# Novel Catalytic Effects of Fullerene for $LiBH_4$ Hydrogen Uptake and Release

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**Our recent novel finding, involving a synergistic experiment and first-principles theory, shows that carbon nanostructures can be used as catalysts for hydrogen uptake/release in aluminum based complex metal hydrides (sodium alanate) and also provides an unambiguous understanding of how the catalysts work. Here we show that the same concepts can be applied to boron based complex hydride such as lithium borohydride, $LiBH_4$. Taking into account electronegtivity and curvature effect a fullerene- $LiBH_4$ composite demonstrates catalytic properties with not only lowered hydrogen desorption temperatures, but regenerative rehydriding at relatively lower temperature of 350 ºC. This catalytic effect likely originates from interfering with the charge transfer from Li to the $BH_4$ moiety, resulting in an ionic bond between $Li^+$ and $BH_4^-$, and a covalent bond between B and H. Interaction of $LiBH_4$ with an electronegative substrate such as carbon fullerene affects the ability of Li to donate its charge to $BH_4$, consequently weakening the B-H bond and causing hydrogen to desorb at lower temperatures as well as facilitating the absorption of $H_2$ to reverse the dehydrogenation reaction. Degradation of cycling capacity is observed and is attributed to forming irreversible intermediates or diboranes.**

## *Introduction*

The ability to control the synthesis of nanostructure building blocks and preserve the nanoscale characteristics of the subsequent assembly is one of the essential foundations for the utilization of nanotechnology to produce effective hydrogen storage materials. In a previous study we showed that co-dopants of graphite and Ti- metal resulted in further enhancement of dehydrogenation and hydrogenation kinetics of sodium aluminum hydride [1]. Our recent experimental data has shown that graphitic nanomaterials are efficient catalysts, enhancing the dehydrogenation and hydrogenation of $NaAlH_4$ even without the use of Ti catalyst [2, 3].

One key component of realizing the hydrogen economy for transportation applications is developing cost effective materials that can store and release hydrogen with large gravimetric and volumetric densities under moderate thermodynamic conditions[4, 5]. One of the most promising classes of materials for hydrogen storage is complex hydrides such as alanates and borohydrides for their high hydrogen capacity. Among these, lithium borohydride ($LiBH_4$) is a widely studied material due to its gravimetric (18.4 wt %) and volumetric (121 $kg/m^3$) hydrogen capacity. The decomposition of $LiBH_4$ is reasoned to occur in two steps:

**Equation 1** $\mathbf{2LiBH_4 \leftrightarrow 2LiH + 2B + 3H_2}$ **[13.8 wt%]**

**Equation 2** $\mathbf{LiH \leftrightarrow Li + 1/2H_2}$ **[18.4 wt%]**

The uncatalyzed, step (1) takes place above 400 °C [6], while decomposition of LiH takes place at ~ 950 °C and is not considered useful.[7] The kinetics of hydrogen uptake and release of these materials are such that catalysts are needed to improve the reaction rates.

Attempts to induce hydrogen sorption reversibility at lower temperatures of $LiBH_4$ have included the use of carbonaceous and metal catalysts, and other metal hydride additives. A recent destabilization strategy via the ball milling of $LiBH_4$ and $1/2MgH_2$ has resulted in a system with improved thermodynamics and hydrogenation reversibility due to the higher electronegativity of the substitution element (e.g. Mg)[8, 9]. In addition, various carbonaceous-metal hydride composites have demonstrated favorable kinetics and thermodynamics. Nano/molecular scale structures offer promising materials properties for hydrogen storage. These structures can enhance hydrogen uptake and release due to short diffusion distances, high-surface area for sorption, potentially new physical phases (e.g., unique electronic environments). They can also play a catalytic role in enhancing the kinetics of formation and decomposition of complex hydrides by acting as a charge donor/acceptor interfering with charge configuration holding the complex hydride together. These properties combined with favored properties of hydrogen storage compounds can result in materials with potentially high storage capacities, reduced temperature and pressure needed for absorption/desorption, faster kinetics, and active surface sites capable of catalyzing hydrogen association/dissociation. In particular, the incorporation of $LiBH_4$ into activated carbon and the addition of single-walled nanotubes (SWNT) have demonstrated improved dehydriding/rehydriding kinetics resulting in systems with partial reversibility at reduced temperature/pressure conditions.[10-12]

