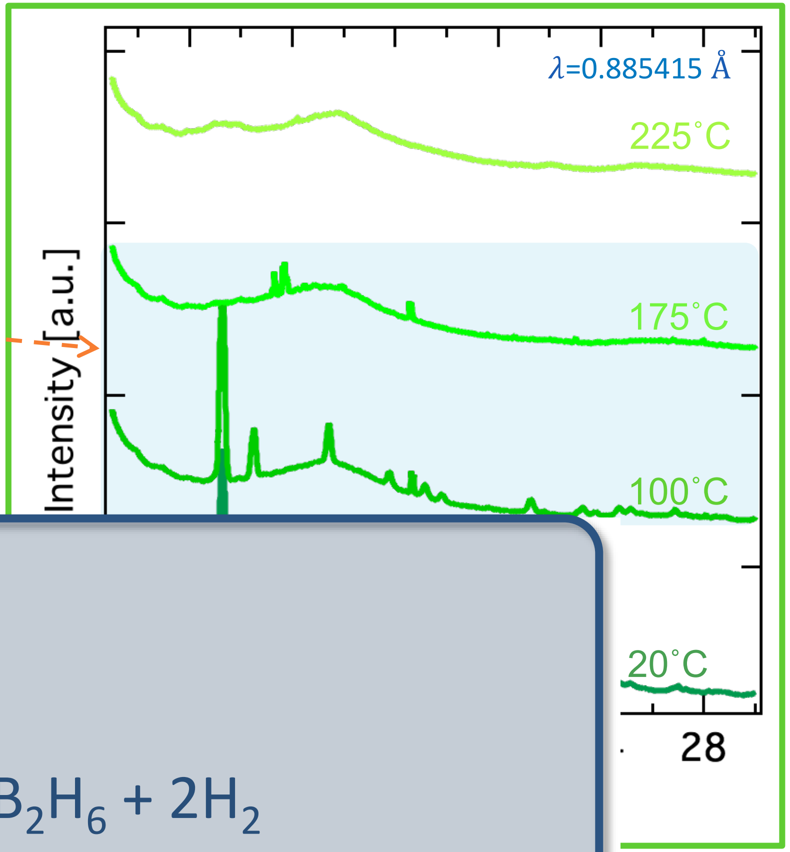
N. Leick et al., *ACS Appl. Energy Mater.* 2021, 4, 2, 1150–1162

$Mg(BH_4)_2$ + ALD of Al_2O_3

Differential Scanning Calorimetry



X-Ray Diffraction - *in situ* heating



loss of crystalline structure

Hydrolysis:

During ALD:

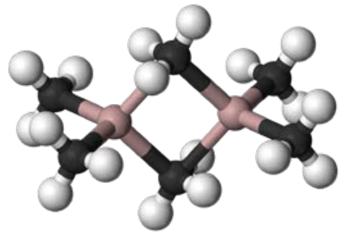
$Mg(BH_4)_2 + 2H_2O \rightarrow Mg(OH)_2 + B_2H_6 + 2H_2$

After ALD – during heating:

