The Role of Impurities in the Complex Hydrides

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Acknowledgements

- **Department of Energy EERE**
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Xianfeng Liu, David Peaslee, Tim Mason, Dongxue Zhao, Gang Wang, Chris Carr, Waruni Jayawardana, Alyssa McFarlane, Henry Hamper, Hua Ning

SNL

Vitalie Stavila, Mark Allendorf, Lennie Klebanoff

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Objectives and Overview

I. Fundamental Limitations
   - density of hydrogen and desorption enthalpy

II. Open Questions in Complex Hydrides
   - growing consensus on reversibility mechanism in $NaAlH_4$
   - important discoveries with unresolved issues in alanates
   - **illustrate the dramatic role of impurities**
   - **provide ideas for basic research**
   - nanoscale confinement and controlling surface chemistry in borohydride and amide/imide systems

Hydrogen Density in Metal Hydrides

Compound	H/M	Å³ / H atom
lattice gas	~0.01	large
$LaNi_5H_6$	1	12
LiH	1	17
TiH_2 or VH_2	**2**	**~10**
MgH_2	2	15
$LiBH_4$	2	14
$NaAlH_4$	2	17
$Mg(BH_4)_2$	2.7	14
solid H_2	--	19 (38 per H_2)
liquid H_2	--	22.5 (45 per H_2)

- New materials are unlikely to exceed these densities

Interstitial hydrides are easily 'tunable'

- H embedding energy in homogeneous e^- gas has a minimum around $n_o=0.01/a_o^3$ [J. K. Norskov, *Phys. Rev. B*, **26**, 2875 (1982)]
- electron density determines the chemical potential
- vary the volume and chemistry of interstitial site
- alloying easy, **can adjust plateau pressure**

Complex ionic hydrides are NOT

- electrostatically dominated cohesive energy
- atomic radii important for structural stability
- alloying more difficult (example: NaCl, NaF)

DOE target 7.5 wt.% and 70g/liter

= 24 Å³ / H atom

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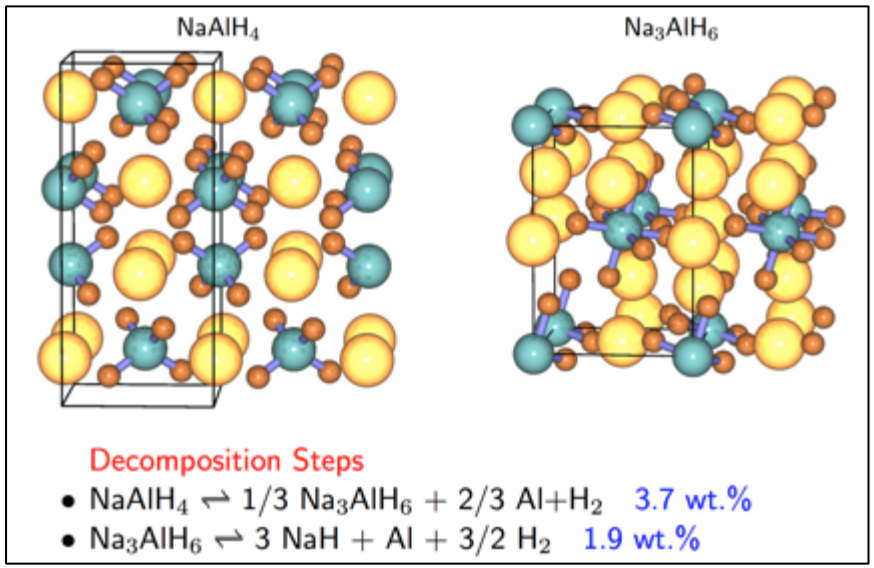
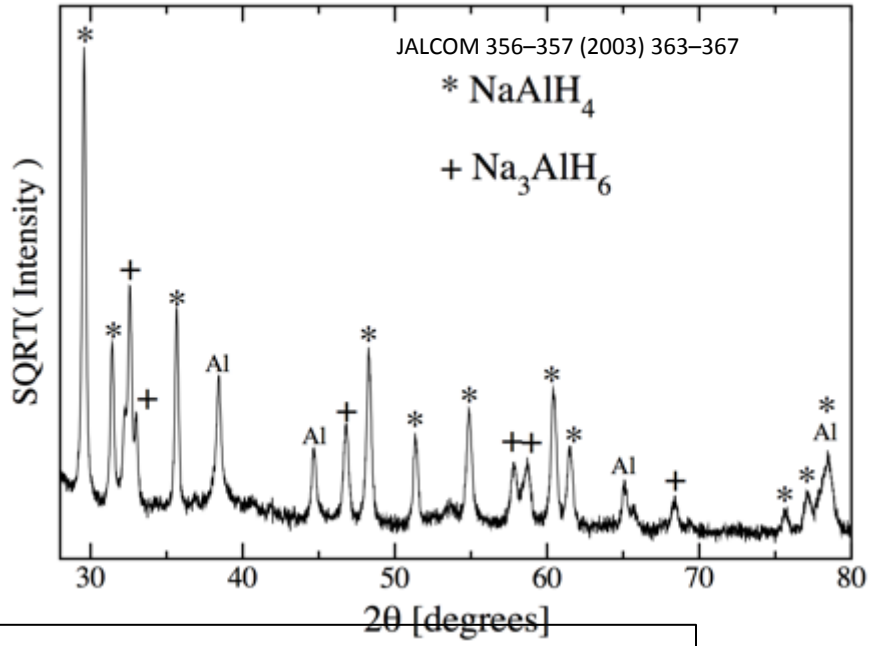
Phase Segregation On Decomposition Introduces Several Problems





- Multiple phases with complex interfaces
- Mass transport problems
- Complicated engineering considerations

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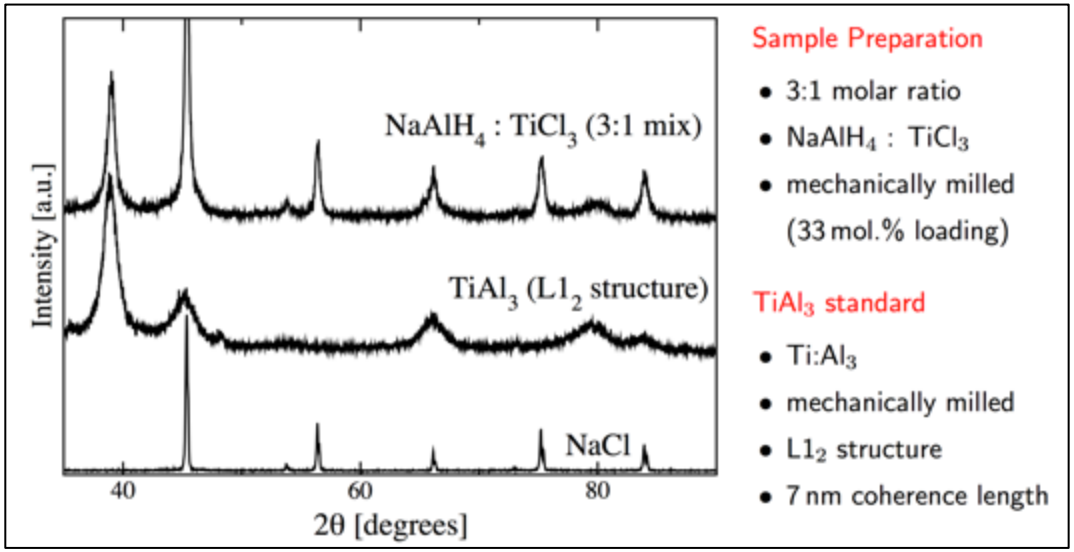
Reversibility in Ti-doped $NaAlH_4$

Titanium Dopant Goes with the Aluminum on Decomposition of $NaAlH_4$



Sample Preparation

- 3:1 molar ratio
- $NaAlH_4$: $TiCl_3$
- mechanically milled (33 mol.% loading)

$TiAl_3$ standard

- Ti:Al_3
- mechanically milled
- $L1_2$ structure
- 7 nm coherence length

Reaction Equation			ΔG_f° [kJ/mol]
3 NaH + 3 Al + $TiCl_3$	→	3 NaCl + 3 Al + 1/2 H_2+TiH_2	-484
3 NaH + 3 Al + $TiCl_3$	→	3 NaCl + $TiAl_3$ + 3/2 H_2	-535

Desorbed Sample
Al (111) reflection asymmetry due to Ti

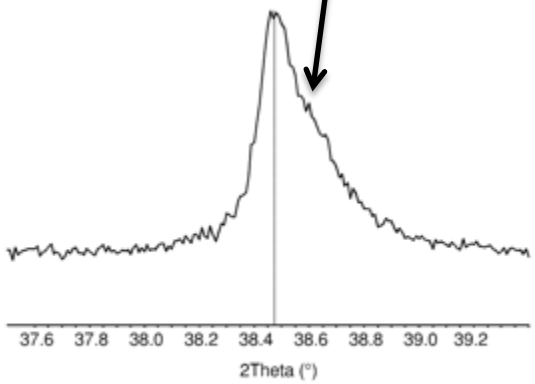


Fig. 6. Powder pattern of sample A4. Aluminum reflection marked by the bar, exhibiting a clear asymmetry at the right side of the reflection.

