IV.D.1 Design of Novel Multi-Component Metal Hydride-Based Mixtures for Hydrogen Storage

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- University of California, Los Angeles, Los Angeles, CA
- Ford Motor Company, Dearborn, MI

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Overall Objectives

- Discover novel mixed hydrides for hydrogen storage, which enable the DOE system-level goals
- Discover a material that has thermodynamics which allow desorbtion of 8.5 wt% hydrogen or more at temperatures below 85°C
- Via the combination of first-principles calculations of reaction thermodynamics and kinetics with material and catalyst synthesis, testing, and characterization, search for combinations of materials from distinct categories to form novel multicomponent reactions

Fiscal Year (FY) 2014 Objectives

- Determine storage capacities, kinetics, and reversibility for reactions predicted to have high capacity and suitable thermodynamics for hydrogen storage applications, $2LiBH_4 + 5Mg(BH_4)_2$ and $B_{20}H_{16}$
- Use combined density functional theory (DFT) and experiment to characterize reaction products from $2LiBH_4 + 5Mg(BH_4)_2$
- Synthesize $B_{20}H_{16}$ and determine hydrogen desorption properties and reaction products
- Develop computational methods to extend calculation of kinetics beyond mass transport to predict dissociation, surface diffusion, and other kinetic barriers

Technical Barriers

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

(O) Lack of Understanding of Hydrogen Physisorption and Chemisorption

(A) System Weight and Volume

(E) Charging/Discharging Rates

Technical Targets

This study is aimed at fundamental insights into new materials and the thermodynamic and kinetic aspects of hydrogen release and reabsorption from them. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- Specific energy: 1.5 kWh/kg
- Energy density: 0.9 kWh/L

FY 2014 Accomplishments

- Used computational tools and high-throughput machinery to survey high-capacity, thermodynamically reversible reactions
- Focused efforts on two main reactions predicted to have high capacity and suitable thermodynamics for hydrogen storage applications, $2LiBH_4 + 5Mg(BH_4)_2$ and $B_{20}H_{16}$
- Determined $B_{20}H_{16}$ to be promising—only known hydrogen storage reaction with high capacity, good thermodynamics, and computational predicted fast mass transport kinetics
- Theoretically predicted that mass transport in $B_{20}H_{16}$ is fast. Subcontract at OSU focused on synthesis of $B_{20}H_{16}$ compound (synthesis and nuclear magnetic resonance [NMR] characterization performed; project ran out of time/funds before full desorption, kinetics, and reaction products could be performed)

- Studied hydrogen desporption and decomposition pathways have been studied in $2LiBH_4 + 5Mg(BH_4)_2$ using NMR; reaction products consistent with theoretically predicted B_2H_6 anion. Using combination of experiments and DFT, able to assign almost all reaction products. Still one uncertain product (~25 ppm).
- Completed computational survey of dopants that lower surface dissociation or diffusion for MgB_2 rehydrogenation
- Confirmed the addition of $ZnCl_2$ (and carbon) to $LiBH_4$+$Mg(BH_4)_2$ mixture results in (slight) increase in hydrogen desorption at lower temperatures

INTRODUCTION

The long-term 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. Specifically, we focus on combinations of materials from distinct categories to form novel multicomponent reactions.

APPROACH

We 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 elucidate the effect of dopants and nanoscale catalysts in achieving fast kinetics and reversibility. And, state-of-the-art storage experiments 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) hydrogen storage measurements and characterization, (2) state-of-the-art computational modeling, (3) detailed catalysis experiments, and (4) an in-depth automotive perspective.

FUTURE DIRECTIONS

This project is complete. $B_{20}H_{16}$ is unique and potentially very interesting as the only hydrogen storage reaction of a known compound with (1) high capacity, (2) good thermodynamics, and (3) predicted fast mass transport kinetics. Of course, there are drawbacks, but because of this unique combination of characteristics, recommend that more future work on this reaction is warranted. Synthesis of $B_{20}H_{16}$ proved difficult, with low yield. However, based on our project accomplishments, we can make several recommendations for future directions for this area.

