Complex Hydrides – A New Frontier for Future Energy Applications

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Program Scope

Hydrogen storage is one of the enabling materials technologies required to assure a successful future transition from fossil to hydrogen-based fuel. The scope of the multidisciplinary effort, which draws on considerable experimental and modeling experience and expertise at the Ames Laboratory and Virginia Commonwealth University, is to achieve a fundamental understanding of the relationships between the chemical composition, bonding, structure, microstructure, properties and performance of hydrogen-rich solids. The specific objectives of this program are to address relevant issues, which have the potential to advance basic materials science of novel hydrides and open up possibilities for their future practical use.

- Synthesize an array of novel non-transition metal-based complex hydrides where the metal, metalloid or nonmetal atom is coordinated by two to six hydrogen atoms by means of solvent-free, mechanochemical technique starting from several parent light-element hydrides.
- Fully characterize the products using state-of-the-art experimental techniques.
- Create a knowledge base relating composition, structure and properties of various classes of complex hydrides by investigating the effects of varying stoichiometry and processing history on their crystal and microscopic structure, chemical, thermodynamic and physical properties.
- Extend and refine the current understanding of the mechanisms of the solid-state transformations occurring in a few model hydrides, which is in a rudimentary state, by examining the effects of various chemical and structural modifications and processing strategies on the structure-property relationships, and dehydrogenation and hydrogenation behavior of novel non-transition metal-based complex hydrides. Special emphasis is placed on bridging lengths scales ranging from a few tenths of a nanometer (a single interatomic distance) to microns (a single grain) and centimeters (assemblies of multiple particles varying in size, shape and structure) in order to fully explore the potential of novel solids.
- Integrate experiment with modeling and first principles theory to provide a fundamental understanding of the nature of hydrogen bonding, the structure and stability of the complex hydride phases, the effect of dopants and catalysts, temperature, and pressure in altering the nature of hydrogen-metal bond, and the role of nanostructuring on the absorption and desorption properties of hydrogen.

In addition to explaining the experimental data, the theory will be used to guide experiments in search of desirable chemical composition, preparation and processing strategy, atomic scale structure and microstructure, and the nature of the substituting element(s) – all related to resultant cyclic hydrogenation and dehydrogenation properties of complex hydrides.

Recent Progress

Mechanochemically-induced transformations have been studied in various systems containing complex metal hydrides such as $NaAlH_4$ (total hydrogen content 7.4 wt. %) and $LiAlH_4$ (10.5%), amides $NaNH_2$ (5.1%) and $LiNH_2$ (8.7%), binary metal hydrides ZrH_2 (2.2%), CaH_2 (4.8%), MgH_2 (7.7%), and LiH (12.5%), and different allotropic forms of carbon (graphite and carbon black). Several previously unknown mechanochemical reactions have been discovered. One of these is a rapidly occurring transformation in the $LiAlH_4 + LiNH_2$ system. The reaction products have been characterized by X-ray powder diffraction and ^{27}Al and ^{7}Li solid state NMR spectroscopy, see Table 1 and Fig. 1.

Table 1. Results of the solid state NMR spectroscopic analysis of an equimolar mixture of $LiAlH_4$ and $LiNH_2$ and of the same ball milled in a Spex-8000 mill for 4, 12 and 30 min. Total mass of the hydrides was ~1g, total mass of balls was ~21 g.

Compound Milling time	$LiAH_4$	$LiNH_2$	Li_3AlH_6	AlN	LiH	Al
0 min	+	+	-	-	-	trace
4 min	+	+	+	+	+	-
12 min	↓	-	↑	↑	+	-
30 min	-	-	-	↑	↑	-