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

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

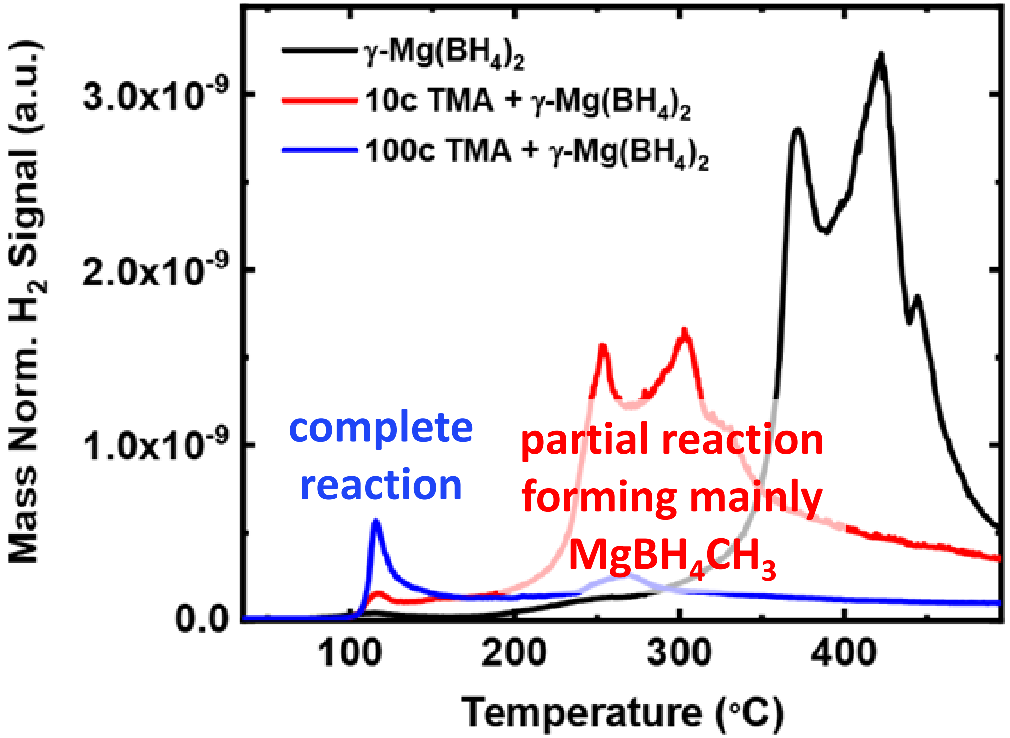
$Mg(BH_4)_2$ + TMA: not self-limiting



vdW radius

BH_4^- = 2.05 Å

$-CH_3$ = 2.0 Å



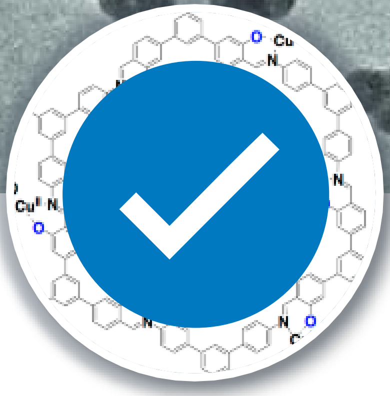
From [11]B, [27]Al NMR, DRIFTS, TPD:

- 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)

