Computational studies of hydrogen interactions with storage materials

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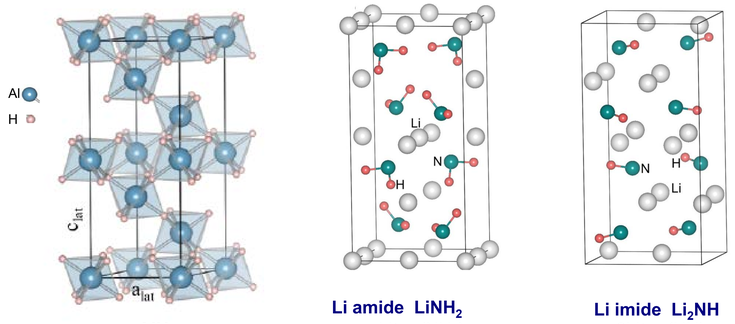
Project ID BES015

Motivation and challenges

- Metal hydrides and complex hydrides as hydrogen-storage materials
- Build understanding of the fundamental mechanisms that control reversible hydrogenation and dehydrogenation processes in hydrides

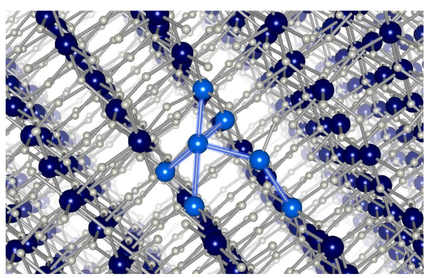
Systems of interest: Aluminum hydride (AlH_3) and lithium amide ($LiNH_2$) as reversible hydrogen-storage materials



α-AlH_3 | Li amide $LiNH_2$ ≈ $Li^+ + (NH_2)^-$ | Li imide Li_2NH ≈ $2Li^+ + (NH)_2^-$

Objectives

- Apply state-of-the-art first-principles calculations as well as other simulation techniques to study the microscopic mechanisms that govern mass transport in hydrogen storage materials
- Determine formation energies and migration barriers of defects related to hydrogen uptake and release
- Interpret experimental results based on calculated activation energies
- Investigate the effect of transition-metal additives on hydrogen kinetics
- Study effects of particle size
- Develop guidelines for designing storage materials with improved storage capacities and favorable kinetics



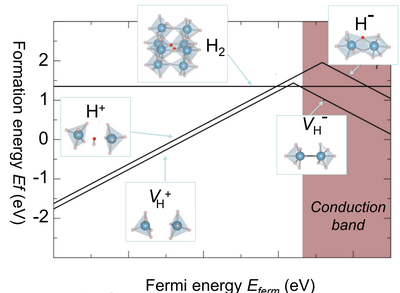
Aluminum metal phase nucleation in AlH_3
The image shows a cluster of bonded Al atoms in an AlH_3 host crystal. Blue balls: Al; white balls: H.

Methods

- Density functional theory (DFT)
  - generalized-gradient approximation (GGA)
  - screened hybrid functional
    - J. Heyd, G. E. Scuderia, and M. Ernzerhof, J. Chem. Phys, **118**, 8207 (2003); **124**, 219906 (2006)
- Kinetic Monte Carlo (KMC) model based on first-principles results
  - Enables direct comparison with experiment

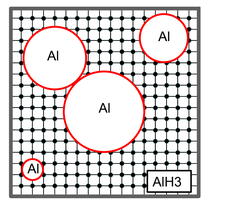
Dehydrogenation of AlH_3

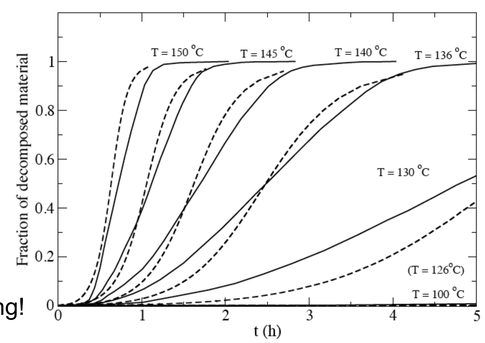
- AlH_3 is thermodynamically unstable at ambient conditions, but kinetic effects inhibit dehydrogenation below 100°C
- Contrary to earlier speculation, surface-oxide layer not responsible for metastability
  - H.Saitoh *et al.*, Appl. Phys. Lett., **93**, 151918 (2008).
- Decomposition of AlH_3 initiates at localized sites throughout the bulk material, as opposed to nucleation at the surface
  - S. D. Beattie *et al.*, Chem. Commun. (Cambridge) **2008**, 4448.
- V_H^+ and V_H^- key defects in the dehydrogenation process
- V_H^+ migrates faster
- Fermi level at the conduction-band minimum ensures the presence of mobile carriers necessary for charge neutrality



Dehydrogenation kinetics modeled using KMC

- V_H^- immobile nucleation centers for Al phase
- V_H^+ Random walkers
- Favorable binding energies (trapping energies) as the vacancy clusters grow in size
- AlH_3 stable for years even without oxide layer
- KMC results agree with experiment
- S-shape-like onset of reaction curve does *not* rule out diffusion-limited mechanism
- Simple rules about shapes of reaction curves can be misleading!





