Computational Design of Hydrogen Storage Materials

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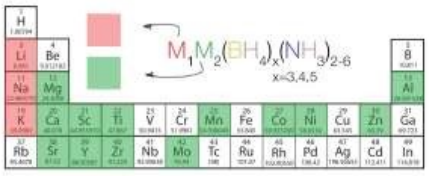
Motivation

Hydrogen and ammonia both have great potential as carbon-neutral energy carriers for the future.

- Storing hydrogen as a gas or liquid is possible but not efficient in terms of energy capacity and cost for on-board applications, due to the requirement of high pressures and cryogenic temperatures, respectively
- Alternatively, hydrogen can also be stored with high capacity in the condensed phase.
- Even though many materials have been proposed for solid state hydrogen storage, none of them are completely promising in terms of a fast, reversible and high-density hydrogen uptake and release.
- Ammine Metal Borohydrides (AMBs) are the most recent promising hydrogen storage medium.
- There are only a few synthesized AMBs reported in the literature.
- In order to investigate the potential of AMBs, a computational screening is necessary.

Computational Screening

- 15 AMB compositions with a general formula of $M_1M_2(BH_4)_x(NH_3)_y$ x=3,4,5 and y=2,3,4,5,6



- For each composition, find template crystal structures.
- This is done by Crystal Structure Prediction via Simulated Annealing (CASPESA) method [1].
- CASPESA requires a model including the crytal structure details (atomic positions and cell parameters).
- CASPESA only expects predefined bond distance thresholds.
- The best lattice structures obtained from CASPESA are further relaxed by employing a planewave DFT approach (Quantum Espresso) [2] using PBE generalized gradient approximation.
- ΔE_{alloy} was inspried from Soloveichik et al [3] and modified as:

$$\Delta E_{alloy} = E_{(M1M2(BH4)x(NH3)y)} - (E_{(M1(BH4)4)} + E_{(M2(BH4)2)} + yE_{((NH3))})$$

- ΔE_{decomp} was inspried from Yang et al [4]

$$M_1M_2(BH_4)_x(NH_3)_y \longrightarrow M_1H + M_2 + NH_3 + BN + B + H_2$$

- Criteria for the screening: $\Delta E_{alloy} < 0$ and $-0.8 \leq \Delta E_{decomp} \leq -0.0$ eV/H_2.

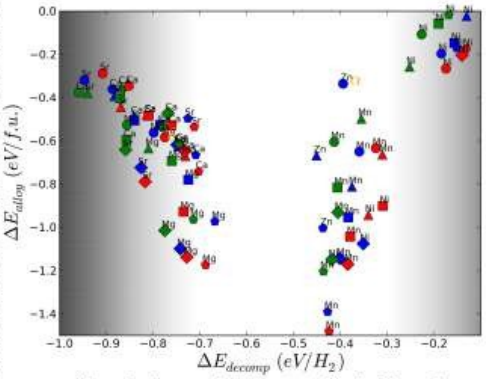


Figure 1 - Decomposition Energy vs Alloying Energy for $M_1M_2(BH_4)_3(NH_3)_x$

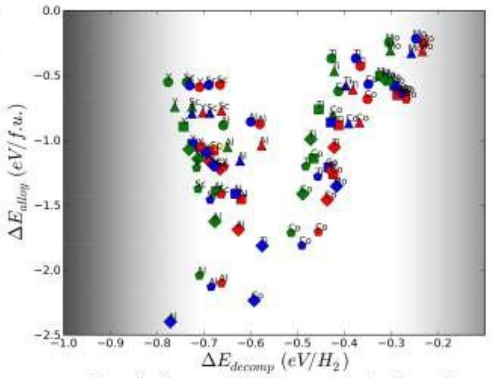


Figure 2 - Decomposition Energy vs Alloying Energy for $M_1M_2(BH_4)_4(NH_3)_x$

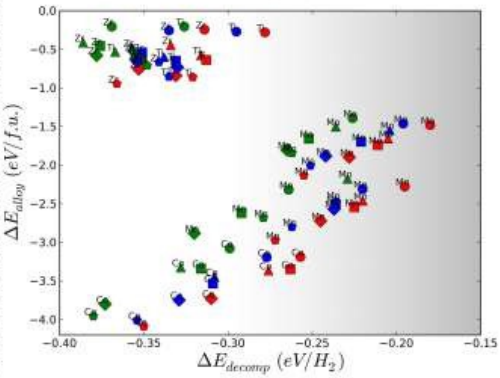


Figure 3 - Decomposition Energy vs Alloying Energy for $M_1M_2(BH_4)_5(NH_3)_x$

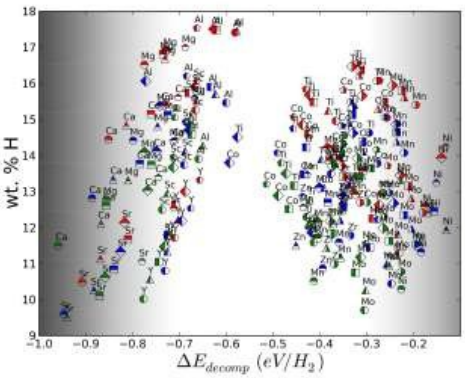


Figure 4 - Hydrogen capacity (wt. %) as a function of the decomposition energy

Li, Na and K. NH_3 content: di (○), tri (△), tetra (□), penta (◇), hexa (⬡).

Results

- CASPESA was successfully applied for all the systems.
- New structures were found for LiMg(BH4)3(NH3)2
- Experimentally known dual cation AMBs $LiMg(BH_4)_3(NH_3)_2$, $NaZn(BH_4)_3(NH_3)_2$ and $LiSc(BH_4)_4(NH_3)_4$ were found in the desired region of our screening
- In accordance with the expreimental study $LiZn(BH_4)_3(NH_3)_2$ was found to be unstable
- Zn was only stable together with Na at certain ammonia content
- Alloys with Ca and Sr are quite stable against decomposition.
- Ni containing alloys have decomposition energies close to zero which makes them unstable.
- Alloy systems with Mn were identified as promising candidates.
- Majority of alloys containing for molecules of BH4 were found to be promising.
- A similar picture was also observed for the alloys containing five molecules of BH4.
- All the promising alloys have a gravimetric hydrogen density above DOE 2015 target.

References

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