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Development and Characterization of Novel Complex Hydrides Synthesized via Molten State Processing

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Abstract:

This study developed novel hydrides for hydrogen storage through a novel synthesis technique utilizing high hydrogen overpressure at elevated temperatures denoted as Molten State Processing, MSP. The ultimate goal is to produce materials that have high hydrogen capacity, are stable after cycling and possess favorable thermodynamic and kinetic characteristics compatible with onboard hydrogen storage for automotive applications. In order to achieve these goals the MSP Process was developed and used to modify and form new complex hydride compounds with desired characteristics. This synthesis technique holds the potential of fusing different known complex hydrides at elevated temperatures and pressures to form new complexes having different sorption and thermodynamic properties. The new complex hydrides produced by this method were identified through structural determination and thermodynamic characterization in order to achieve a more fundamental understanding of their formation and dissociation mechanisms.

Introduction and Background

Renewed interest in hydrogen as the ultimate clean fuel of the future has spawned major R&D efforts in the area of fuel cell and other hydrogen technology. One issue that still needs to be resolved before the hydrogen economy becomes realty is developing a safe and efficient hydrogen storage device. Despite decades of research and the discovery of new intermetallic hydrides none of these intermetallics proved suitable for widespread commercial implementation of hydrogen [1]. However, the recent activities in the area of alanate hydrides have created much excitement and stimulated extensive interest into the potential use of these alanates as practical hydrogen storage media [2-5]. It has been known for decades that complex hydride alanates such as lithium aluminum hydride and sodium aluminum hydride ($LiAlH_4$ and $NaAlH_4$) have high hydrogen capacity and favorable dehydriding thermodynamics. However, difficulties in rendering these complex hydrides reversible in the solid state under practical pressure and temperature conditions and the slow kinetics of their decomposition prevented their consideration as useful hydrogen storage materials in the past. Recently, Bogdanovic et al showed that sodium aluminum hydrides could be modified to reversibly store hydrogen [2-4], opening the door to new possibilities for a practical hydrogen storage material. However, despite extensive research into complex hydrides, these systems require additional research to reach a product that has a stable hydrogen capacity with cycling and enhanced kinetics compatible with application requirements. Further modification of complex hydride systems and the understanding of the formation and decomposition of these complex hydrides are needed.

As was done with metal hydrides, attempts were made to alter their composition and form new stoichiometries of these complexes. For example, in the case of sodium aluminum hydride an elemental substitution using elements other than Na and Al was conducted and compositions such as Na_2LiAlH_6 have been reported [3-6]. The substitution of a sodium atom by a lithium atom and the transformation of the compound from Na_3AlH_6 to Na_2LiAlH_6 have caused the dehydriding plateaus pressure to change, with resultant altered thermodynamics.

Past attempts to modify alanates and other complex hydrides were conducted using wet chemistry methods or ball milling. Unfortunately, the use of wet chemistry limits the number of possible chemical combinations. The complexes have to be soluble in a solvent and many complexes are insoluble in the solvents used. Ball milling is also useful technique with practical limitations since it produces small quantities of material and in many cases the yield of the substitute complex is so small that it takes hours of high energy milling to have a significant yield [7-9].

An alternate methodology of synthesizing complex hydrides used here is to maintain them at or slightly below the melting temperature under high hydrogen pressure [10]. This takes advantage of the high atomic mobility, where diffusion and formation of new stoichiometric compositions can occur. Melt processing may be a superior methodology compared to milling as the molten chemical reactants are allowed to intimately mix the components via stirring facilitating solution of the non-molten components. Thus the molten state processing allows for intimate contact of all the constituent phases. In near-molten state processing, where the sample is kept slightly below the melting temperature of all the components, high solid state diffusional atomic mobility can be achieved as well, but not on the same scale as occurs in the liquid state.