Examples of how ALD can benefit H_2 storage materials

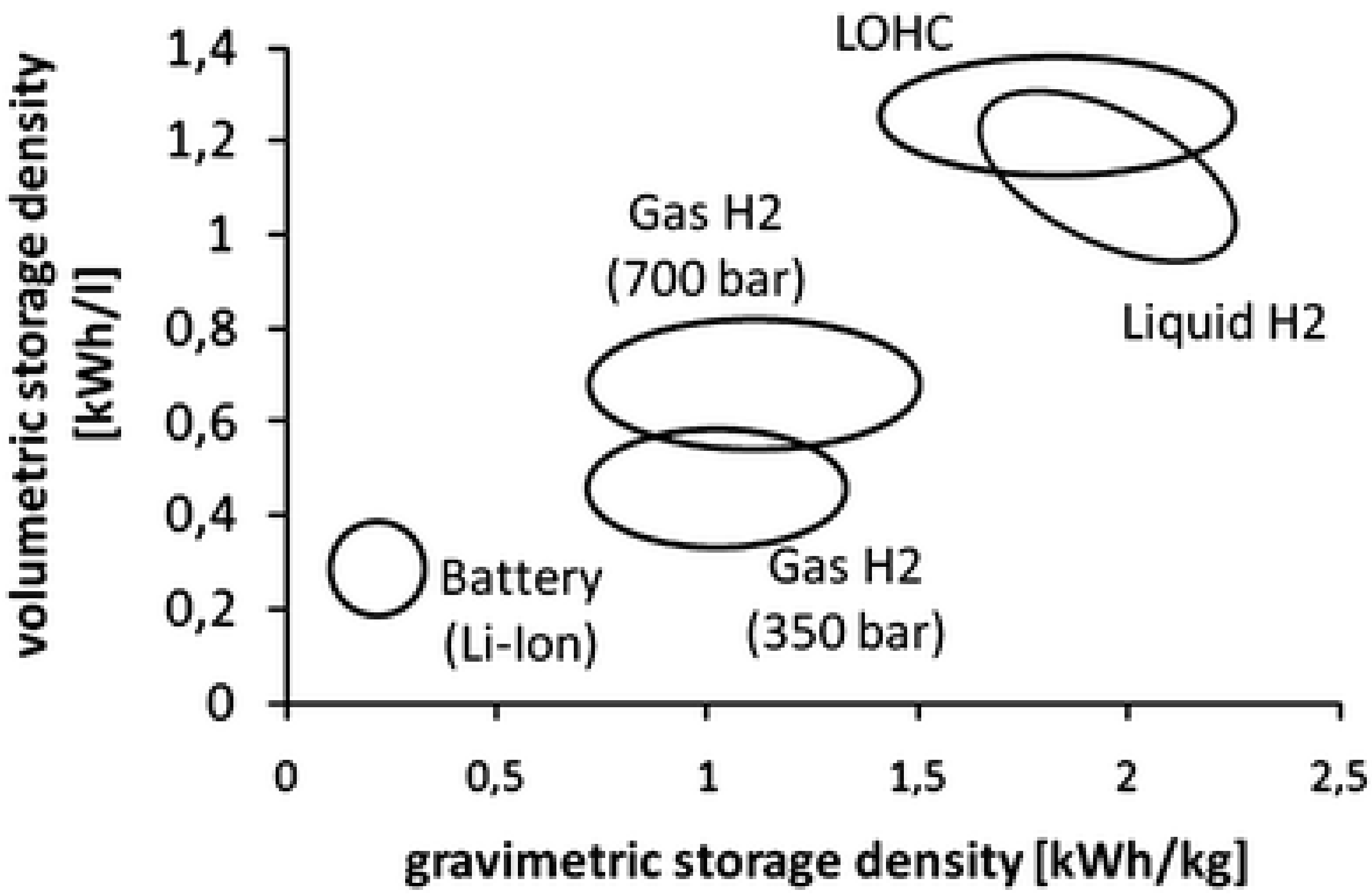


ALD is a promising technique to engineer open metal sites in COFs

Encapsulation of metal hydrides and/or infiltration of additives can be tuned using ALD

Catalysis for de-/rehydrogenation of LOHCs

Liquid Organic Hydrogen Carriers (LOHC)