- Validate future experimental work should try to validate predicted beneficial attributes of $B_{20}H_{16}$ material; if validated, more focused effort should be performed to overcome any potential drawbacks (e.g., low yield synthesis, low-cost synthesis, possible kinetic limitations)
- Perform computations of observed reaction products to confirm results and provide predictions of thermodynamics/kinetics
- Extend NMR experiments and DFT-NMR calculations to "recharged" $2LiBH_4$+$5Mg(BH_4)_2$ samples, to determine portion(s) of the reaction that are reversible
- Explore the potentially promising avenue for "fast kinetics" borohydrides: low melting point combinations (i.e., low-lying eutectics); direct some computational effort to finding these low-lying eutectics (AIMD and λ-integration)

PUBLICATIONS

1. *Theoretical prediction of different decomposition paths for $Ca(BH_4)_2$ and $Mg(BH_4)_2$* Yongsheng Zhang, Eric Majzoub, Vidvuds Ozolins and C. Wolverton Phys. Rev. B **82**, 174107 (2010)

2. *First-principles prediction of phase stability and crystal structures in Li-Zn and Na-Zn mixed-metal borohydrides* Dilpuneet S. Aidhy and C. Wolverton Phys. Rev. B **83**, 144111 (2011)

3. *Prediction of a $Ca(BH_4)(NH_2)$ quaternary hydrogen storage compound from first-principles calculations* Dilpuneet S. Aidhy, Yongsheng Zhang and C. Wolverton Phys. Rev. B **84**, 134103 (2011)

4. *First-principles prediction of high-capacity, thermodynamically reversible hydrogen storage reactions based on (NH4)2B12H12* W.H. Sun, C. Wolverton, A.R. Akbarzadeh and V. Ozolins Phys. Rev. B 83, 064112 (2011)

5. *Transition Metal-Decorated Activated carbon Catalysts for Dehydrogenation of NaAlH4*, Sean S.-Y. Lin, Jun Yang, and Harold H. Kung, Int. J. Hydrogen Energy **37**, 2737 (2012)

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7. *Crystal structures, phase stabilities, and hydrogen storage properties of metal amidoboranes* Yongsheng Zhang and C. Wolverton J. Phys. Chem. C **116**, 14224 (2012)

8. *First-principles insight into the degeneracy of ground state $LiBH_4$ structures* Yongsheng Zhang, Yongli Wang, Kyle Michel and C. Wolverton Phys. Rev. B **86**, 094111 (2012)

9. *Structure determination of an amorphous compound AlB_4H_{11}* Xuenian Chen, Yongsheng Zhang, Yongli Wang, Wei Zhou, Douglas A. Knight, Teshome B. Yisgedu, Zhenguo Huang, Hima K. Lingam, Beau Billet, Terrence J. Udovic, Terrence J. Udovic, Gibert M. Brown, Sheldon G. Shore, Christopher M. Wolverton and Ji-Cheng Zhao Chem. Sci. **3**, 3183 (2012)

10. *First-principles studies at intermediate products in the decomposition of metal amidoboranes* Yongsheng Zhang, Tom Autrey and C. Wolverton J. Phys. Chem. C **116**, 26728 (2012)

11. *The kinetics of mass transport in $B_{20}H_{16}$* Kyle Michel, Yongsheng Zhang and C. Wolverton J. Phys. Chem. C **117**, 19295 (2013)

12. *First principles studies of phase stability and crystal structures in Li-Zn mixed-metal borohydrides* Yongli Wang, Yongsheng Zhang and C. Wolverton Phys. Rev. B **88**, 024119 (2013)

13. *Hydrogen Storage Properties of Complex Metal Hydride-Carbon Materials* Sean S.-Y. Lin, Jun Yang, Harold H. Kung, Mayfair C. Kung Topics in Catalysis 56, 1937 (2013)

14. *Crystal structure, phase stability, and decomposition of the quaternary Mg-B-N-H hydrogen storage system* Yongsheng Zhang, David Farrell, Jun Yang, Andrea Sudik and C. Wolverton, J. Phys. Chem. C 118, 11193 (2014)

15. *Stability of transition metals on the Mg-terminated MgB2 (0001) surface and their effects on hydrogen dissociation and diffusion* Yongli Wang, Kyle Michel, Yongsheng Zhang and C. Wolverton, submitted to Phys. Rev. B (2014)

16. *Hydrogen diffusion in MgB2 bulk* Y.L. Wang, K. Michel, and C. Wolverton, in prep. (2014)

17. *A strategy for designing hydrogen storage materials with moderate thermodynamic properties* Y.L. Wang, K. Michel, and C. Wolverton, in prep. (2014)