B. Bogdanović et al. / Journal of Alloys and Compounds 350 (2003) 246–255

Journal of Alloys and Compounds 356–357 (2003) 363–367

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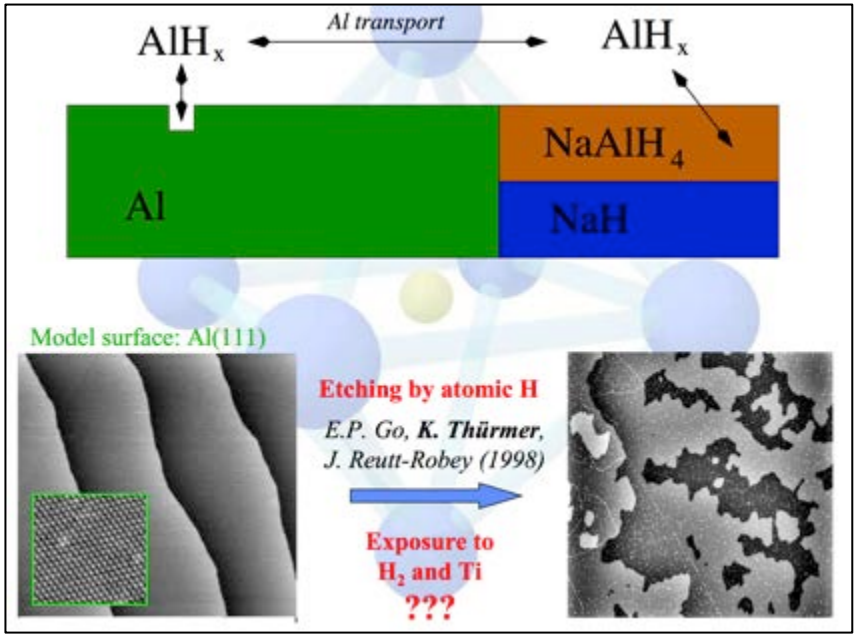
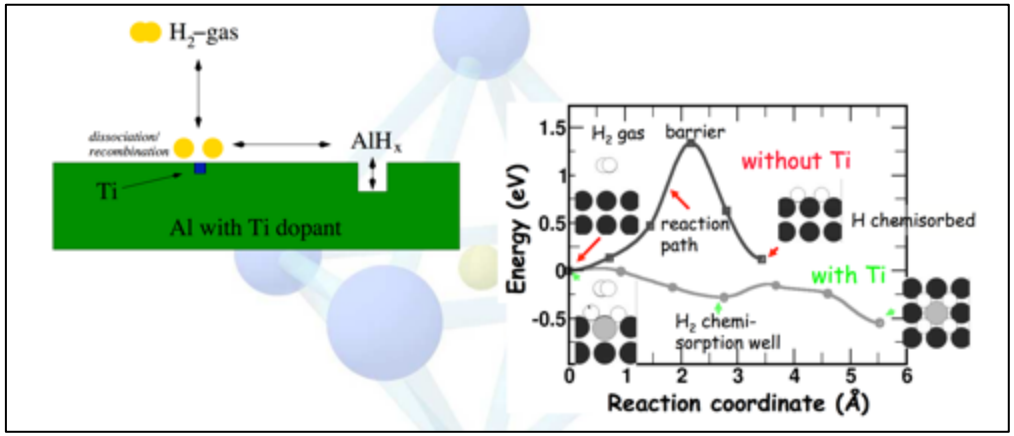
AlH_x Formation Occurs on Al (111) Surface and is Mobile



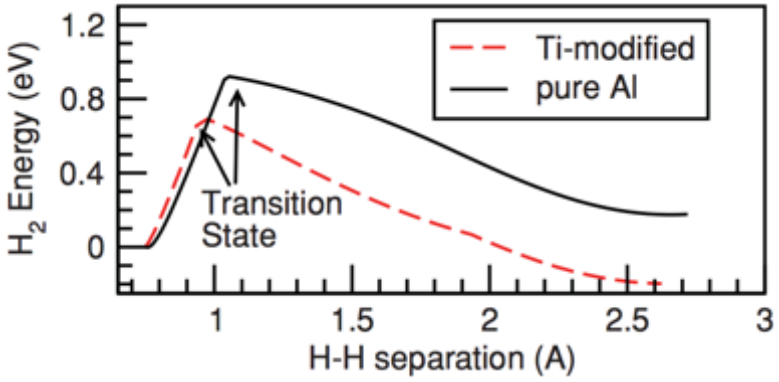


- **Requires atomic H**
- **Subsurface Ti in Al lowers barrier for H_2 bond dissociation**

PHYSICAL REVIEW B 83, 195419 (2011)

Catalytic effect of near-surface alloying on hydrogen interaction on the aluminum surface

Yan Wang,[1] Feng Zhang,[1] R. Stumpf,[2] Pei Lin,[1] and M. Y. Chou[1]
[1]*School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332-0430, USA*
[2]*Sandia National Laboratories, Albuquerque, New Mexico 87185-1415, USA*
(Received 4 November 2010; revised manuscript received 22 March 2011; published 9 May 2011)



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Mass Transport in $NaAlH_4$ Mediated via AlH_x and Na Vacancies

THE JOURNAL OF PHYSICAL CHEMISTRY C

ARTICLE

pubs.acs.org/JPCC

J. Phys. Chem. C 2011, 115, 21443–21453

Native Defect Concentrations in $NaAlH_4$ and Na_3AlH_6

Kyle Jay Michel and Vidvuds Ozoliņš*

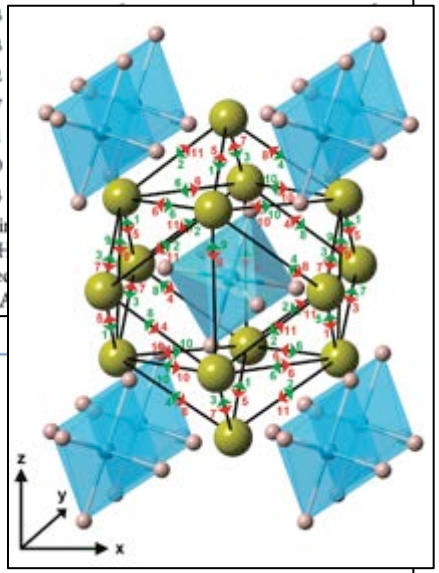
Department of Materials Science and Engineering, University of California, Los Angeles, P.O. Box 951595, Los Angeles, California 90095-1595, United States

- Free energies of formation and concentrations of native defects in $NaAlH_4$ and Na_3AlH_6
- determined at possible two-phase interfaces

Table 2. Defect Formation Energies and Concentrations in $NaAlH_4$ at $T = 400$ K, Including Vibrational and Gas-Phase H_2 Enthalpies and Entropies[a]

	$Na_3AlH_6/NaAlH_4/H_2$			$Al/NaAlH_4/H_2$		
defect	ΔH_{form}^{400K}	ΔG_{form}^{400K}	C^{400K}	ΔH_{form}^{400K}	ΔG_{form}^{400K}	C^{400K}
$[Al]^{3-}$	0.99	1.60	2.50×10^{-20}	0.70	0.58	2.12×10^{-7}
$[AlH]^{2-}$	1.11	1.41	6.11×10^{-18}	1.06	0.62	6.67×10^{-8}
$[AlH_2]^{-}$	0.96	1.01	7.55×10^{-13}	1.13	0.44	1.06×10^{-5}
$[AlH_3]$	0.87	0.71	4.74×10^{-9}	1.27	0.37	8.56×10^{-5}
$[AlH_4]^{+}$	0.82	0.43				
$[Na]^{-}$	0.16	0.43				
$[NaH]$	1.38	1.42				
$[H]^{+}$	1.26	1.07				
$[H]^{-}$	1.01	0.61				
$^{i}H^{+}$	1.36	1.70				
$^{i}H^{-}$	0.44	0.64				

[a] Values are given at the i
well as Al, $NaAlH_4$, and H
given in units of eV/defe
of defects per f.u. of Na



Kinetic Monte Carlo Results and transition state theory

- **$NaAlH_4$: AlH_x vacancies**
- **Na_3AlH_6: Na vacancies**

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YSICAL CHEMISTRY C

J. Phys. Chem. C 2011, 115, 21465–21472

Vacancy Diffusion in $NaAlH_4$ and Na_3AlH_6

Kyle Jay Michel and Vidvuds Ozoliņš*

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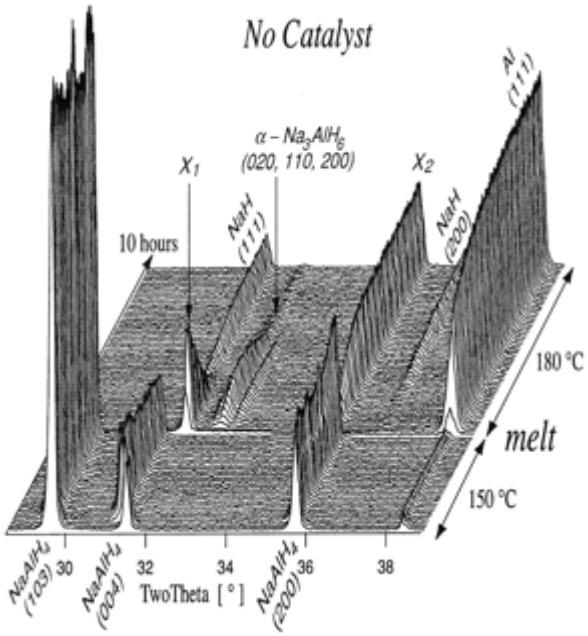
Explanation for $NaAlH_4$ Reversibility is Incomplete

- Intermediates observed in XRD
  - X1 and X2 phases
- **X1, X2 very sensitive to overpressure**
- 0.1 < P < 1 or 2 bar
- These phases have never been conclusively identified
- Experiments near operating conditions are important



K.J. Gross et al. / Journal of Alloys and Compounds 297 (2000) 270–281

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Discovery of Phase "S105" - Fast Al Motion In $NaAlH_4$

THE JOURNAL OF PHYSICAL CHEMISTRY Letters

J. Phys. Chem. Lett. 2010, 1, 2412–2416

pubs.acs.org/JPCL

Discovery of A New Al Species in Hydrogen Reactions of $NaAlH_4$

Timothy M. Ivancic,*,† Son-Jong Hwang,† Robert C. Bowman, Jr.,§ Derek S. Birkmire,‖ Craig M. Jensen,‖ Terrence J. Udovic,⊥ and Mark S. Conradi*,†

S105 first observed when heating $NaAlH_4$ *under H_2 overpressure near the melting temperature*

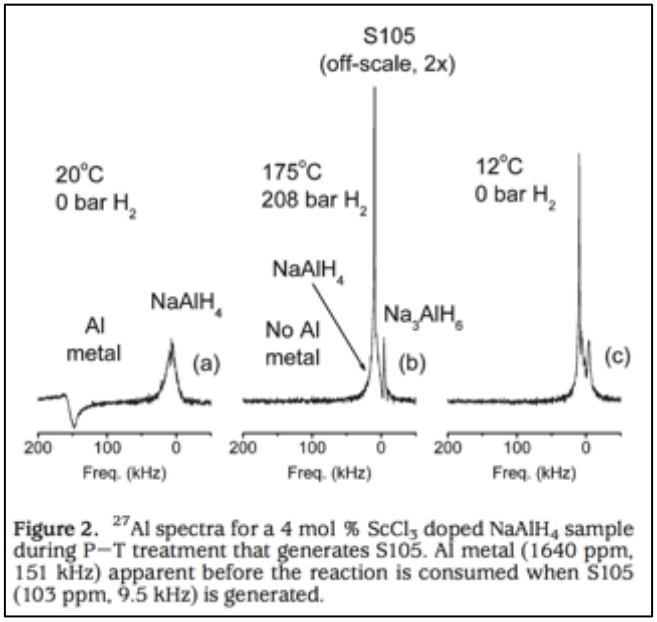

Figure 2. ^{27}Al spectra for a 4 mol % $ScCl_3$ doped $NaAlH_4$ sample during P–T treatment that generates S105. Al metal (1640 ppm, 151 kHz) apparent before the reaction is consumed when S105 (103 ppm, 9.5 kHz) is generated.