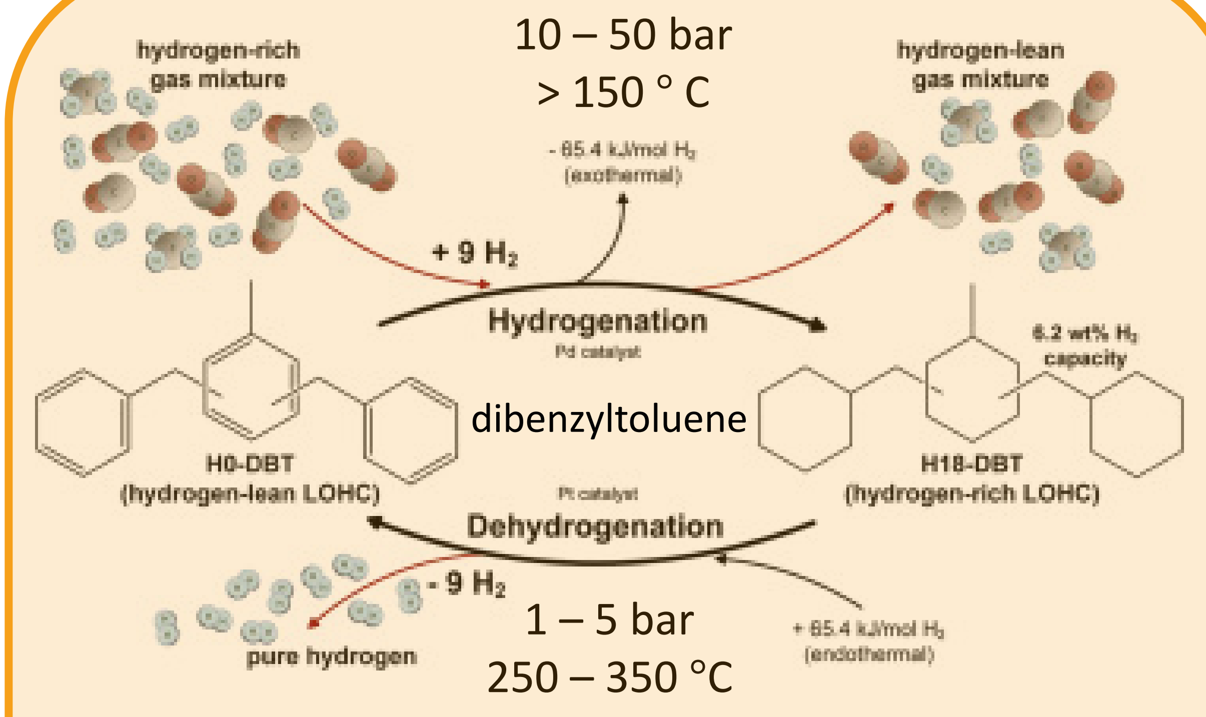


D. Teichmann et al., *Energy Environ. Sci.*, 2011, 4, 2767-2773

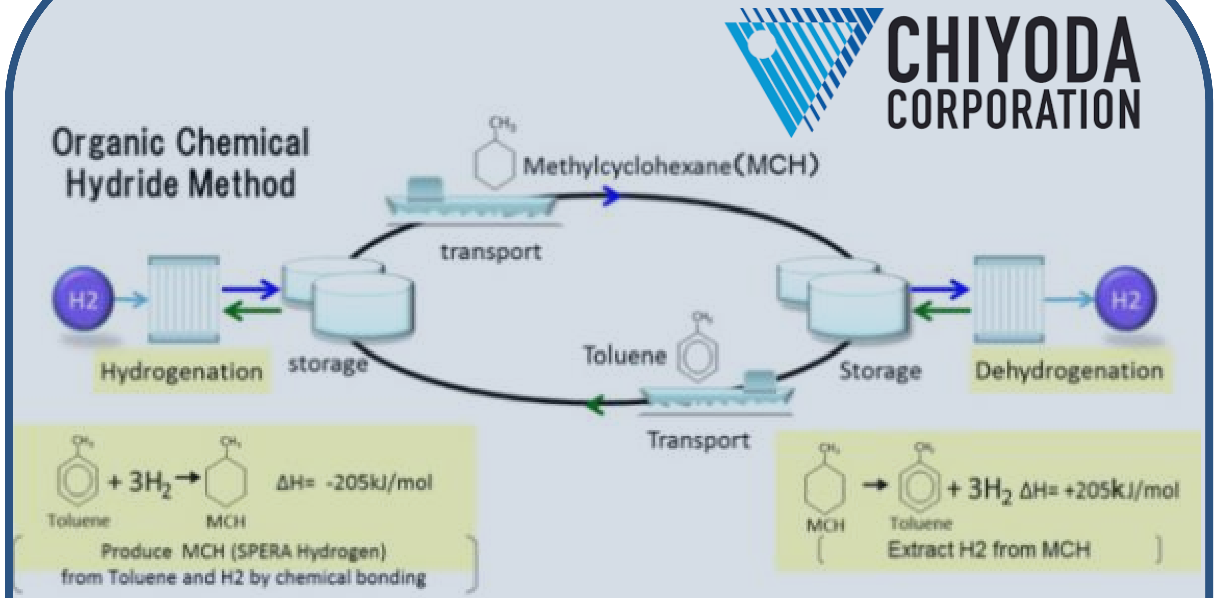
LOHCs…

- Have a high energy density
- Store H_2 at ambient temperatures and pressures
- Can have low (eco)toxicity
- Conformable different types of tanks

