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Facile Cycling of Ti-Doped $LiAlH_4$ for High Performance Hydrogen Storage

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The discovery and development of high-capacity solid-state hydrogen storage materials is the focus of intensive efforts worldwide. Aluminum hydrides and complexes such as AlH_3, $LiAlH_4$, and $NaAlH_4$ and have attracted much attention in this regard.[1−6] These materials are characterized by theoretical hydrogen contents of 10.0, 7.9, and 5.6 wt %, respectively, and possess low H_2 release temperatures (∼150 °C) when doped with small amounts of transition-metal catalysts (usually Ti); furthermore, Al is cheap, plentiful, and widely used in 21st century technologies. However, the major impediment to their widespread application for hydrogen storage remains their lack of reversibility. Of these three materials, only $NaAlH_4$ has been recharged with hydrogen gas under acceptable conditions (∼100 bar H_2 pressure at 120 °C), but the U.S. Department of Energy's 2010 goals for a hydrogen storage system (6.0 wt % H_2 and 45 kg H_2/m^3) rule out $NaAlH_4$ as a viable material for transportation applications.

Both $LiAlH_4$ and $NaAlH_4$ release hydrogen in two stages:

$$3MAlH_4 \rightarrow M_3AlH_6 + 2Al + 3H_2 \qquad (1)$$

$$M_3AlH_6 \rightarrow 3MH + Al + 1.5H_2 \qquad (2)$$

For $NaAlH_4$, eqs 1 and 2 are both endothermic, whereas in the case of $LiAlH_4$, eq 1 is actually exothermic ($\Delta H_1 = -10$ kJ/mol of H_2, $\Delta H_2 = +25$ kJ/mol of H_2).[7] The reaction enthalpy for eq 1 when M = Li is dominated by the high lattice energy of Li_3AlH_6, with its small cations and triply charged anion. As the entropy change corresponding to release of H_2 must be positive, the implication for $LiAlH_4$ is that eq 1 as written is thermodynamically irreversible under all practical conditions. Thus, although $LiAlH_4$ contains over 40% more hydrogen by weight than its Na congener, it appears to have been widely accepted that $LiAlH_4$ cannot be recharged,[8−10] and there have been no reports of its use for reversible hydrogen storage.

However, the unfavorable thermodynamics of eq 1 may be altered by carrying out the reaction in solution, with the solvation of $LiAlH_4$ contributing to an (ideally) endothermic ΔH value. As early as 1963, Ashby et al.[11] reported that a mixture of LiH and activated Al in THF or diglyme solvent reacted with 350 bar H_2 at 120 °C to produce $LiAlH_4$. This THF synthesis has been improved recently by Graetz et al.[12] using Ti doping to significantly lower the pressure and temperature required. A variation on this method employing high-energy ball milling of a LiH/Al/H_2 mixture in the presence of THF has also been reported by Ritter and co-workers.[13]

While the methods of Ashby et al. and Ritter and co-workers result in the ultimate formation of $LiAlH_4$ from LiH, Al, and H_2, they demand a large energy investment in the temperature, pressure, and/or mechanical energy required as well as for the removal of the THF solvent (by vacuum drying at 60 °C for several hours). Ashby et al. noted that it is very difficult to remove the final vestiges of THF; however, their attempts to prepare $LiAlH_4$ in Et_2O met with little success.[11] The prolonged baking in vacuo required to remove THF compromises the integrity of a Ti-activated product, which, as noted above, is only kinetically stable. Thus, for example, Ritter and co-workers' and Graetz et al.'s multistep schemes for hydrogen storage by $LiAlH_4$ necessitate separation by filtration of the Ti catalyst and unreacted LiH and Al before removal of coordinated THF, with redoping required for each successive cycle.[12,13]

Here we report a simple, effective, and energy-efficient single-stage procedure for the direct rehydrogenation of Ti-doped $LiAlH_4$ under mild conditions, and we present the first study of its performance as a high-capacity hydrogen storage material at moderate temperatures. Our recharging process exploits low-boiling dimethyl ether (Me_2O; bp = −24 °C) as the reaction medium to stabilize the nascent $LiAlH_4$. The reaction is carried out in an autoclave at ambient temperature, and the volatile solvent can be vented easily along with excess H_2 upon completion of the reaction, leaving a fine, dry powder product that requires no further processing and releases large amounts of H_2 rapidly and at moderate temperatures.

