

VI.A Metal Hydrides

VI.A.1 Catalytically Enhanced Hydrogen Storage Systems

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Objectives

- Determination of the chemical nature of the titanium species responsible for the enhanced kinetics of Ti-doped NaAlH₄.
- Determination of the mechanism of action of the dopants of Ti doped NaAlH₄ in the dehydrogenation and re-hydrogenation processes.
- Apply insights gained from fundamental studies of Ti-doped NaAlH₄ to the design and synthesis of hydrogen storage materials that meet the U.S. DOE 2010 hydrogen storage system targets, especially cost, specific energy, and energy density.

Technical Barriers

The final year of this project addressed the following technical barriers from the Hydrogen Storage section of the Hydrogen Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- B. Weight and Volume
- E. Refueling Time
- M. Hydrogen Capacity and Reversibility
- N. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

In the final year of this project, we conducted fundamental studies of Ti-doped NaAlH₄. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the DOE 2010 hydrogen storage targets of cost: \$4/kWh net; specific energy: 2 kWh/kg; and energy density: 1.5 kWh/L.

Approach

- Determination of the influence of doping on structure and composition through X-ray and neutron diffraction studies (in collaboration with the University of Geneva).
- Direct characterization of Ti-dopants through electron paramagnetic resonance (EPR) studies (in collaboration with the University of Denver).
- Direct studies of the effects of doping on hydrogen through infrared and anelastic spectroscopy (in collaboration with the University of Geneva and the University of Rome).

Accomplishments

- Discovery that the enhanced hydrogen cycling kinetics that arise following the mechanical doping process are not only a consequence of hydride particle size reduction and Ti dispersal but are also linked to a distortion of the hydride's microstructure.
- Discovery that the enhanced hydrogen cycling kinetics of Ti-doped NaAlH₄ are due to a minority Ti species and that the majority of the Ti is in a kinetically irrelevant resting state.
- Discovery that highly mobile, hydrogen containing point defects arise upon thermal treatment of Ti-doped NaAlH₄.

Future Directions

This project is now completed; however, our group at the University of Hawaii is continuing to develop advanced hydrogen storage materials. A new DOE funded project, that will be administrated as part of the Metal Hydride Center of Excellence, was initiated in March 2005. A detailed description of this new project appears elsewhere in this report.

Introduction

We have developed methods of doping sodium aluminum hydride, NaAlH₄, with titanium and/or zirconium that give rise to state-of-the-art hydrogen storage materials. However, less than that ~5 weight percent hydrogen can be reversibly released from these materials under conditions that are required for the practical operation of an onboard fuel cell. In light of this and other practical limitations, it has become apparent that improved variations of this material must be produced to achieve commercial viability. Recently it has been found that the phenomenon of kinetic enhancement upon transition metal doping extends to the reversible dehydrogenation of LiNH₂ and LiBH₄/MgH₂. A better understanding of the fundamental basis of the enigmatic kinetic enhancement of reversible dehydrogenation of the doped materials in the solid state would be invaluable to the effort to develop improved hydrogen storage materials. Therefore, a major thrust of our efforts has been focused on gaining a fundamental understanding of the nature of the dopants and the structural effects

they exert on alanates and related materials. During the final year of this project, we have elucidated several key fundamental aspects of the unprecedented solid chemistry occurring in doped complex hydrides.

Results

Doping of NaAlH₄ through mechanical milling results in a broadening of the X-ray diffraction peaks. Rietveld analysis of this broadening indicates that in addition to the reduction of hydride grain size, the process also results in a distortion of the lattice (primarily in the c direction). Thus the enhanced hydrogen cycling kinetics that arise following the mechanical milling appear to be linked to a distortion of the hydride's microstructure.

Our EPR studies have shown that the majority of titanium is transformed from Ti(III) to Ti(0) during early cycles of dehydrogenation/re-hydrogenation. This finding is in agreement with our synchrotron X-ray studies (collaboration with the Norwegian Institute for Energy Research) which established that