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Article

pubs.acs.org/JPCC

J. Phys. Chem. C 2013, 117, 8105−8113

Mobile Species in $NaAlH_4$

Eric G. Sorte,*,† Robert C. Bowman, Jr.,‡ Eric H. Majzoub,§ Margriet H. W. Verkuijlen,‖ Terrence J. Udovic,⊥ and Mark S. Conradi*,†

S105 is due to the presence of oxygen impurities. H_2O or NaOH exposure.

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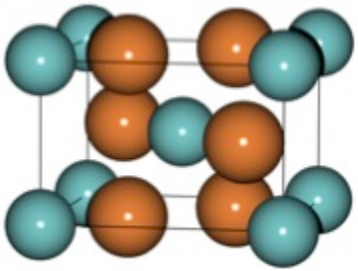
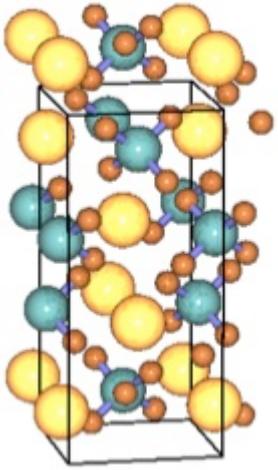
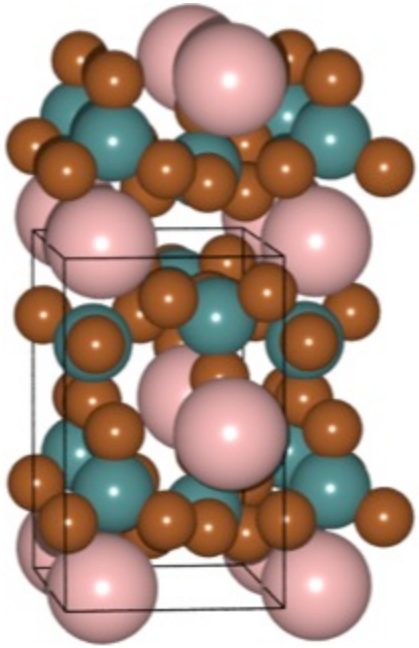
Monte Carlo Method (PEGS) Generally Obtains Observed Crystal Structures



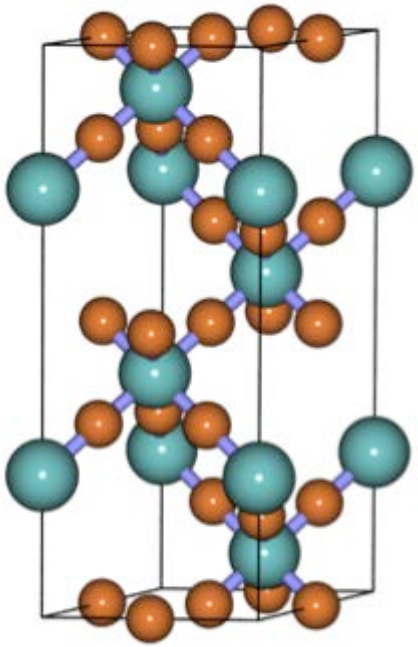
MgH_2



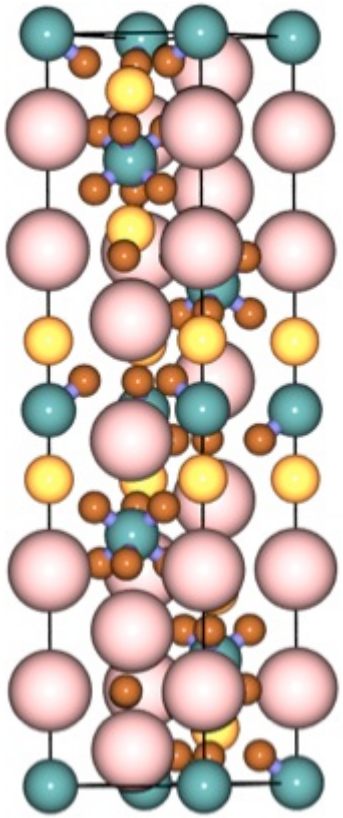
$NaAlH_4$



$Ca(BH_4)_2$



AlH_3



K_2LiAlH_6

- PEGS method -
Majzoub & Ozolins, Phys. Rev. B, 77, 104115, (2008)

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Search for Intermediates in $NaAlH_4$

PRL 103, 185901 (2009) PHYSICAL REVIEW LETTERS week ending 30 OCTOBER 2009

Dynamics and Thermodynamics of a Novel Phase of $NaAlH_4$

Brandon C. Wood* and Nicola Marzari
Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
(Received 17 January 2009; published 28 October 2009)

Article

Ultrafast Bulk Diffusion of AlHx in High-Entropy Dehydrogenation Intermediates of NaAlH4

Feng Zhang, Brandon C. Wood, Yan Wang, Cai-Zhuang Wang, Kai-Ming Ho, and Mei-Yin Chou
J. Phys. Chem. C, **Just Accepted Manuscript** • DOI: 10.1021/jp504550m • Publication Date (Web): 21 Jul 2014
Downloaded from http://pubs.acs.org on July 24, 2014

First-Principles Study of Structural Prototypes for $NaAlH_4$: Elevated Pressure Polymorph in Symmetry *Fmm*2 Leads to a Single-Step Decomposition Pathway

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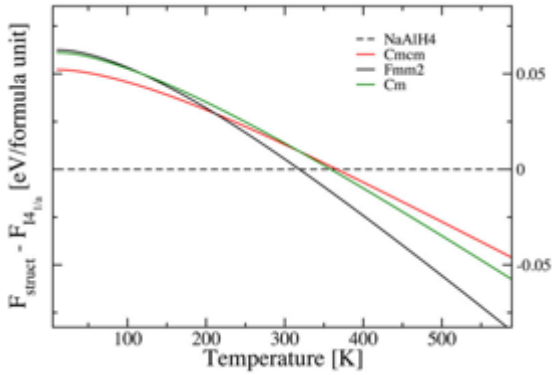
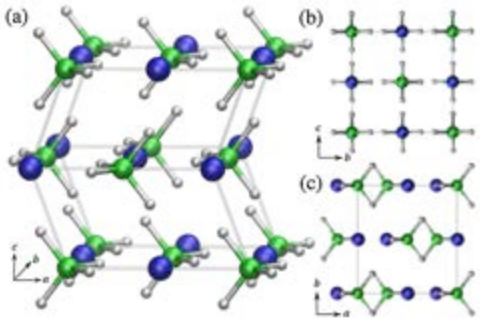
E. Hazrati and G. A. de Wijs
Radboud University Nijmegen, Institute for Molecules and Materials, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands

- gamma-$NaAlH_4$ stable above 320K
- Charged AlH_4 and neutral AlH_3 vacancies: computed barriers for diffusion are less than 0.1 eV

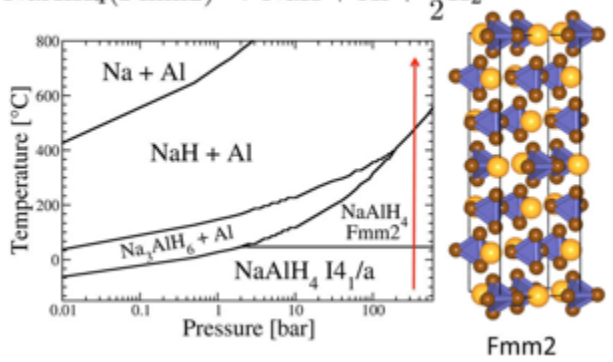




Cmcm and Fmm2

- Larger volume available to AlH_4 units
- **XRD not consistent with X1, X2 phases**

$$NaAlH_4(Fmm2) \rightarrow NaH + Al + \frac{3}{2}H_2$$



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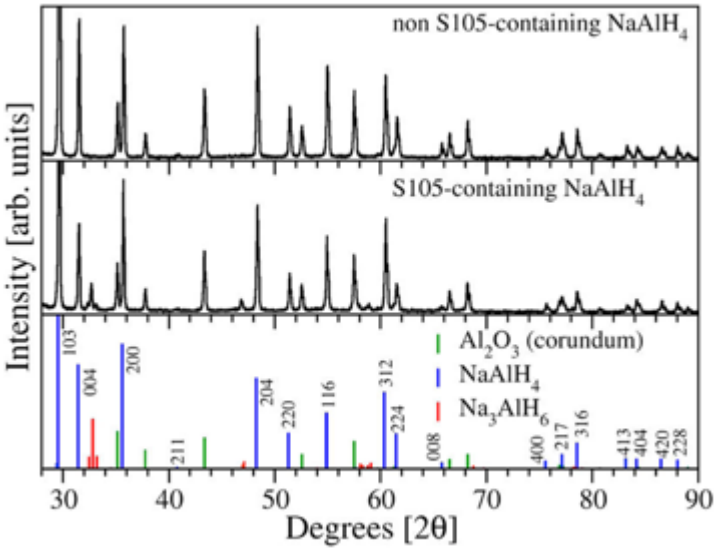
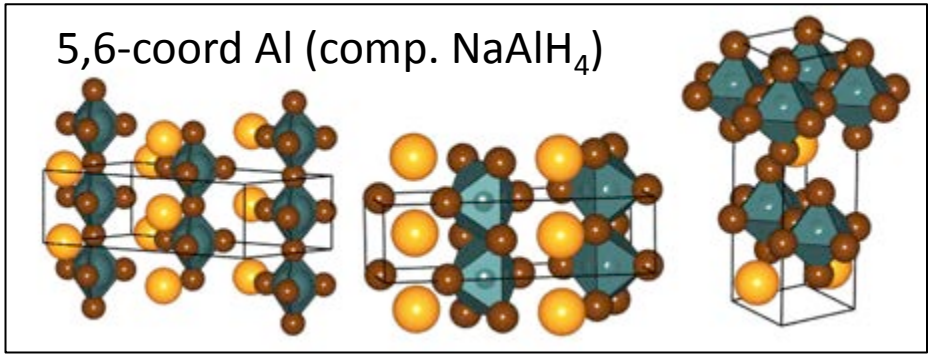
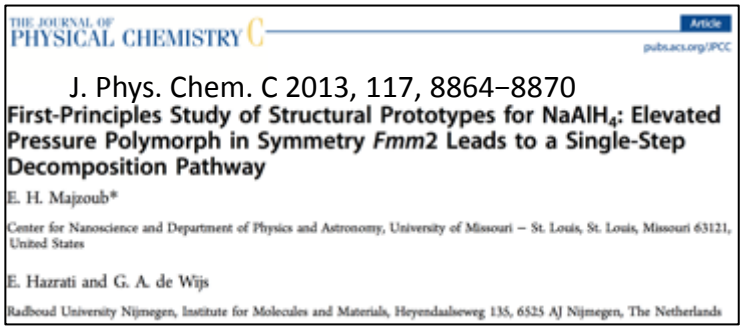
S105 Must Contain 4-coordinate Al



