Potential of High-Throughput Experimentation with Ammonia Borane Solid Hydrogen Storage Materials

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Energy Efficiency and Renewable Energy

(Chemical) Hydrogen Storage

at PNNL

DOE EERE Chemical Hydrogen Center

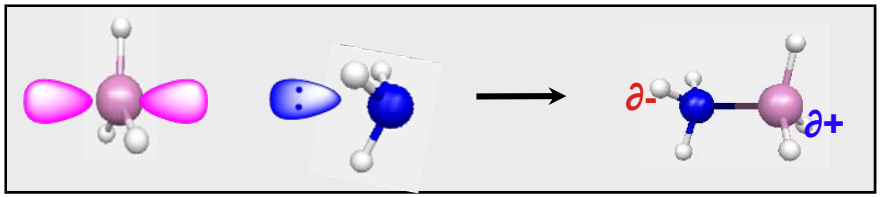
- Controlling release of hydrogen from NH_3BH_3
  - Regeneration of NH_3BH_3
  - Engineering, experiment and theory
  - Materials Discovery

DOE BES Hydrogen Fuel Initiative

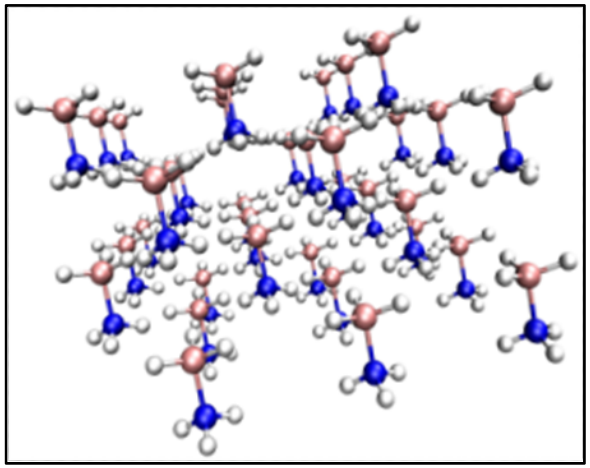
- Structure and dynamics (Neutron and NMR)
  - Experimental and computational studies of di-hydrogen bonding interactions (H-/H+)
- Catalysis (XAFS and NMR)
  - In-situ spectroscopy and mechanistic investigations

(amine boranes; T = 5 – 500K)