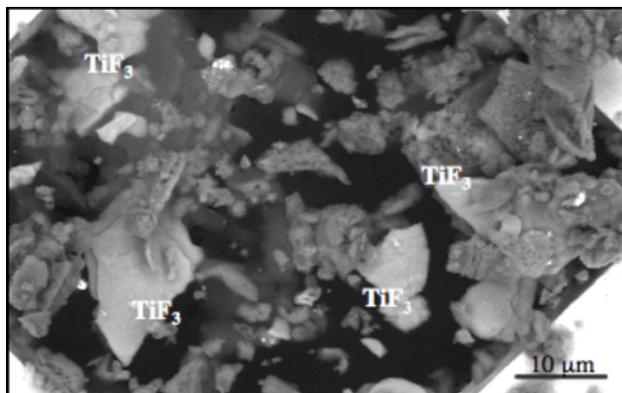


Figure 1. Back-scattered electron SEM image of sample of NaAlH₄ ball milled with 2 mol % TiF₃ prior to initial dehydrogenation.

the increasing amounts of a solid solution with an approximate composition of Al_{0.93}Ti_{0.07} forms over the course of repeated cycling. During the past year, we have obtained further confirmation of our conclusions through scanning and tunneling electron microscopy studies (collaboration with the Norwegian University of Science and Technology) and X-ray absorption fine structure studies (collaboration with GE Global Research). For example, segregated particles of TiF₃ can clearly be seen in a BSE SEM image (Figure 1) of NaAlH₄ following ball milling with TiF₃. We observe only a relatively minor change in the hydrogen cycling kinetics whether a Ti(III) to Ti(0) species predominates. Therefore, our studies strongly suggest that the enhanced hydrogen cycling kinetics of Ti-doped NaAlH₄ are due to a minority Ti species and that the majority of the Ti is in a resting state. This conclusion is supported by our finding that all known TiAl alloys are ineffective in promoting the dehydrogenation/re-hydrogenation kinetics of NaAlH₄.

Our anelastic spectroscopy studies have shown that point defects arise upon thermal treatment of Ti-doped NaAlH₄ as seen in Figure 2. These entities very likely involve hydrogen and are highly mobile ($\sim 5 \times 10^3$ jumps/s at 70 K). The conclusion that Ti-doping perturbs Al-H bonding and induces a population of highly mobile hydrogen is in agreement with our previous infra (collaboration with the University of Geneva) and nuclear magnetic resonance spectroscopy studies.

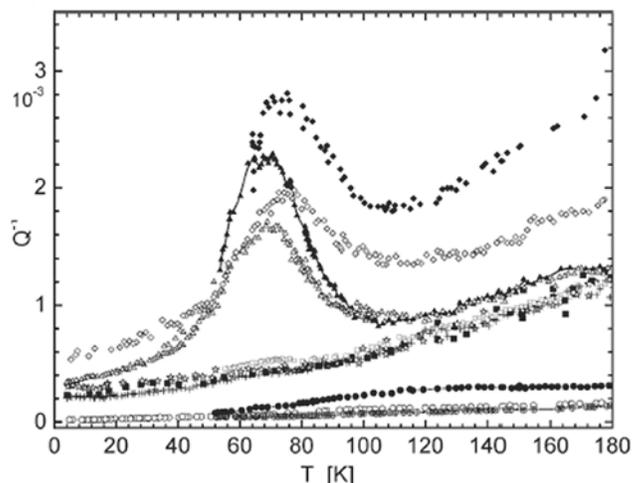


Figure 2. Low temperature dependence elastic energy loss of: ○ KBr only; ● KBr, H₂ treated; ▽ undoped NaAlH₄; □ undoped NaAlH₄ after thermal treatment (TT); △ doped NaAlH₄, after TT, 1.1 Hz; ▾ doped NaAlH₄, after TT, 4.8 Hz; ▲ doped NaAlH₄, TT, 1.1 Hz, aged; + doped NaAlH₄, TT, 4.8 Hz, aged.

Conclusions

- High valent Ti dopant precursors are transformed Ti(0) species during the first few cycles dehydrogenation-rehydrogenation.
- The observation that only a relative minor change in the hydrogen cycling kinetics occurs whether the majority of titanium is transformed from Ti(III) to Ti(0) during early cycles of dehydrogenation/rehydrogenation strongly suggests that the enhanced hydrogen cycling kinetics are due to a minority Ti species and that the majority of the Ti is in a resting state.
- Mechanical milling of NaAlH₄ not only reduces grain size and disperses Ti but also results in distortion of the microstructure of the hydride.
- Ti-doping perturbs Al-H bonding and induces a population of highly mobile hydrogen.
- Ti-doping of NaAlH₄ induces a thermally activated process that generates point-defects. These entities very likely involve hydrogen and are highly mobile, performing about 5×10^3 jumps/s at 70 K.