- XRD shows structure is still $I4_1/a$
- Structure factor changes only

J. Phys. Chem. C 2013, 117, 8105−8113





THE JOURNAL OF PHYSICAL CHEMISTRY C — Article — pubs.acs.org/JPCC

J. Phys. Chem. C 2013, 117, 8864−8870

First-Principles Study of Structural Prototypes for $NaAlH_4$: Elevated Pressure Polymorph in Symmetry *Fmm*2 Leads to a Single-Step Decomposition Pathway

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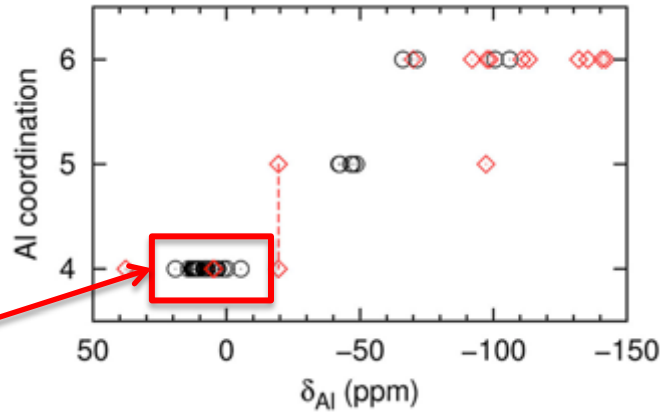

S105 must contain 4-coordinate Al

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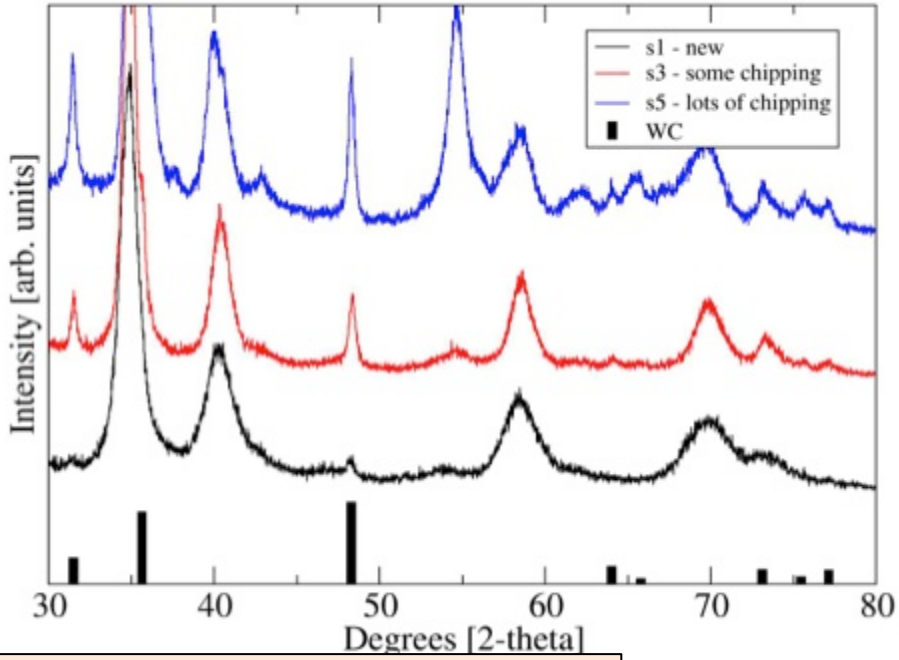
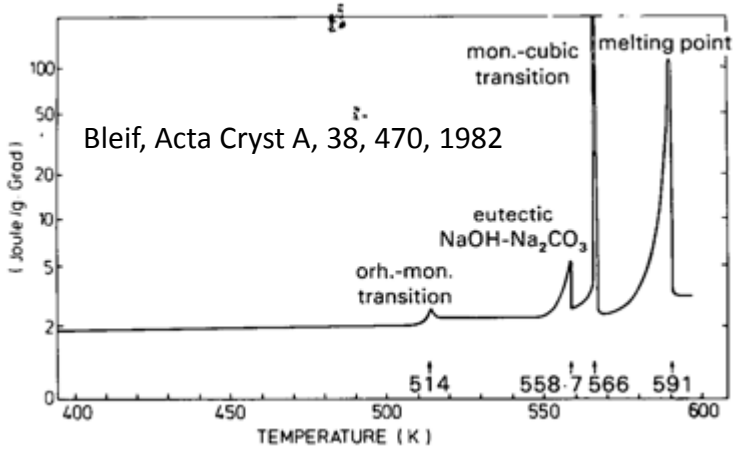
Oxygen Contamination? Many Hydride Preparation Techniques Introduce Impurities



- Mill type: shaker mills, planetary mills
- Ball construction: steel, WC, ceramic
- Mill wall construction: steel, WC, ceramic, etc.
- Mill seal allows for leaks – contamination from atmosphere

Effect of Oxygen in Na-Al-H?

Oxygen In Alkali Metal Hydrides



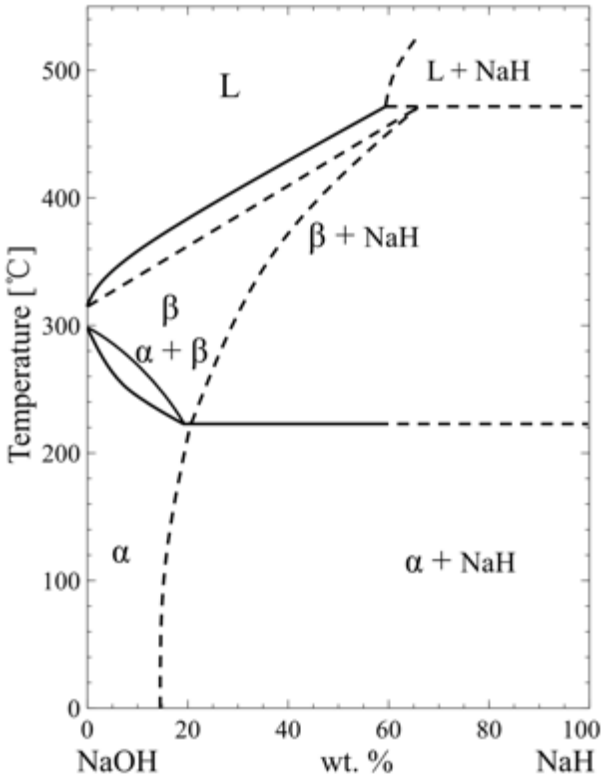
Bleif, Acta Cryst A, 38, 470, 1982

Phases of NaOH:

- low temp phase: Bmmb (orth)
- alpha-phase: $P2_1/m$ (mono)
- beta phase: Fm3m

Q: What is the temperature dependence of the formation of solid solution phase NaH/NaOH?

NaH-NaOH Pseudo-binary



Mikheeva, et al., Russian J. Inorg. Chem. **7**, 1251 (1962).

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THE JOURNAL OF PHYSICAL CHEMISTRY C

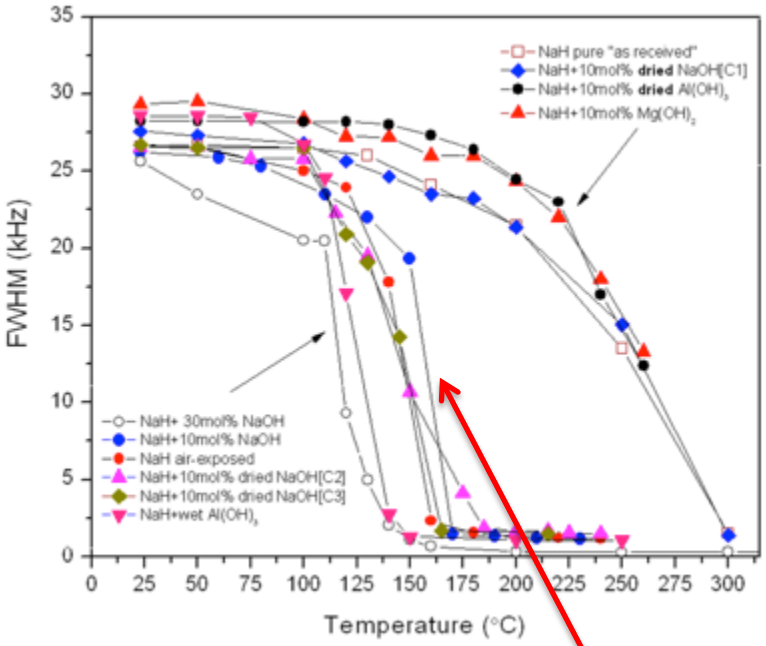
Article

pubs.acs.org/JPCC

Effects of NaOH in Solid NaH: Solution/Segregation Phase Transition and Diffusion Acceleration

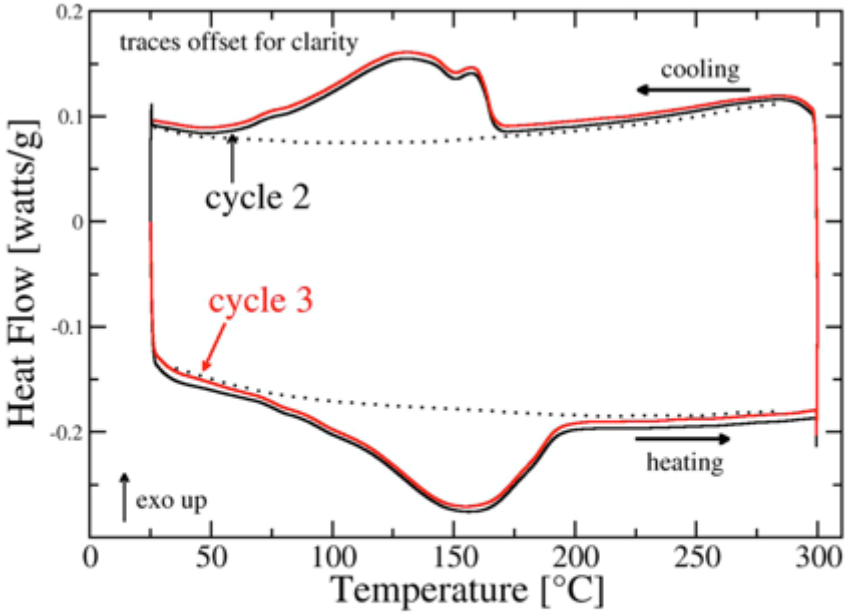
Eric G. Sorte,*,† E. H. Majzoub,‡ Tim Ellis-Caleo,† Blake A. Hammann,§ Gang Wang,‡ Dongxue Zhao,‡ Robert C. Bowman, Jr.,‖ and Mark S. Conradi*,†,§