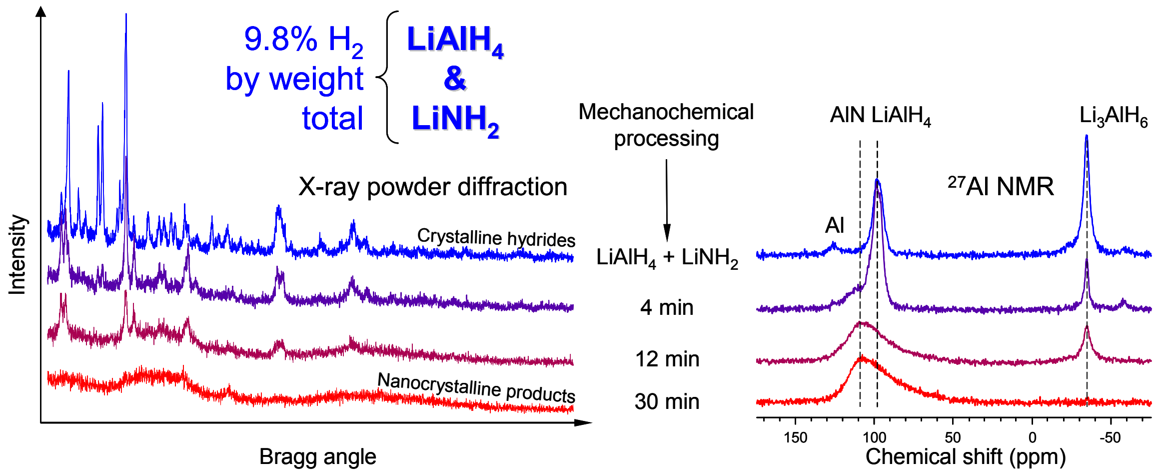

Fig. 1. X-ray powder diffraction (left) and ^{27}Al solid state NMR (right) traces of an equimolar mixture of $LiAlH_4$ and $LiNH_2$ and of the same ball milled in a Spex-8000 mill for 4, 12, and 30 min. Total mass of the hydrides was ~1g, total mass of steel balls was ~21 g.

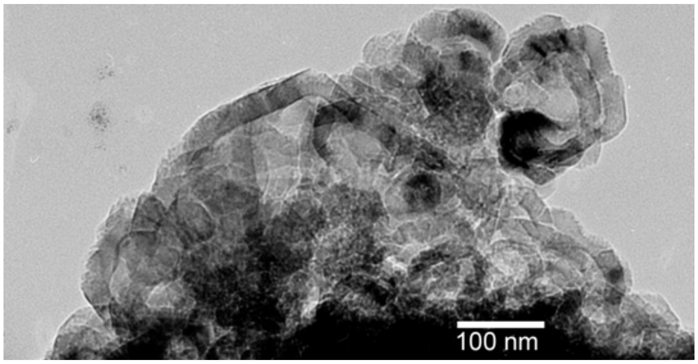

Fig. 2. TEM micrograph of the products of the mechanochemical reaction between $LiAlH_4$ and $LiNH_2$ taken in a 1:1 (molar) ratio after ball milling for 30 min.

Identification of the reaction products from the X-ray powder diffraction data is impossible because they are formed as a few micron size conglomerates of much smaller, nanometer-scale particles, see Fig. 2. Solid state NMR analysis, however, provides the much needed information in order to establish the nature of the final reaction products (Eq. 1) leading to a conclusion that several competing solid state reactions are likely (some possible examples are shown in Eqs. 2 through 4). Although the exact mechanism remains unclear, we show that a total of 6.6 wt.% hydrogen can be easily obtained from the $LiAlH_4 + LiNH_2$ system. The reversibility of reaction (1) has not been yet demonstrated but the process is fundamentally reversible (this effort will commence as soon as the construction of a high hydrogen pressure milling vial is completed).

$$LiAlH_4 + LiNH_2 \rightarrow AlN + 2LiH + 2H_2\uparrow \quad [6.6\text{ wt.\% }H_2] \qquad (1)$$

$$Al\text{ (trace)} + LiNH_2 \rightarrow AlN + 2LiH + \tfrac{1}{2}H_2\uparrow \qquad (2)$$

$$LiAlH_4 + 2LiH \rightarrow Li_3AlH_6 \qquad (3)$$

$$Li_3AlH_6 + LiNH_2 \rightarrow AlN + 4LiH + 2H_2\uparrow \qquad (4)$$

Synergistic effect of these two individual compounds ($LiAlH_4$ and $LiNH_2$) enables one to destabilize both the complex hydride and the amide without adding halides of Ti. The latter renders as much as 9 mol.% of an alanate irreversible (assuming a ~3 mol.% doping level by any Ti^{3+} halide), contaminates the hydride with an alkali metal halide, and reduces both the reversible and total hydrogen contents of the hydride. For example, 0.03 mol.% $TiCl_3$ doped $LiAlH_4$ has a total hydrogen content of 8.5 wt.% H_2 instead of 10.5%, and its theoretical reversible capacity becomes 6.4 wt.% H_2 instead of 7.9%. Examination of equimolar systems containing alanates and amides of both lithium and sodium indicates that following mechanochemical transformations also proceed quite rapidly.