Invited Presentations (5/02-6/03)

1. International Symposium on Metal Hydrogen Systems, Crakow, Poland, 9/4/04.
2. Leiden University, The Netherlands, 9/14//04.
3. Utrecht University, The Netherlands., 9/15/04.
4. Symposium on the Hydrogen Economy, meeting of the American Society for Materials, Columbus, OH, 10/18/04.
5. Symposium on Hydrogen Storage, Fifth Pacific Rim International Conference on Advanced Materials and Processes (PRICM-5), Beijing, China, 11/3/04.
6. Nankai University, Tainjin, China, 11/5/04.
7. Fudan University, Shanghai, China, 11/8/04.
8. Cornell University, 11/30/04.
9. Symposium on Hydrogen Storage, 2004 Materials Research Society fall meeting, Boston, MA, 11/29/04.
10. Gordon Research Conference on Hydrocarbon Resources, Ventura, CA, 1/12/05.
11. Session on "Crystalline Hydrogen Storage Materials, 2005 meeting of the American Crystallographic Association, Orlando, FL, 5/29/05.
4. Structure and Hydrogen Dynamics of Pure and Ti-doped Sodium Alanate. Jorge Iniguez, T. Yildirim, T.J. Udovic, M. Sulic, C.M. Jensen; *Phys. Rev. B.* 2004 65, 235433.
5. Preparation of Ti-doped Sodium Aluminum Hydride from Mechanical Milling of NaH/Al with Off-the-Shelf Ti Powder. P. Wang, C.M. Jensen; *J. Phys. Chem. B.* 2004 108, 15829.
6. Electron Microscopy Studies of NaAlH₄ Doped with TiF₃: Hydrogen Cycling Effects. C.M. Andrei, J. Walmsley, H.W. Brinks, R. Homestad, C.M. Jensen, B.C. Hauback; *Appl. Phys. A.* 2005, 80, 709.
7. Point Defect Dynamics and Evolution of Chemical Reactions in Alanates by Anelastic Spectroscopy. Oriele Palumbo, Rosario Cantelli, Annalisa Paolone, Sessa S. Srinivasan, Craig M. Jensen; *J. Phys. Chem. B.* 2005, 109, 1168.
8. Effects of Milling, Doping and Cycling of NaAlH₄ Studied by Vibration Spectroscopy and X-ray Diffraction. S. Gomes, G. Renaudin, H. Hagemann, K. Yvon, M.P. Sulic, C.M. Jensen; *J. Alloys Compd.* 2005 390, 305.
9. Synthesis and Crystal Structure of Na₂LiAlD₆. H.W. Brinks, B.C. Hauback, C.M. Jensen, R. Zidan; *J. Alloys Compd* 2005 392, 27.

Publications (6/04-6/05)

1. Synchrotron X-ray and Neutron Diffraction Studies of NaAlH₄ Containing Ti Additives. H.W. Brinks, C.M. Jensen, S.S. Srinivasan, B.C. Hauback, D. Blanchard, K. Murphy; *J. Alloys Compd.* 2004, 376, 215.
2. Long Term Cycling Behavior of Titanium Doped NaAlH₄ Prepared through Solvent Mediated Milling of NaH and Al with Titanium Dopant Precursors. Sessa S. Srinivasan, Hendrik W. Brinks, Bjorn C. Hauback, Dalin Sun, Craig M. Jensen; *J. Alloys Compd.* 2004 377, 283.
3. Method for Preparing Ti-doped NaAlH₄ Using Ti powder: Observation of Unusual Reversible Dehydrogenation Behavior. Ping Wang, Craig M. Jensen; *J. Alloys Compd.* 2004 379, 99.
10. Synchrotron X-ray Studies of Al_{1-y}Ti_y Formation and Re-hydriding Inhibition in Ti-enhanced NaAlH₄. Hendrik W. Brinks, Bjorn C. Hauback, Sessa S. Srinivasan, Craig M. Jensen; *J. Phys.Chem. B.* 2005 in press.
11. Transmission Electron Microscopy Studies of Cycled NaAlH₄ with Titanium Additives. Carmen M. Andrei, John C. Walmsley, Randi Homestad, Bjorn C. Hauback, Sessa S. Srinivasan, Craig M. Jensen; *Mater. Res. Bull.* 2005 in press.
12. Characterization of Titanium Dopants in Sodium Alanate by Electron Paramagnetic Resonance Spectroscopy. Meredith T. Kuba, Sandra S. Eaton, Christine Morales, and Craig M. Jensen; *J. Mater. Res.* 2005 in press (invited contribution to special issue on materials for energy and the environmental applications).