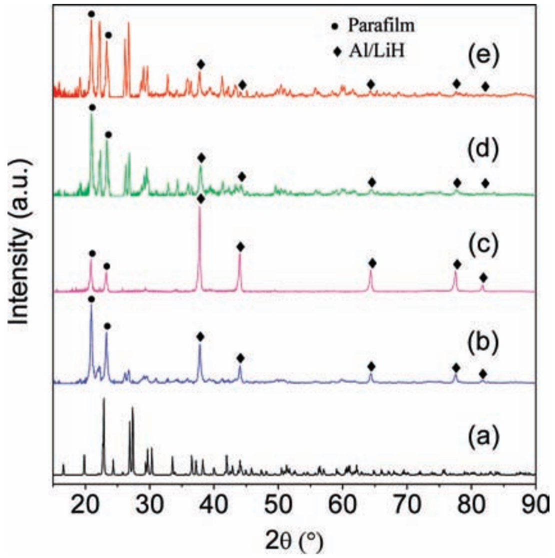

Figure 1. XRD patterns of $LiAlH_4$ samples: (a) ICDD reference plot; (b) ball-milled (2.0 mol % $TiCl_3$); (c) fully dehydrogenated (0.2 mol % $TiCl_3$); (d) rehydrogenated (2.0 mol % $TiCl_3$); (e) rehydrogenated (0.2 mol % $TiCl_3$).

In a typical procedure, as-received $LiAlH_4$ was doped with $TiCl_3$ by mechanochemical milling and then dehydrogenated in vacuo at 120 °C for 5 h. Complete desorption of H_2 according to eqs 1 and 2 to leave LiH and Al was confirmed by powder X-ray diffraction

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(XRD) measurements (Figure 1c). In a glovebox, ~650 mg of the resulting material was transferred to a 500 mL reaction vessel, which was then charged with Me_2O (55 g) using a solvent pump. H_2 gas (100 bar) was added to the vessel, which was sealed and stirred at room temperature. After 24 h, the pressure was vented cautiously, and the reactor was transferred to a glovebox, where the solid contents were removed for analysis by powder XRD (Figure 1) and temperature-programmed desorption (TPD) measurements (Figure 2).

Initial experiments employed a Ti content of 2.0 mol %, as this amount was shown by Bogdanović and Schwickardi[14] to work optimally in the activation of $NaAlH_4$. However, as the catalyst activates both hydrogen uptake and release and as eq 1 is exothermic for $LiAlH_4$, this level of Ti resulted in some instability of the product at ambient temperatures, leading to residual Al in the XRD pattern and to a lower amount (5.0 wt %) of desorbed H_2 (Figures 1d and 2c). Such instability was also evident in our attempts to activate as-received $LiAlH_4$ directly: ball milling with 2.0 mol % $TiCl_3$ resulted in the loss of ~80% of the available hydrogen, with desorption of only 1.4 wt % below 200 °C (Figures 1b and 2b). This sensitivity is consistent with previous reports describing the H_2 desorption properties of doped $LiAlH_4$.[15] Decreasing the catalyst level to 0.5−0.2 mol % rendered the material significantly more stable toward decomposition and resulted in almost quantitative regeneration of $LiAlH_4$ (Figures 1d and 2e,f), raising the amount of desorbable H_2 as high as 7.0 wt %, as compared with 7.5 wt % for the as-received material. As is also evident from Figure 2, the Ti catalyst lowers the H_2 desorption temperature significantly, with release commencing at ~80 °C (in contrast to 180 °C for the as-received material; Figure 2a). Hydrogen release was rapid between 100 and 150 °C for the Ti-doped samples and was effectively complete at ~180 °C. As described above, Ti-doped $LiAlH_4$ can be completely dehydrogenated at 120 °C in vacuo over a period of several hours.