^{1}H NMR linewidths



J. Phys. Chem. C 2013, 117, 23575−23581

rapid hydrogen motion



Differential scanning calorimetry indicates excellent reversibility of NaH/NaOH solid solution formation

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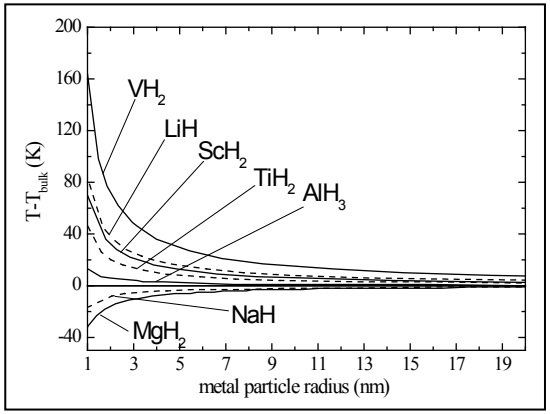
Comments

- Oxygen (OH^-) content in NaH, $NaAlH_4$ will vary strongly with temperature and may have a significant impact on kinetics
- Computationally expensive to predict intermediate phases and their stability from first principles – depend sensitively on T and P (harmonic vs. quasi-harmonic, etc.)

- Test materials closer to operating conditions
- Experiments with very high purity starting materials to identify contaminant issues
- Q: Could impurity doping improve the kinetics in other interesting complex hydride systems?

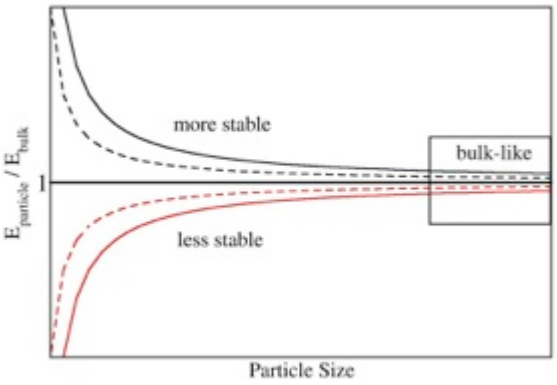
Interfaces and Surfaces

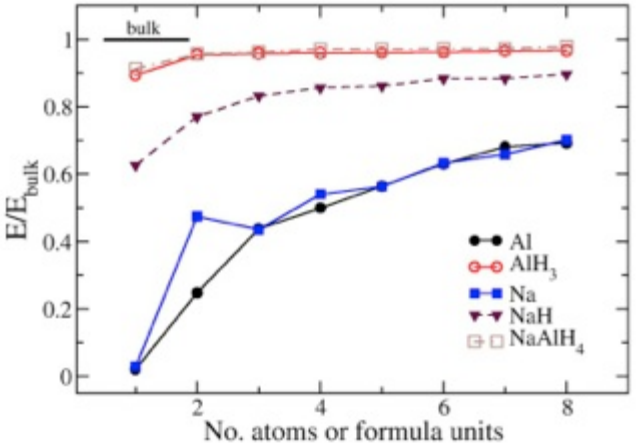
Free Nanoparticle Stability Is a Function of Size



Predicted hydride destablization as a function of particle size, using the Wulff construction

Kim, *et al.*, *Nanotechnology*, **20**, 204001 (2009)





Free Nanoparticles in the Na-Al-H System

Majzoub, *et al.*, *JPCC*, **115**, 2636 (2011)

Q: How does nanoconfinement alter thermodynamics?

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Benefits of Nanoconfinement

- Improves kinetics and reversibility
- Can impact thermodynamics
- Safety
- Surface functionalization allows for selectivity of reactions
- Frameworks can be active, e.g. Li intercalation in carbon
- Difficult to handle computationally -- work is needed here

Nano-confined $LiBH_4$ is Reversible

J. Phys. Chem. C **2008,** *112,* 5651−5657

Enhanced Hydrogen Storage Kinetics of $LiBH_4$ in Nanoporous Carbon Scaffolds

Adam F. Gross, John J. Vajo,* Sky L. Van Atta, and Gregory L. Olson
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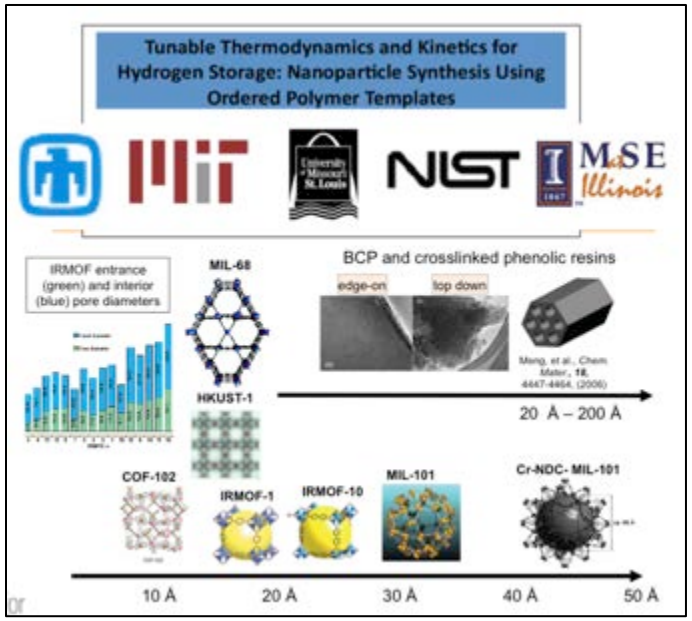
Carbon Aerogels



U.S. DEPARTMENT OF ENERGY

Ordered Nanoporous Materials

- J. Phys. Chem. C., 118, 8843-8851, (2014)
- J. Phys. Chem. C., 118, 8852-8858, (2014)
- J. Materials Chemistry A, 1, 9935-9941 (2013)
- J. Mater. Chem. A, 1, 3926-3931 (2013)
- ACS Nano, 6, 9807-9817 (2012)
- Phys. Chem. Chem. Phys., 14, 8160-8169 (2012)
- Phys. Chem. Chem. Phys., 14, 6611-6616 (2012)
- J. Phys. Chem. C, 115, 2636-2643 (2011)
- Chem. Mater.,23, 1331-1336 (2011)
- J. Phys. Chem. C, 114, 14036-14041(2010)

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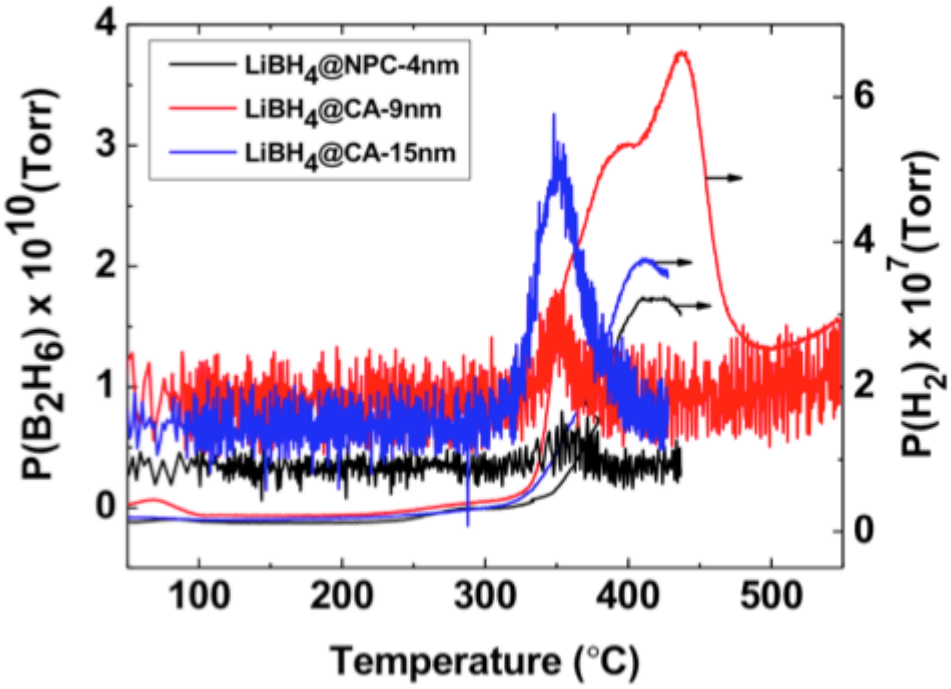
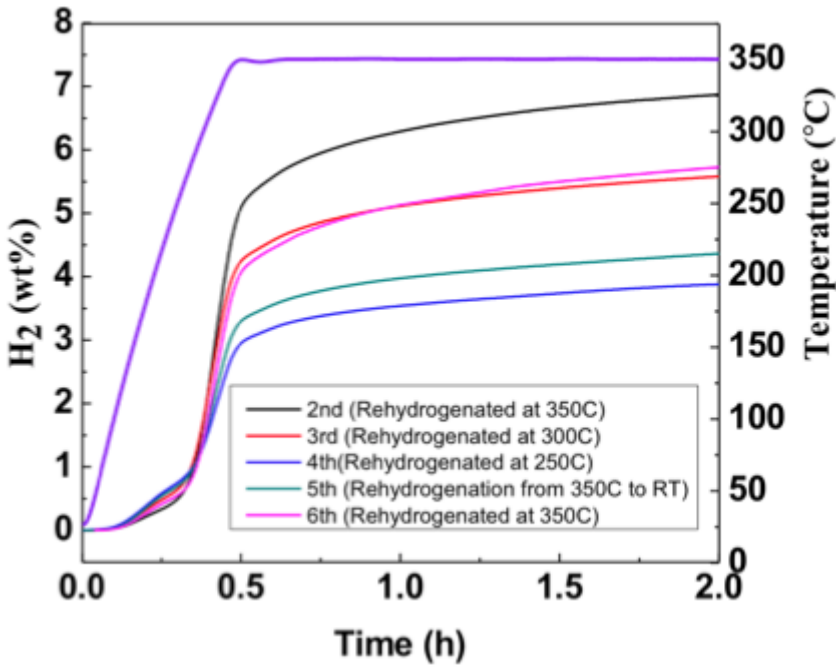
Nanoconfined $LiBH_4$ is Reversible and Reaction Pathway is Changed