$$NaAlH_4 + NaNH_2 \rightarrow AlN + 2NaH + 2H_2\uparrow \quad [4.3\text{ wt.\% }H_2] \qquad (5)$$

$$NaAlH_4 + LiNH_2 \rightarrow AlN + NaH + +LiH + 2H_2\uparrow \quad [5.2\text{ wt.\% }H_2] \qquad (6)$$

$$LiAlH_4 + NaNH_2 \rightarrow AlN + NaH + LiH + 2H_2\uparrow \quad [5.2\text{ wt.\% }H_2] \qquad (7)$$

Other mechanochemical reactions that have been studied are as follows:

$$LiAlH_4 + MgH_2 \rightarrow LiMgAlH_6 \rightarrow LiH + Al + MgH_2 + 1\tfrac{1}{2}H_2\uparrow \quad [4.7\text{ wt.\% }H_2] \qquad (8)$$

$$3LiAlH_4 + C\text{(graphite)} \rightarrow Li_3AlH_6 + 2Al + C\text{(graphite)} + 3H_2\uparrow \quad [5.3\text{ wt.\% }H_2] \qquad (9)$$

$$3CaH_2 + NaNH_2 \rightarrow CaNH + NaH + H_2\uparrow \quad [2.5\text{ wt.\% }H_2] \qquad (10)$$

$$3CaH_2 + LiNH_2 \rightarrow CaNH + LiH + H_2\uparrow \qquad [3.1 \text{ wt.\% } H_2] \qquad (10)$$

Controlled nanostructuring experiments exploring micellar self-assembly of alanates in Et_2O in order to prepare mesoporous hydrides encountered some difficulties in synthesis of desired hydrocarbon-fluorocarbon compounds. While synthesis work continues, we attempted self assembly using simpler, commercially available surfactants in a system $2LiAlH_4 + MgCl_2$ in Et_2O expecting to prepare mesoporous $Mg(AlH_4)_2$. To date we established that surfactants have a considerable effect on both the size and topology of sub-micrometer scale hydride particles.

Theoretical effort included two model systems studied from first principles: $NaAlH_4$ and MgH_2, both extensively studied experimentally in the past. In the alanate system, Na vacancies and stabilization of the AlH_3 clusters, rather than substitutions by Ti have been found to have the greatest effect on lowering the energy required to dehydrogenate the alanate. In the MgH_2, on the other hand, small substitutions of Nb in Mg sublattice during mechanochemical reactions with Nb_2O_5 catalyst appear to play a major role.

Future Plans

Considering preliminary transformation mechanisms (see Eqs. 2-4), understanding their details and identifying all possible solid state reactions is a critical enabling step in discovering the most suitable pathways toward rehydrogenation of the respective decomposition products. The most promising mixed light metal hydride systems exhibiting synergistic effects will be modeled from first principles and these theoretical results will guide our experimental efforts. Simultaneously, experiments will be designed to verify our models (e.g. reaction of Eq. 2) and refine theoretical predictions. We will also focus on the preparation and characterization of $LiAlH_4$, $NaAlH_4$, $LiNH_2$ and $NaNH_2$ nanocomposites with various volume fractions of AB_5-, AB_2-, and AB-type conventional hydrides to establish the most active combinations of the two.

In order to provide a better control over nano-structured metal hydrides, understand the role of surface effects, and exploit the potential of the nano-scale, we will continue our effort on self-assembled micelles of known alanates and other complex hydrides. The rates of absorption and desorption of hydrogen as well as the cycling properties of these materials at various temperatures and pressures will be studied.

When our PCT system arrives (HyEnergy LLC, planned shipment on May 15, 2006) and becomes operational we will begin experiments to establish whether the transformations shown in Eqs. 1, 5-10 can be induced thermally. Ball milling experiments on mechanochemically induced hydrogenation of the decomposition products shown in Eqs. 1-10 will be initiated upon completion of the construction of a high pressure vial (up to 300 bar H_2).

Publications in 2005

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3. S. Li, P. Jena and R. Ahuja, Dehydrogenation mechanism in catalyst activated MgH_2, Phys. Rev. Lett., submitted.