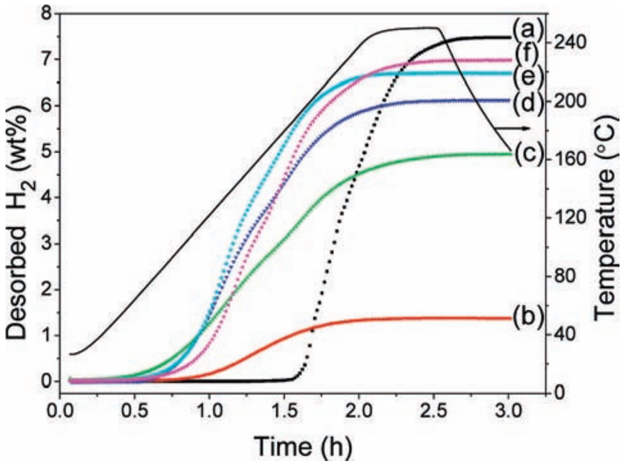

Figure 2. TPD plots for $LiAlH_4$ samples: (a) as-received; (b) ball-milled (2.0 mol % $TiCl_3$); (c) rehydrogenated (2.0 mol % $TiCl_3$); (d) rehydrogenated (1.0 mol % $TiCl_3$); (e) rehydrogenated (0.5 mol % $TiCl_3$); (f) rehydrogenated (0.2 mol % $TiCl_3$).

We ascribe our success in recharging $LiAlH_4$ in this way to the high dipole moment of Me_2O (1.30 D), which exceeds that of Et_2O (1.15 D; compare with 1.63 D for THF, all values for the gas-phase molecules). As appreciated by Ashby et al.,[11] Et_2O is too feeble a solvent to reverse the thermodynamics of eq 1. The interaction between Me_2O and Li^+ is clearly strong, such that a $Li \cdot x(Me_2O)AlH_4$ adduct is the immediate reaction product; it is this complexation of the small Li^+ ion that allows eq 1 to become reversible in solution by leveling the thermodynamic playing field that is otherwise dominated by the high lattice energy of Li_3AlH_6 (see above). However, the high vapor pressure of Me_2O (~5 bar) then allows the coordinated solvent to desorb cleanly and rapidly at room temperature once the pressure is reduced, leaving dry Ti-activated $LiAlH_4$ while avoiding the protracted and compromising treatment required to desolvate the THF adduct.

While the majority of current research into hydrogen storage is focused on the quest for new materials, we have shown here that the development of new processes that establish sustainable cycles for known materials is an equally valid approach that could provide a solution to the hydrogen storage Grand Challenge. Previous attempts to prepare $LiAlH_4$ directly by hydrogenation of LiH and Al metal had established that the key to success was the identification of a solvent that is sufficiently coordinating to support the nascent $LiAlH_4$ in the reaction environment yet also volatile enough to be removed easily once it has served this purpose; we have now found this long-sought solvent. Hence, we have demonstrated that Ti-doped $LiAlH_4$ can operate as a reversible hydrogen storage material that can release up to 7 wt % hydrogen commencing at temperatures as low as 80 °C and that the material can be recharged almost quantitatively under remarkably mild conditions by employing liquid Me_2O as a solvent. Our simplification of the hydrogenation half-cycle may provide the key to harnessing the long-recognized potential of this lightweight, high-capacity material as a practical hydrogen carrier. We have subjected Ti-doped $LiAlH_4$ prepared as described above to subsequent hydrogenation/dehydrogenation cycles, and although there is some drop-off in the amount of hydrogen released over several such experiments, it remains above 6 wt %. We are currently exploring in detail how the extended cycling behavior of activated $LiAlH_4$ produced in this way depends on the concentration of the Ti dopant and on the exact recharging conditions and handling procedures employed.

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Note Added after ASAP Publication. After ASAP publication on March 18, 2009, the first sentence after eq 2 was modified. The corrected version was published March 20, 2009.

Supporting Information Available: Experimental details and XRD patterns for doped, dehydrogenated, and recharged samples of $LiAlH_4$ with various levels of Ti catalyst. This material is available free of charge via the Internet at http://pubs.acs.org.

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