Controlled Reaction Pathway: Diborane Release

Demonstrated Low Temperature Reversibility

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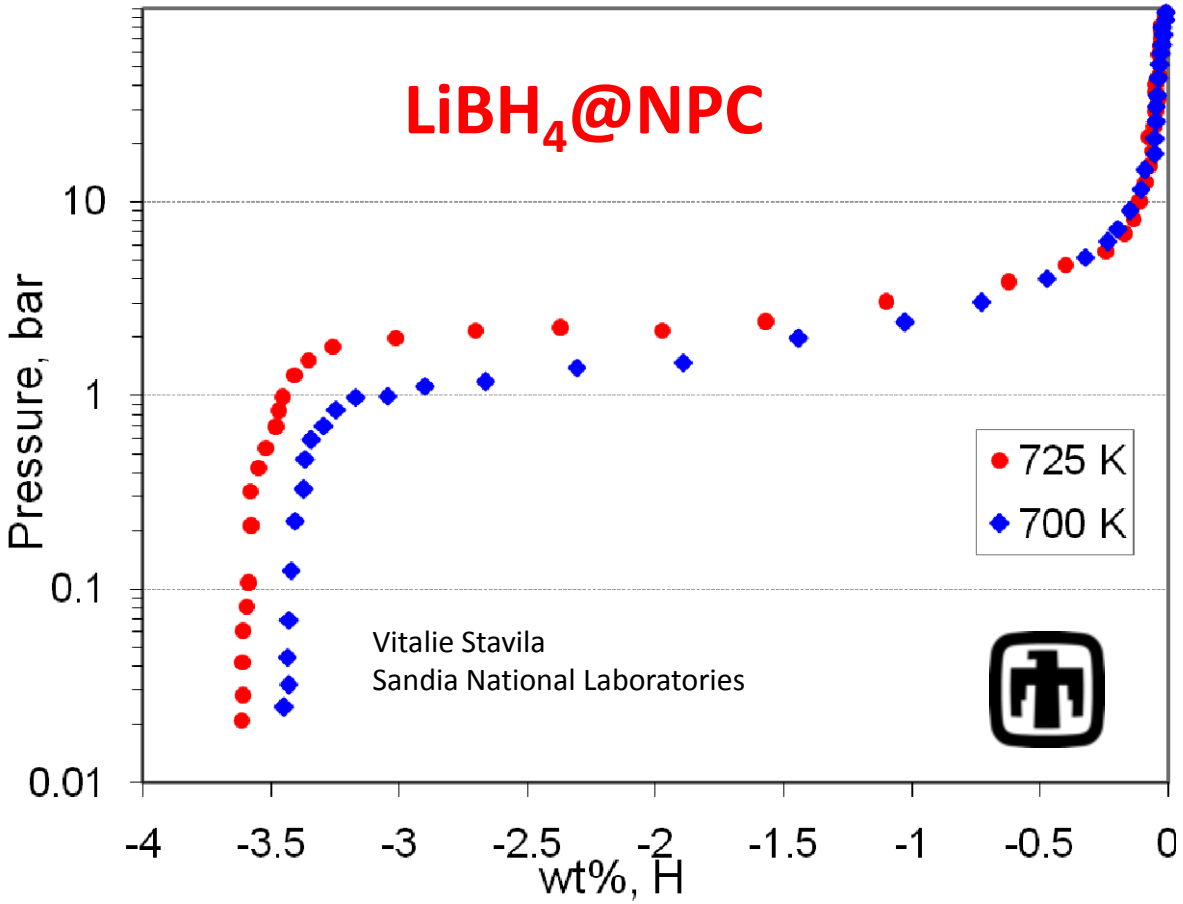
PCT of $LiBH_4$@NPC Indicate No Change From Bulk Thermodynamics



- 4nm NPC
- 20 wt.% LiBH4
- Flat plateau
- Enthalpy: 75 kJ/mol H_2

Note: New sample each cycle

Vitalie Stavila, Sandia

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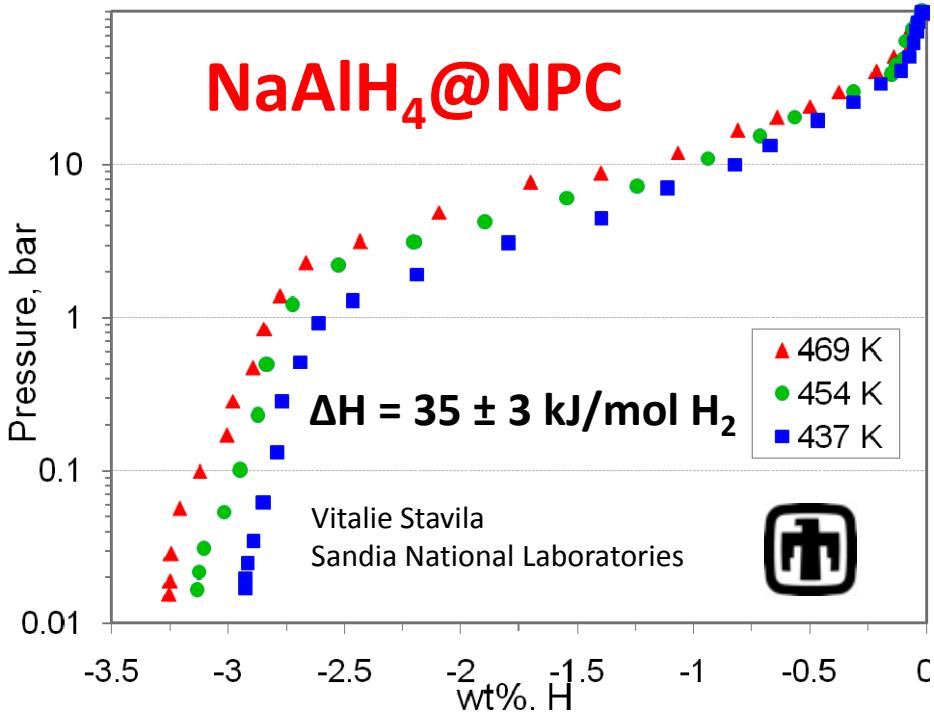
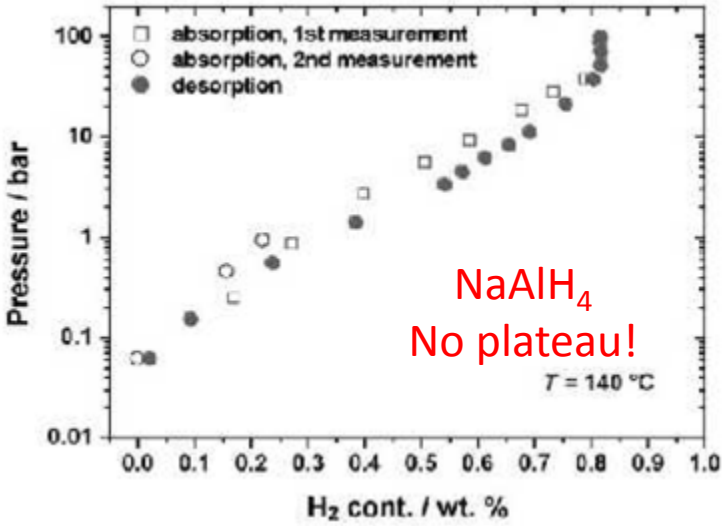
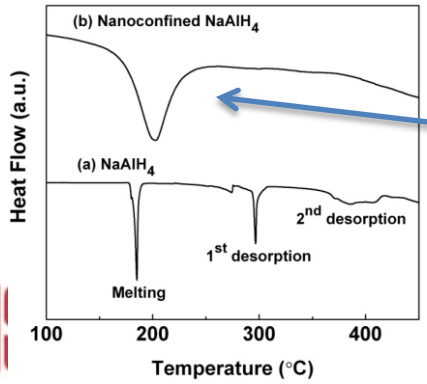
PCT of $NaAlH_4$@NPC Indicate A Single Step Reaction And Altered Thermodynamics





Lonstron, et al., Chem Phys Chem, **11**, 789, 2010



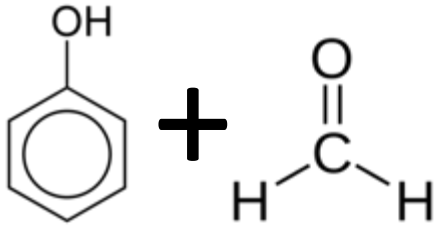
DSC indicates single step for $NaAlH_4$@NPC

Lohstroh *et al.*
- Activated carbon fiber
- 0.5 – 4 nm pore size
- Melt-infiltrated
- 1800 m^2/g

What can we explain computationally?

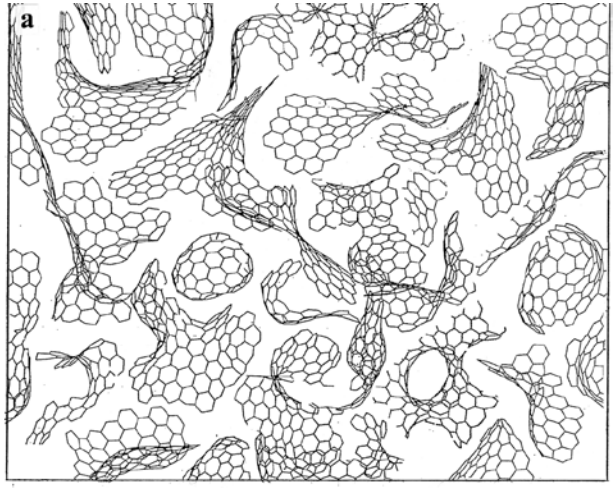
- Wetting is observed for molten $LiBH_4$ (Gross, et al., J. Phys. Chem. C 2008, 112, 5651-5657)
- Can explain the wetting computationally?