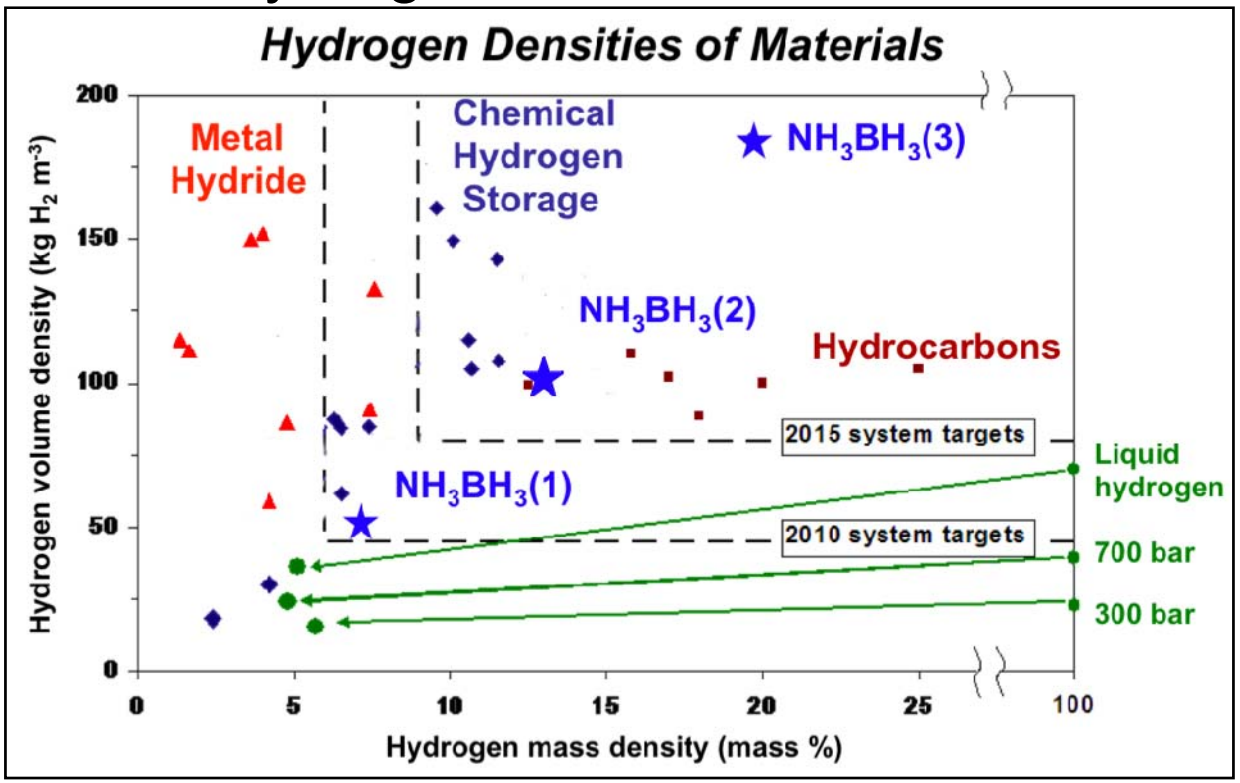
Ammonia Borane for Hydrogen Storage



- Hydridic B-H and protonic N-H hydrogens impart unique ability to store and release hydrogen



Molecular crystal held together by network of dihydrogen bonds density = ~0.75 g/cm³

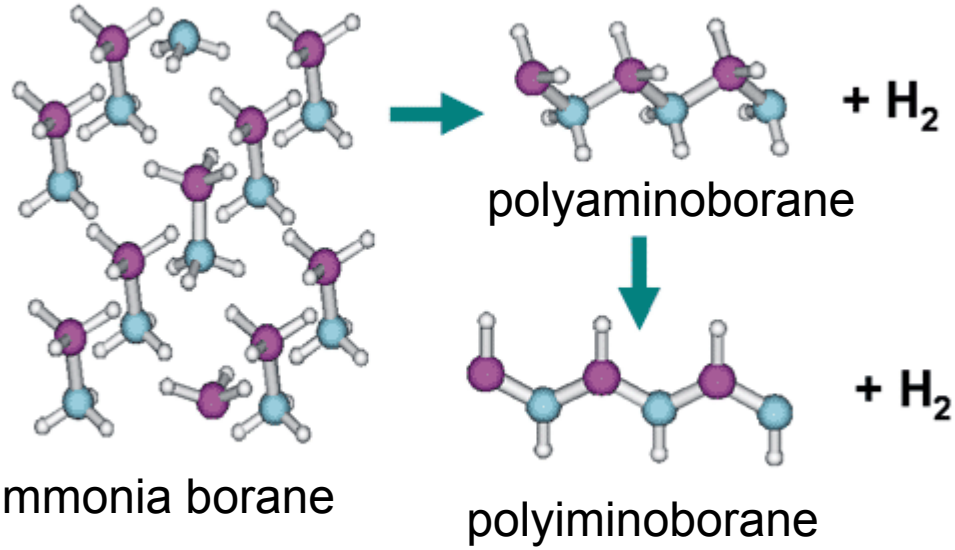


Thermolysis of Ammonia Borane

$nNH_3\text{-}BH_3 \rightarrow (NH_2BH_2)_n + (n\text{-}1)H_2$ (<120 °C) (Intramolecular)

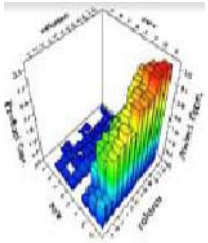
$(NH_2BH_2)_n \rightarrow (NHBH)_n + H_2$ (> 150 °C) (Intermolecular)