Examples of LOHC uses

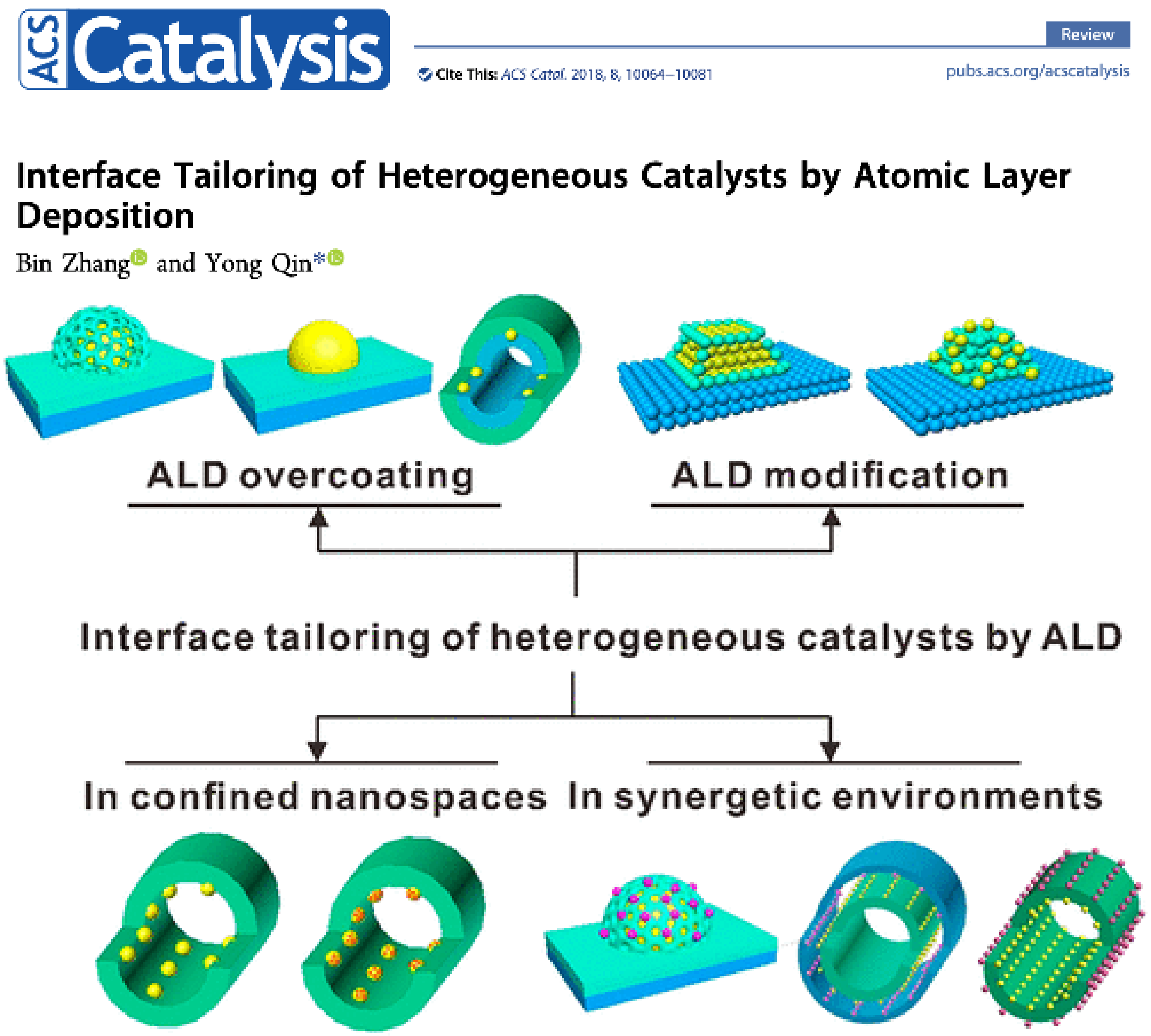


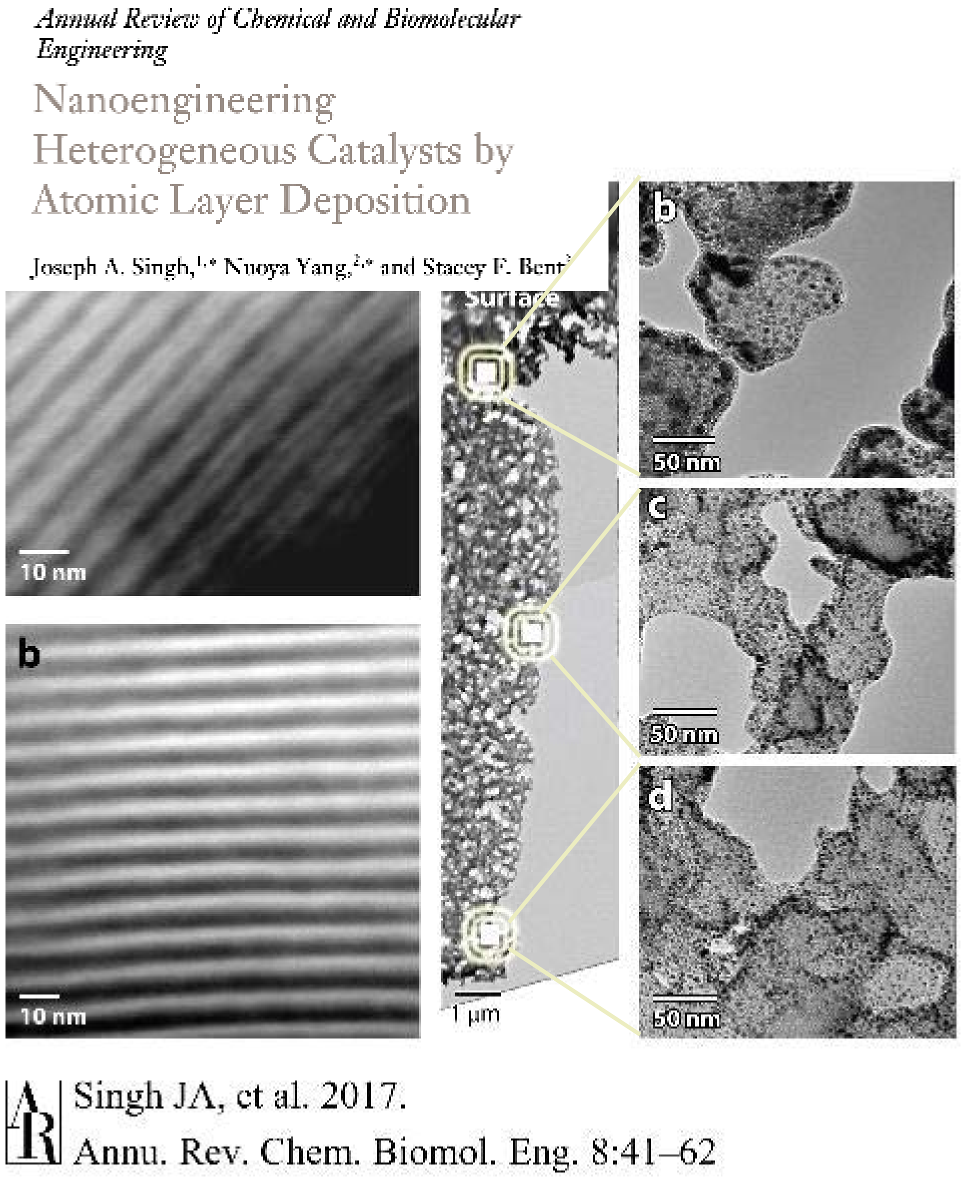
H. Jorschick et al., *Int. J. Hydro. Energ*. 2019, 44, 59, 31172-31182
S. Duerr et al., ChemSusChem 2017, 10, 42 – 47