High- and Low-temperature Carbonized Phenolic Resins Show Different Character and Defect Density



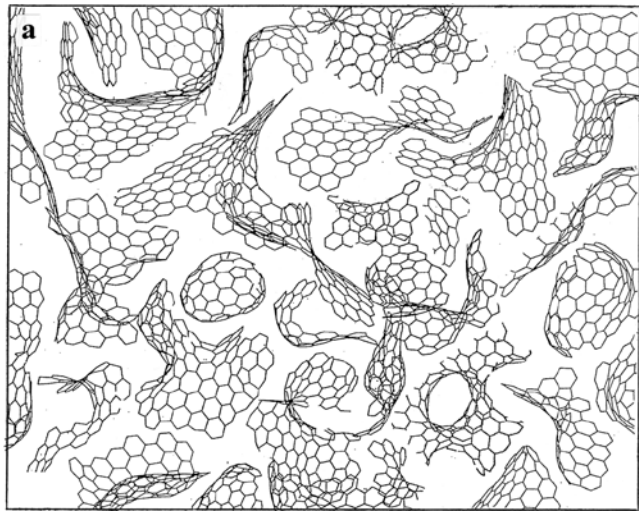
+ = Bakelite

Baekland, 1907



~ 1000°C

~3000°C

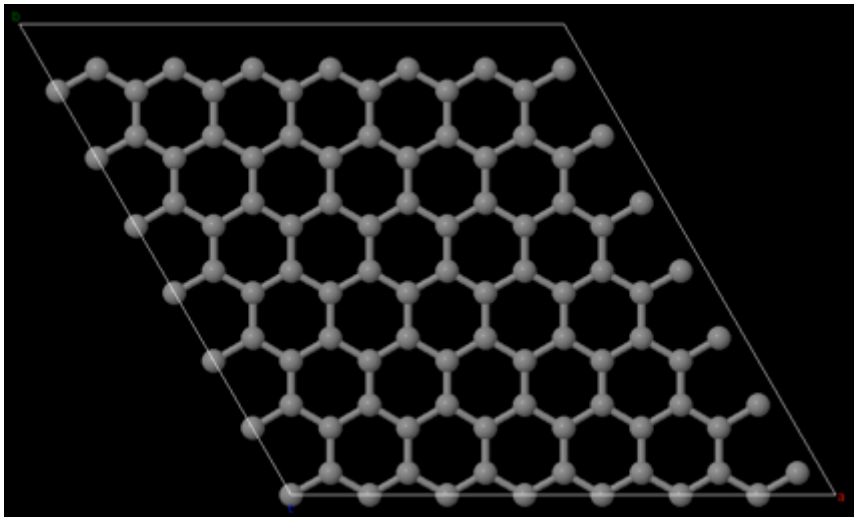


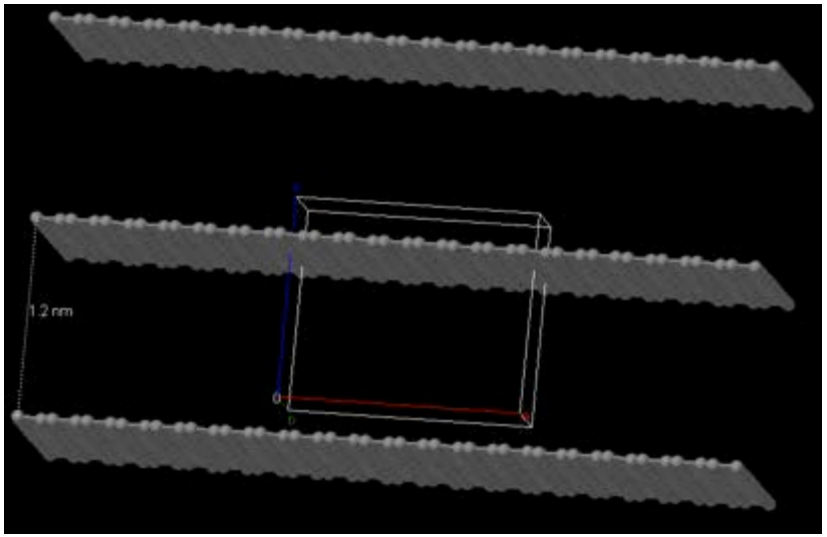
More dangling bonds

More sp2 character

Harris, P.J.F., Philosophical Magazine, **2004**, 84, 3159–3167

Model the Carbon Environment Using a Sheet of Graphene





- 7 X 7 super cell of graphene with 17 Angstrom vacuum layer
- Crude but no tractable amorphous structure models

J. Phys. Chem. C 2014, 118, 8852−8858

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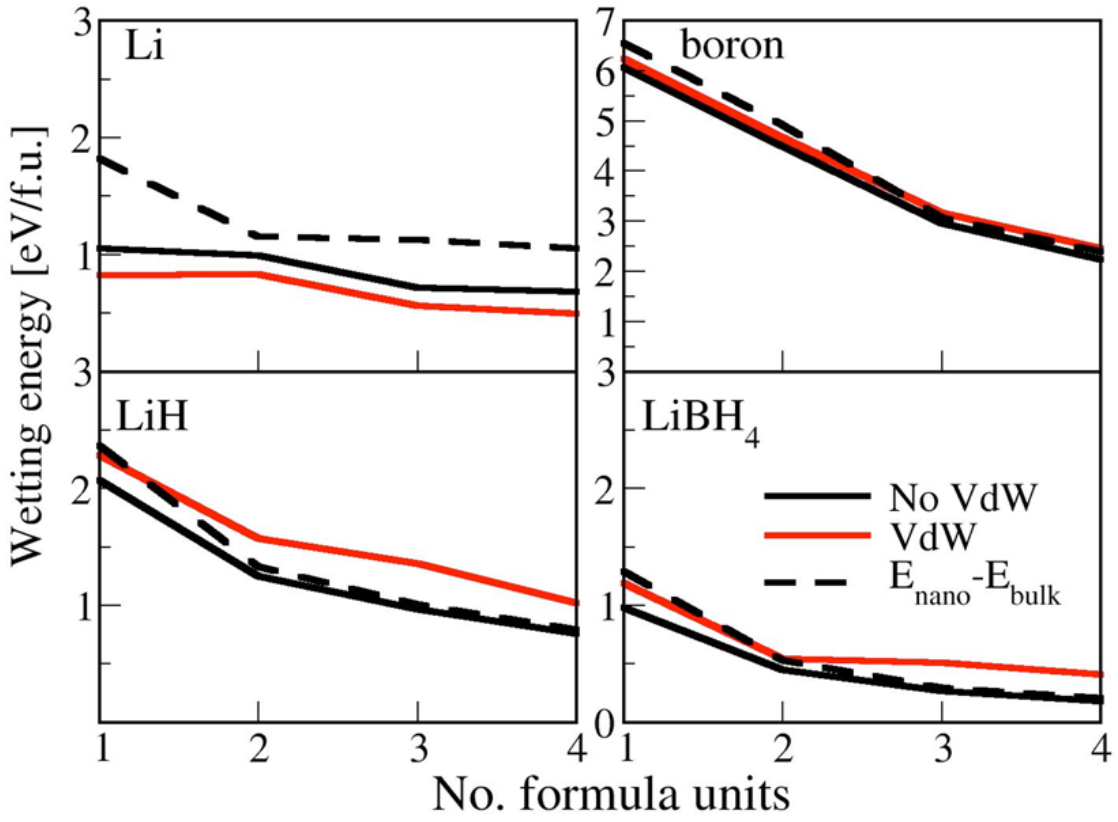
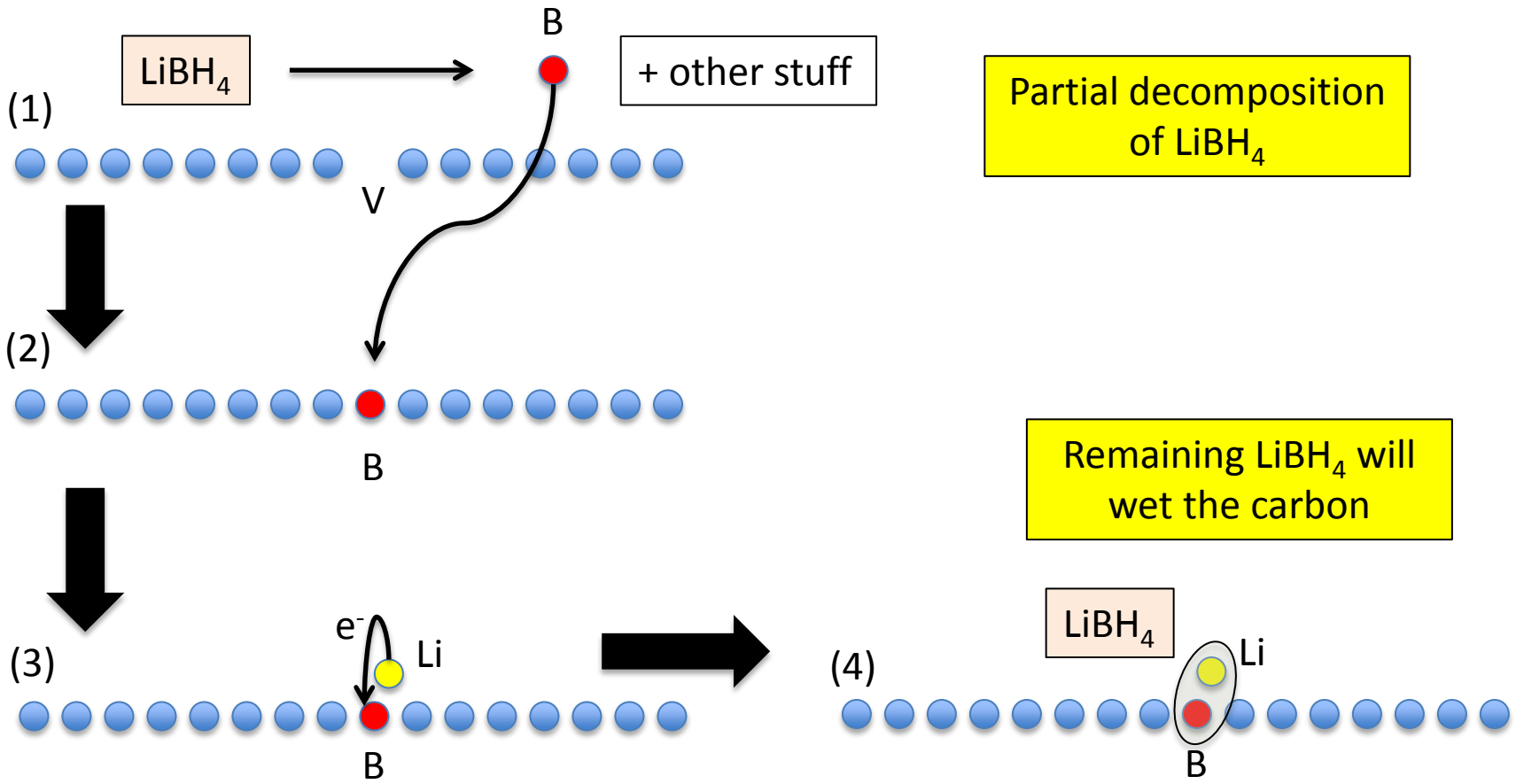
No Wetting for $LiBH_4$ or Other Likely Decomposition Products on Graphene Sheet



- contradicts experimental observation of wetting
- Note: *Free*-nanoparticle reference energy will show wetting

Four-step Process Results in $LiBH_4$ Wetting of Carbon



Partial decomposition of $LiBH_4$

Remaining $LiBH_4$ will wet the carbon

LiH does not wet this surface!

