IV.A.2 Design of Novel Multi-Component Metal Hydride-Based Mixtures for Hydrogen Storage

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Objectives

The objective of the project is to discover novel mixed hydrides for hydrogen storage, which enable the DOE 2010 system-level goals. Since prior Argonne National Laboratory/TIAX system-level modeling has shown that there will likely be a ~50% penalty on the material's gravimetric capacity due to balance-of-plant issues, our goal is to find a material that desorbs 8.5 wt% H_2 or more at temperatures below 85°C. The project will combine first-principles calculations of reaction thermodynamics and kinetics with material and catalyst synthesis, testing, and characterization.

- Three materials classes (chemical, metal/complex, physisorptive) divided into DOE Centers of Excellence.
- Our project: Combine materials from distinct categories to form novel multi-component reactions.
- Systems to be studied include mixtures of complex hydrides and chemical hydrides (e.g. $LiNH_2$+NH_3BH_3) and nitrogen-hydrogen-based borohydrides (e.g. $Al(BH_4)_3(NH_3)_3$).

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

(A) System Weight and Volume

(E) Charging/Discharging Rates

Technical Targets

This project is conducting fundamental studies of novel multi-component mixtures of complex and chemical hydrides. Insights gained from these studies will be applied toward the development of hydrogen storage materials and reactions that meet the following DOE 2010 hydrogen storage targets:

- Specific energy: 1.5 kWh/kg
- Energy density: 0.8 kWh/L

Approach

The 2010 and 2015 FreedomCAR/DOE targets for hydrogen storage systems are very challenging, and cannot be met with existing materials. The vast majority of the work to date has delineated materials into various classes, e.g., complex and metal hydrides, chemical hydrides, and sorbents. However, very recent studies indicate that *mixtures* of storage materials, particularly mixtures *between various classes*, hold promise to achieve technological attributes that materials within an individual class cannot reach. Our project involves a systematic, rational approach to designing novel multicomponent mixtures of materials with fast hydrogenation/dehydrogenation kinetics and favorable thermodynamics using a combination of state-of-the-art scientific computing and experimentation. We will use the accurate predictive power of first-principles modeling to understand the thermodynamic and microscopic kinetic processes involved in hydrogen release and uptake and to design new material/catalyst systems with improved properties. Detailed characterization and atomic-scale catalysis experiments will elucidate the effect of dopants and nanoscale catalysts in achieving fast kinetics and reversibility. And, state-of-the-art storage experiments will give key

storage attributes of the investigated reactions, validate computational predictions, and help guide and improve computational methods. In sum, our approach involves a powerful blend of: 1) H_2 storage measurements and characterization, 2) state-of-the-art computational modeling, 3) detailed catalysis experiments, 4) in-depth automotive perspective.

Accomplishments

- Recently discovered a novel hydrogen storage medium that combines the $[B_{12}H_{12}]_2$- anion with the ammonium *complex cation* to form $(NH_4)_2B_{12}H_{12}$, ammonium dodecaboro-closo-dodecahydride, at 11.3 wt% H_2 (Figure 1). By using a combination of first-principles total energy calculations and finite-temperature phonons, with the recently-developed Grand Canonical Linear Programming approach [1] we show that the thermodynamically-preferred decomposition reaction sequence for $(NH_4)_2B_{12}H_{12}$ releases all 11.3 wt% H_2 between 20-30 kJ/mol H_2. Experimental testing of this reaction is underway.
- Currently calculating the formation energies and thermodynamic properties of all binary, ternary, quaternary, and quinary Li-Mg-B-N-H compounds from the Inorganic Crystal Structure Database. The calculated free energies will be used as inputs to the grand-canonical linear programming approach for determining reaction pathways in multinary systems.
- Refining the prototype electrostatic ground state search method for predicting crystal structures of currently unknown materials. Implementing a dramatically more efficient algorithm for finding the ground states using the recently proposed Wang-Landau Monte Carlo method. We have completed extensive tests for simple Lennard-Jones systems and are in a position now to conduct extensive searches for the crystal structures of new hydrogen storage compounds, with ammoniated borohydrides and metal-substituted derivatives of amido boranes and borohydrides as the first targets.
- Initiated a general experimental/theoretical study of the amide-borohydride mixture phase space involving reactions of the type: $X\ M_1(NH_2) + Y\ M_2(BH_4) \rightarrow M_1M_2(NH_2)_x(BH_4)_y$. First principles calculations show promising low-energy solid-state synthesis routes. Initial thermally programmed desorption-mass spectrometry data have been taken from the first series of mixtures we have investigated involving $NaNH_2 + NaBH_4$ with varying ratios of amide to borohydride.

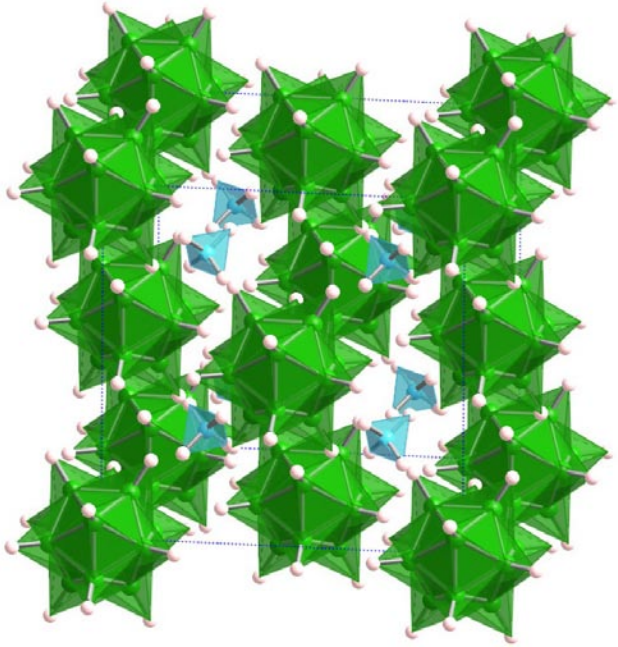

FIGURE 1. Crystal Structure of the $(NH_4)_2B_{12}H_{12}$ Compound

FY 2009 Publications/Presentations

1. Presentation at 2009 Hydrogen Program Annual Merit Review Meeting, C. Wolverton.

References

1. Akbarzadeh, A.; Ozolins, V.; Wolverton, C. *Adv. Mater.* **19**, 3233 (2007).