Experimental

The molten/near-molten state processing was conducted in a high temperature and pressure reactor, sealed with PTFE O-rings. The use of PTFE limits the upper operating temperature to 350^{o}C, but in practice the maximum operating temperature was limited to ~320^{o}C to prevent leaks resulting from PTFE flow. Simultaneously, the maximum working pressure limit is held to ~340 bar (5000 psi). A 3-5 grams sample of a mixture was placed in the reactor with a magnetic PTFE coated stirring bar. The reactor was attached to a volume calibrated manifold while seated on top of a magnetic stirrer/heating unit. Heating was conducted via a temperature controlled heating mantle. Over temperature protection was supplied via a separate over-temperature probe. A 340 bar (5000 psi) pressure transducer was mounted near the sample reactor and was part of the sample volume reactor. Sample temperature and pressure, heating mantle temperature, and manifold pressure were monitored and logged by a data acquisition computer. Specific temperature and pressure conditions depended on the material being processed. For example, for $NaAlH_4$, whose melting point is ~185^{o}C, the reactor was heated to 190-200^{o}C at 200–340 bar (3000-5000 psi) for 2-5 hours. The melt was cooled under pressure to prevent decomposition. Once the temperature dropped below the point where significant hydride material decomposition was expected to occur, the reactor was vented to near atmospheric pressure, whereupon the reactor was removed and returned to an inert atmosphere glovebox for sample removal for analysis. All sample preparation and analysis were conducted under an inert atmosphere.

Sample preparation can consist of any desired level of pre-mixing, from simple hand shaken mixes prepared in closed vials, through mortar and pestle hand-milled mixes, to ball-milled mixtures; which often show some extent of chemical reaction prior to melting. Typically $TiCl_3$ was used to catalyze sodium alanatebased mixtures to insure reversibility, but other catalysts were used as well. After melt processing, samples were characterized using powder x-ray diffraction, XRD, analysis using Cu-K_α radiation. Temperature programmed desorption, TPD, experiments were also utilized to ascertain material reactivity and hydrogen content. Hydrogen desorption analyses were conducted in a modified Sieverts apparatus. Heating rates of 2.5-3^o/min are routinely obtained for TPD experiments. Sample sizes were typically 1 gram.

Results and Discussion

Initial experiments utilizing molten state process (MSP) were made in synthesizing Na_2LiAlH_6 by mixing appropriate amounts of LiH, NaH, $NaAlH_4$ and 4 mol% $TiCl_3$. The mixture was maintained at 200 bar (3000 psi) hydrogen pressure and heated to 190^{o}C, slightly higher than the melting temperature of $NaAlH_4$. Fig. 1 shows the XRD spectrum of the resultant composition. From the indexing of this pattern, Na_2LiAlH_6 was clearly identified. Similar procedures were used to prepare solvent free sample for neutron diffraction study [11].

In Fig. 2 the formation of $NaMgH_3$ by combining $NaAlH_4$, Mg and 4m% $TiCl_3$ was achieved while Figure 3 shows that K_3AlH_6 results from molten state processing of $LiAlH_4$, KH and 4m%$TiCl_3$.

Through Molten State processing, it has been shown that ionic exchange between the different mixed cations has been demonstrated to take place. Furthermore, the formation of complex hydride can occur free from solvent contaminants. Elemental substitution occurs where it otherwise would be difficult to achieve using wet chemistry. The yield of the desired complex hydride is higher than that achieved by conventional ball milling techniques alone. The molten state process can also be used as a method for off-board rehydriding.

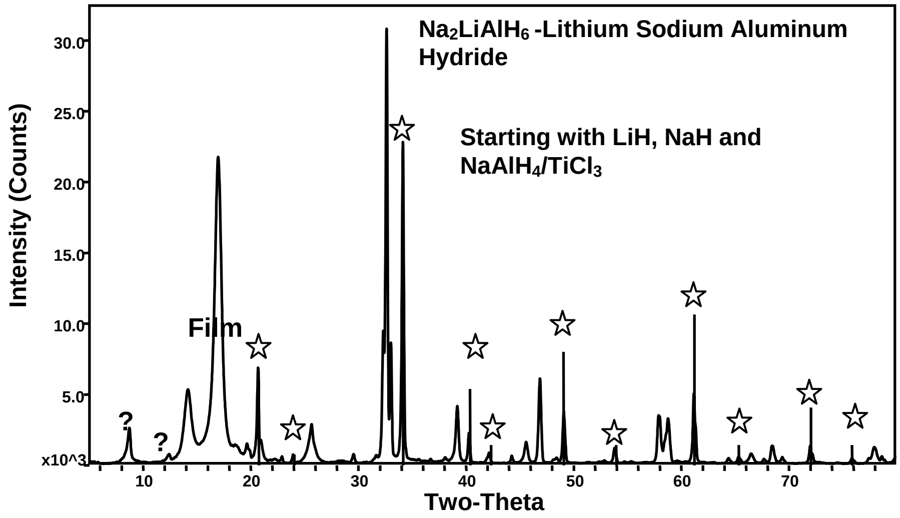

Fig. 1 X-ray diffraction pattern of Na_2LiAlH_6 synthesized using MSP.