Point defects and diffusion in lithium amide

$$LiNH_2 + LiH \leftrightarrow Li_2NH + H_2$$

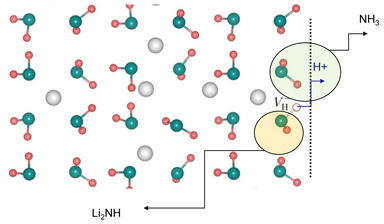
- All possible native defects investigated: structure, energetics, migration
- All native defects can be interpreted in terms of H_i^-, V_H^-, $(H_2)_i$, Li_i^+, V_{Li}^-, and V_{NH2}^+

Defect	E^f (eV)	E_m (eV)	Complex
H_i^+	1.28	0.61	
H_i^-	1.34	0.34	
V_H^-	0.63	0.71	
$(H_2)_i$	1.75	0.19	
Li_i^+	0.51	0.30	
V_{Li}^-	0.51	0.20	
Li_H^0	0.48	0.71*	$Li_i^+ + V_H^-$
H_{Li}^0	1.17	0.61*	$H_i^+ + V_{Li}^-$
$V_{NH_2}^+$	0.62	0.87	
V_{NH}^0	0.40	0.87*	$V_{NH_2}^+ + H_i^-$
V_N^+	1.64	0.87*	$V_{NH_2}^+ + (H_2)_i$
V_N^-	1.77	0.87*	$V_{NH_2}^+ + 2H_i^-$

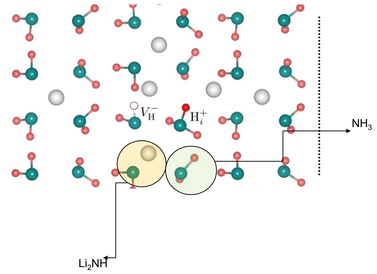
Hydrogen desorption kinetics of lithium amide

- Charge neutrality maintained by Li-related Frenkel pairs
- Two mechanisms for dehydrogenation of $LiNH_2$ suggested:

Mechanism I (bulk): self-diffusion of (H_i^+, V_H^-) rate-limiting process



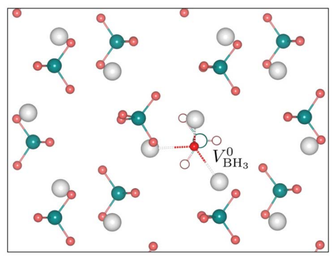
Mechanism II (surface): self-diffusion of V_H^- rate-limiting process

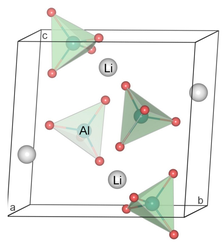


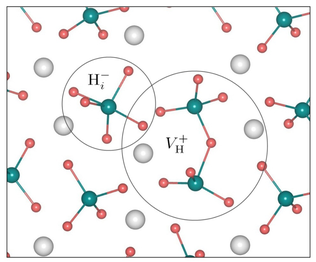
- Dominant mechanism for decomposition depends on particle size (specific surface area): explains variation of activation energy with duration of ball milling
- Hydrogen Frenkel pairs at the core of decomposition mechanism

Decomposition mechanisms of $LiBH_4$ and $LiAlH_4$

- Comprehensive study of point defects and dehydrogenation mechanisms
- Investigated effects of transition-metal additives







Future directions

- Role of hydrogen-related Frenkel pairs in dehydrogenation kinetics
  - Systematic studies in a range of materials: $LiBH_4$, $Li_4BN_3H_{10}$, $LiNH_2$, MgH_2, Mg_2(Fe/Ni)-hydride, $LiAlH_4$, etc.
- Role of transition-metal doping in MgH_2:
  - Formation energies and migration barriers in Mg_2-TM and MgH_2 matrix in the dilute limit

Overall summary and impact

- Consideration of charged point defects and impurities (and not just neutral states) in hydrides: an essential physics issue previously not addressed
- State-of-the-art first principles calculations to accurately describe defects
- Multiscale modeling to address realistic system sizes and temperature
- Broader conclusions: shapes of reaction curves, particle-size dependence

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