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Experimental Confirmation via TEM

THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

pubs.acs.org/JPCC

Characterization of the Dehydrogenation Process of $LiBH_4$ Confined in Nanoporous Carbon

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[‡]College of Materials Science and Optoelectronic Technology, University of Chinese Academy of Sciences, Beijing, 10049, P. R. China

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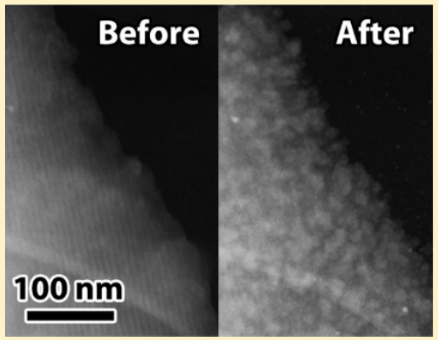
Supporting Information

ABSTRACT: Annealing in the transmission electron microscope allows direct comparison of the same nanoporous carbon scaffold particles following dehydrogenation of the confined $LiBH_4$. At a nominal temperature of 200 °C, a granular crust of cubic and cuboidal LiH nanocrystals ~8−15 nm wide grew on the outer surface of the scaffold. Furthermore, these crystals migrated on the carbon support film away from the scaffold. Ejection of material from the scaffold also occurred upon dehydrogenation in a differential scanning calorimeter. The form of the ejected material was different, being bristles instead of cubes or cuboids. This ejection of LiH and thus preferential segregation of lithium from boron is proposed to explain the observed continual decrease in hydrogen storage capacity with the number of cycles.



***in situ* observation of LiH ejection from the material**

Stephen House, Ian Robertson

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N-doped Carbons Through Melt-infiltration of $Li_4BN_3H_{10}$

Journal of Materials Chemistry A 2013, **1**, 3926 RSC Publishing

PAPER

Tailoring the hydrogen storage properties of $Li_4BN_3H_{10}$ by confinement into highly ordered nanoporous carbon†

Cite this: *J. Mater. Chem. A*, 2013, **1**, 3926

Xiangfeng Liu,*[ab] David Peaslee[a] and E. H. Majzoub*[a]

$$LiBH_4 + 3\ LiNH_2 = Li_4BN_3H_{10}$$

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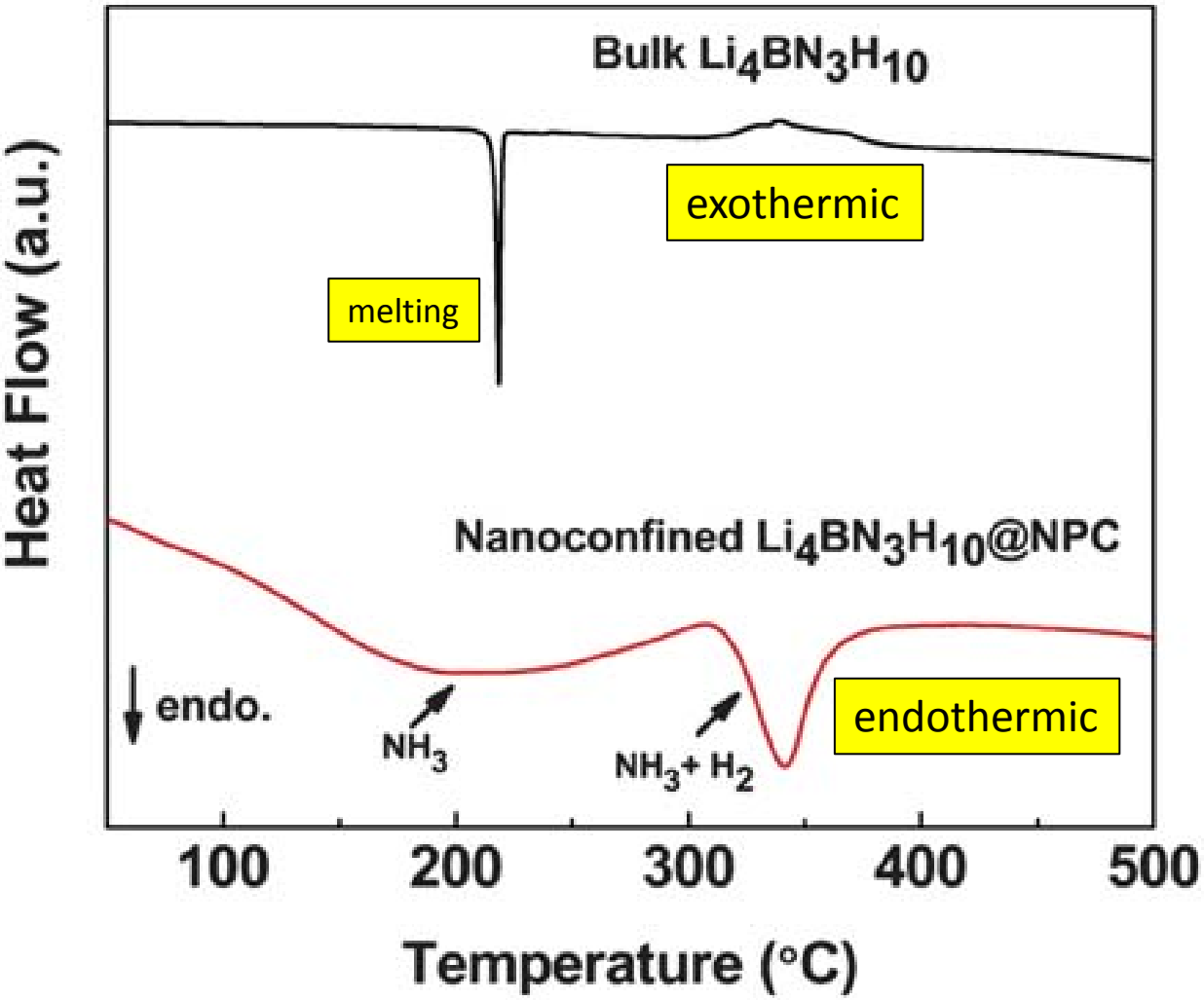
Nanoconfinement of $Li_4BN_3H_{10}$ Changes Enthalpy from Exothermic to Endothermic



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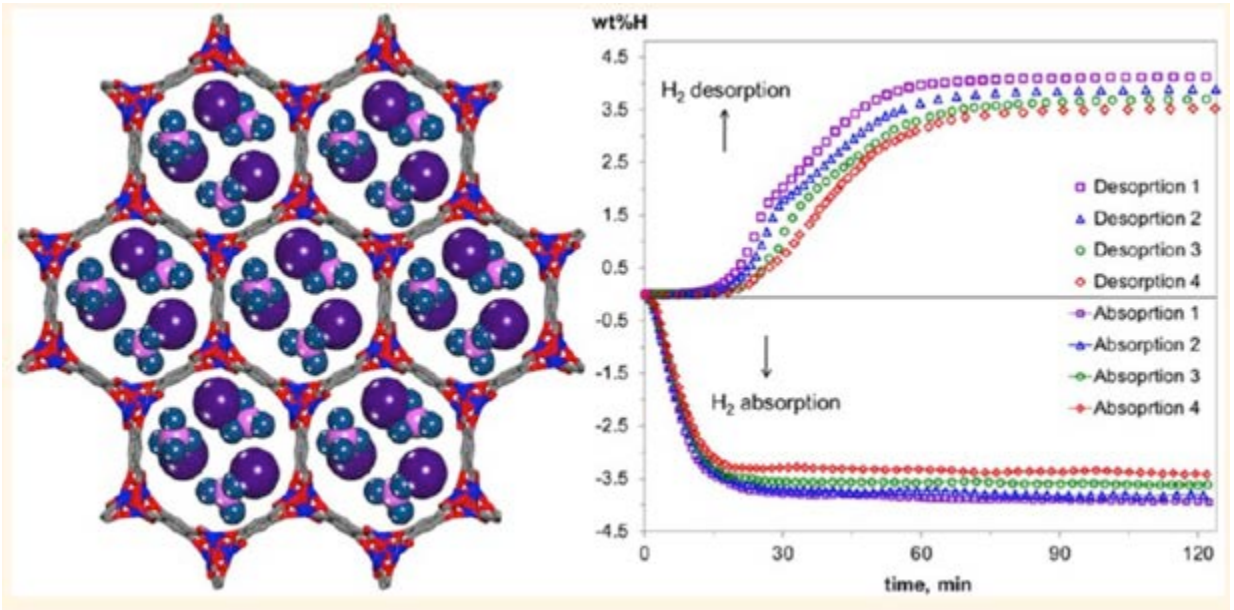
Infiltration in MOFs Also Show Dramatic Effects

ARTICLE

Reversible Hydrogen Storage by $NaAlH_4$ Confined within a Titanium-Functionalized MOF-74(Mg) Nanoreactor

ACS Nano, 6, 9807, 2012

Vitalie Stavila,[†,*] Raghunandan K. Bhakta,[†] Todd M. Alam,[‡] Eric H. Majzoub,[§] and Mark D. Allendorf[†,*]



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Conclusions

- Nanoconfinement alters the properties we are interested in controlling
- Limited work to date on functionalization of carbons
- Limited work to date on the vast array of MOFs available
- Computational work needed to address catalysis and interfaces

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- **Department of Energy EERE**
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UMSL

Xianfeng Liu, David Peaslee, Tim Mason, Dongxue Zhao, Gang Wang, Chris Carr, Waruni Jayawardana, Alyssa McFarlane, Henry Hamper, Hua Ning

SNL

Vitalie Stavila, Mark Allendorf

END