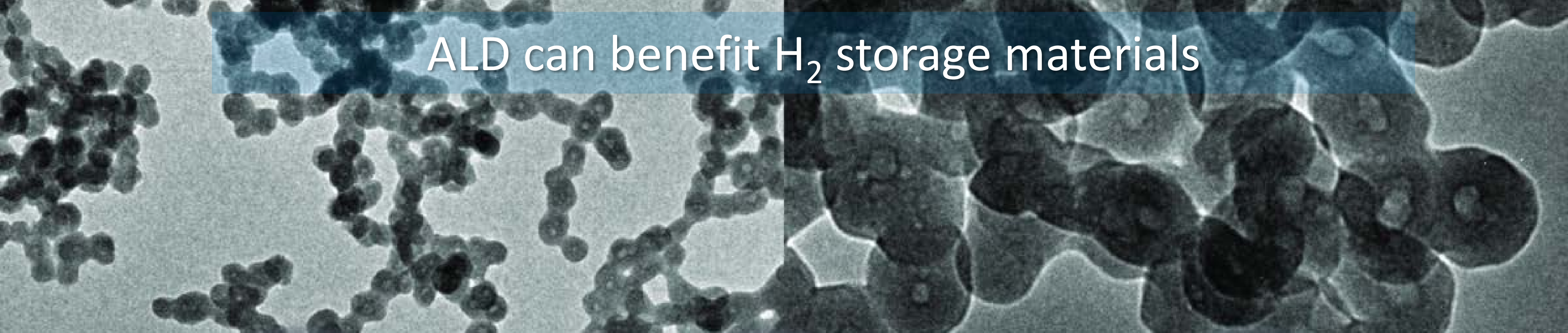
https://www.greencarcongress.com/2017/07/20170728-ahead.html

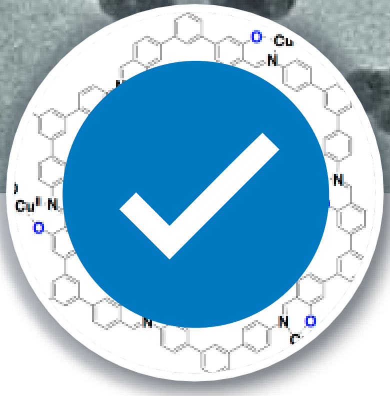
Atomic Layer Deposition of heterogenous catalysts





ALD can benefit H_2 storage materials





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Encapsulation of metal hydrides and/or infiltration of additives can be tuned using ALD

The ALD catalyst development can be leveraged for optimized de-/rehydrogenation of LOHCs

Acknowledgements

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NREL/PR-5900-81276

Hydrogen Materials Advanced Research Consortium

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