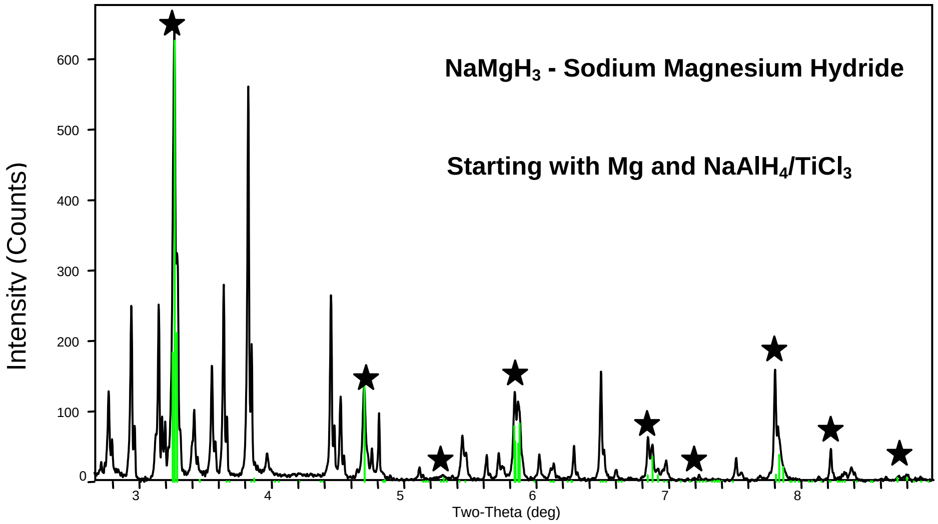

Fig. 2 XRD pattern $NaMgH_3$ synthesized using MSP

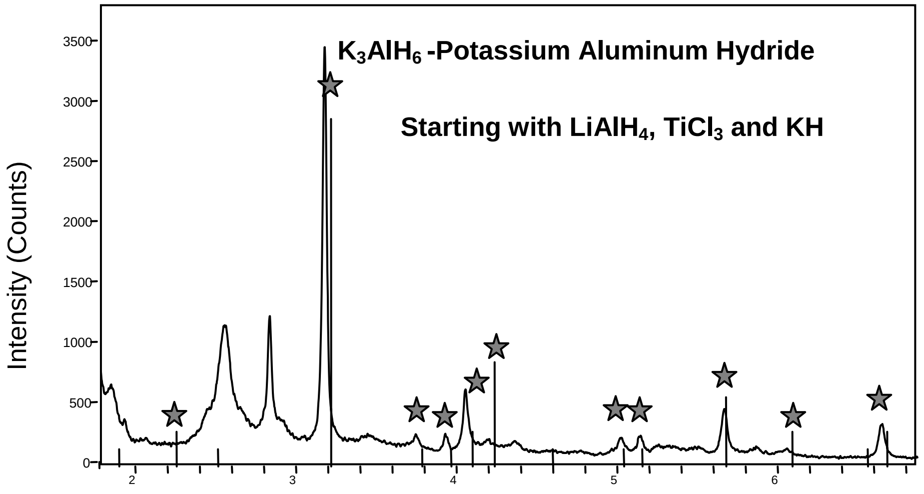

Fig. 3 XRD pattern K_3AlH_6 synthesized using MSP.

Conclusions

Molten State Processing, MSP, has been demonstrated as a viable method for producing mixed cation alanate compounds. Through the simulations melting of alanate compounds with either binary hydrides or metals and exposure to high hydrogen pressures, the compounds $NaMgH_3$, K_3AlH_6 and Na_2LiAlH_6 have been readily formed in the presence of a $TiCl_3$ catalyst. This new process holds the potential to rapidly and economically synthesis many mixed cation complex hydrides at high yields. In addition, new mixed cation hydrides can also be synthesized readily. It is the possibility of forming new and yet unidentified compounds which hold the highest promise for meeting the very demanding requirements of high hydrogen storage capacity while being reversible at moderate temperature and pressure conditions.

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