$2(NHBH)_n \rightarrow (NHB—NBH)_n + H_2$ (< 150 °C) (Cross linking)

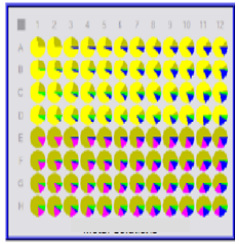


- Ammonia borane releases a hydrogen molecule, forming polyaminoborane.
- Release of a second hydrogen molecule leaves polyiminoborane.
- Crosslinking of polyiminoborane leads to polyborazylene analogues

High-Throughput Experimentation Process



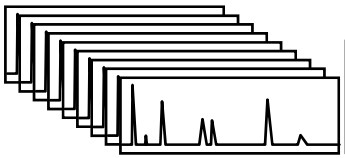
Confirmation of leads discovered from high-throughput experimentation



jmp™

Purification of chemicals

Inferential engine - molecular modeling & data mining



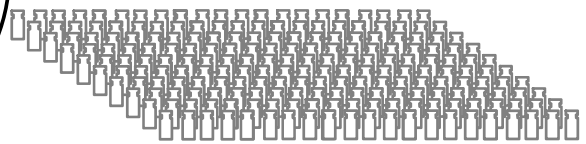
Leads

Plan

Analyze

Database

Make Arrays of Materials to Test

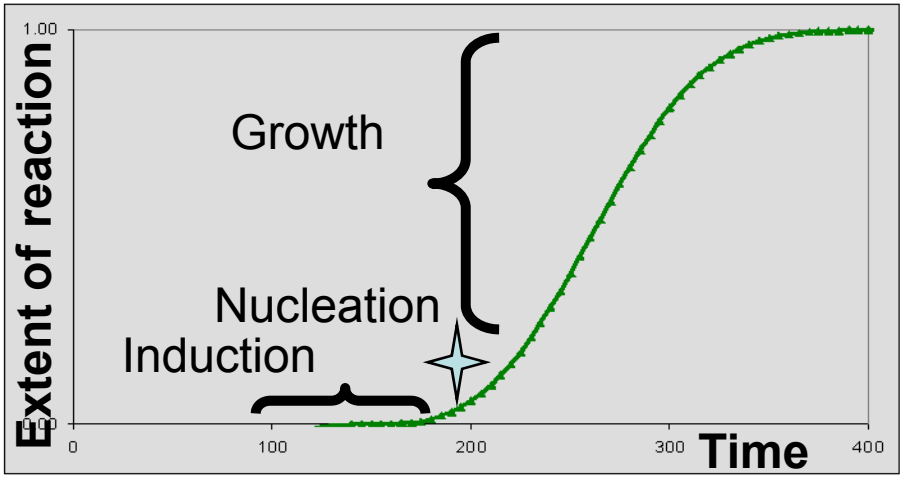


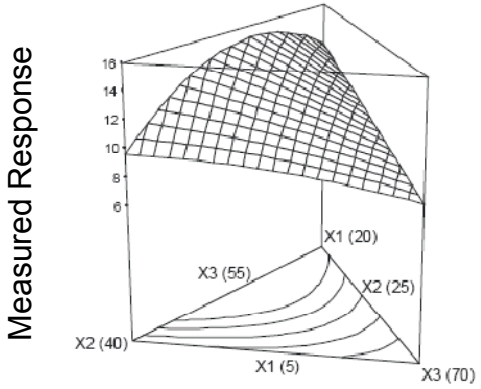
Test (Reaction, Screening)

Control of Hydrogen Release

- Sigmoidal kinetic behavior: Induction, Nucleation & Growth
- Purity and additives profoundly effect reaction
- Ammonia borane dimers catalyze hydrogen release

Optimization of additives design space enables control





3D Response surface for a mixture design

Anderson, M. J.; Whitcomb, P. J. 08/08/06

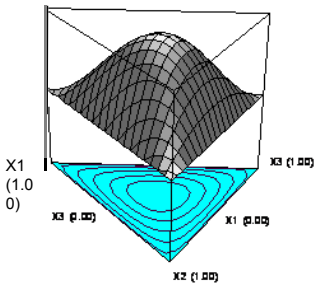
http://www.statease.com/pubs/doe for coatings.pdf

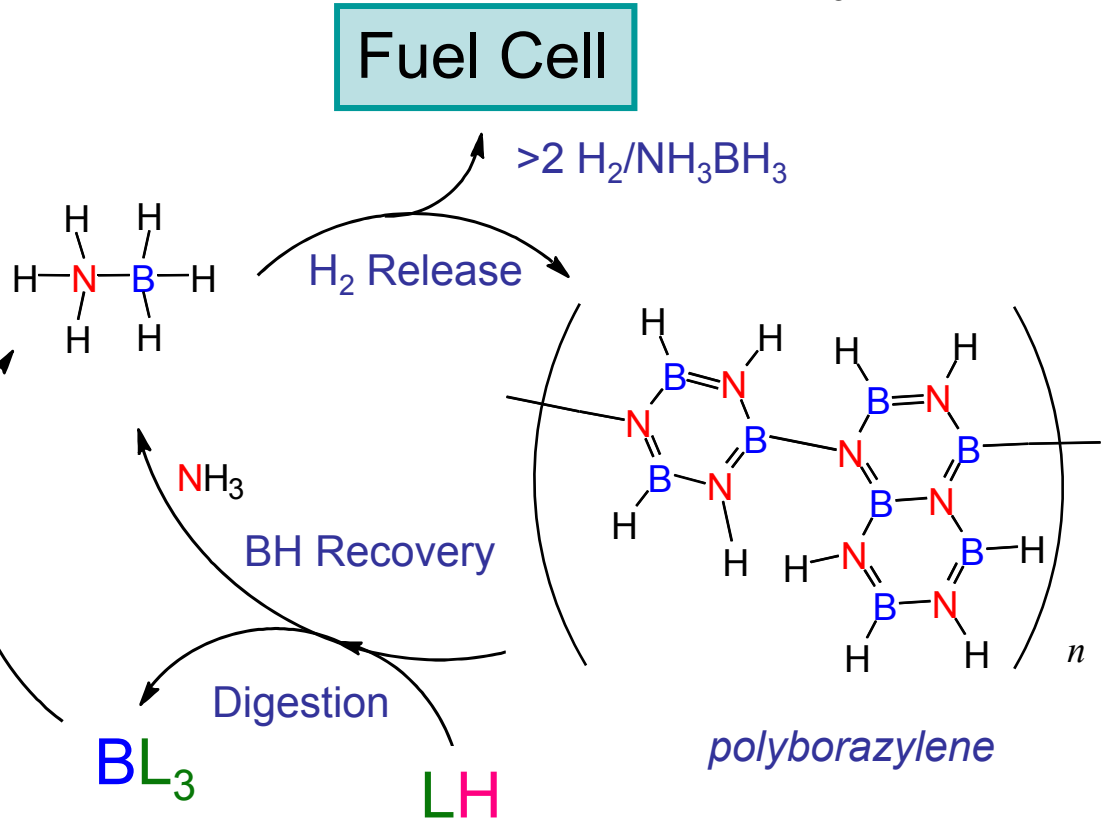
Regeneration of NH_3BH_3

- Polyborazylene-like material cannot be reformed with practical H_2 over-pressures
- Chemical processing pathways are required to regenerate the chemical hydrogen storage material (digestion: alcohols, diglyme and NH_3)

Large parameter space to obtain optimum combinations of M and L suited to HTE

$3\ (RO)_2BH \leftrightarrows 2\ (RO)_3B + BH_3$





Ammonia Borane Metal Composites

- International cooperation – United States, New Zealand, Singapore, United Kingdom
- Combination of Amine Boranes with MgH_2 & $LiNH_2$ for High Capacity Reversible Hydrogen Storage
- Synthesize and characterization of hybrid materials that combine light element metal hydrides with the amine borane chemical based hydrogen storage through a coupled endothermic-exothermic approach for hydrogen storage
- Binary and ternary designs with complex synergies - HTE

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