Analogous work has been performed by several groups in the use of carbon materials as possible catalysts for the metal hydride $NaAlH_4$[13-17]. Four of these groups report that carbon materials are catalysts for the dehydrogenation and rehydrogenation of $NaAlH_4$[13-16]. However, all of the studies utilize ball milling which is known to degrade fragile carbon nanostructures[18, 19] and is known to introduce Fe contamination from the ball mill vial and/or balls[20, 21], and Fe is an excellent catalyst for hydrogen sorption of $NaAlH_4$[22]. When studying carbon materials as catalysts for metal hydrides, care must be taken in the preparation of samples not to mix causes of observations. We were interested in investigating this property of carbon nanomaterials with sample preparation techniques which *avoid* introduction of metal contaminants and degradation of the carbon nanostructures. We used a solvent preparation technique to intimately mix the $LiBH_4$ and carbon without introducing metal contaminants.

In this paper we not only show that carbon nanostructures such as $C_{60}$ fullerenes can be used as catalysts for dehydrogenation and rehydrogenation of lithium borohydride, but also builds on our fundamental understanding of how these catalysts work. This has significance beyond just $LiBH_4$ and can apply to other complex metal hydride materials. $C_{60}$ fullerene, carbon nanotubes, and graphene are models of zero, one, and two dimensional carbon nanostructures, and their chemistry can be manipulated by changing their curvature and dimensionality. Previous first-principles calculations show that the energies needed to remove a hydrogen atom from $NaAlH_4$ supported on a (5,0) carbon nanotube or $C_{60}$ fullerene are significantly smaller than those in pure sodium alanate and are nearly the same as when Ti is substituted at the Na site in sodium alanate.[3] Interestingly, no structural changes of the carbon nanostructures take place, the carbon nanotubes and fullerenes behave as true catalysts. The results can be explained in very simple terms by using the chemistry of the carbon substrates and that of the $NaAlH_4$ and $LiBH_4$ clusters. Note that the $LiBH_4$ cluster is stabilized by the formation of the $(BH_4)^-$ anion, charge balanced by having $Li^+$ in the cationic form. As $LiBH_4$ interacts with a substrate that is as electronegative as $BH_4$, the ability of Li to donate the electron to form the $(BH_4)^-$ anion is compromised and hence the covalent bond between B and H is weakened. This weakening of the boron-hydrogen bond leads to lowering of the hydrogen desorption energy and hence to improved kinetics. In the following we establish this picture through experiment and our understanding of the analogous $C_{60}$-$NaAlH_4$ composite system.[3]

***Experimental***

Samples were prepared as in a similar fashion to graphitic-$NaAlH_4$ composites as previously published.[3] The $C_{60}$-$LiBH_4$ composite was formed by combining fullerene and $LiBH_4$ as 1.6 mole % composite (e.g. 0.887 and 1.622 g, respectively) in a Schlenk flask within an Argon-filled glove box. Tetrahydrofuran (THF) was added and the mixture stirred with a Teflon coated magnetic stir bar for 30-60 minutes. The solvent was removed under reduced pressure, resulting in a dark brown powder, and was collected for further characterization.

Chemicals were used as provided by the supplier and are listed by supplier as follows. Acros: THF (anhydrous, 99.9%, inhibitor-free). Albemarle: $LiBH_4$. Sigma-Aldrich: $C_{60}$ (98%), THF (anhydrous, ≥99.9%, inhibitor-free). Measurements were made on a Sievert's apparatus, a Hy-Energy PCT Pro 2000. Dehydrogenation experiments were run at approximately $1.0 \times 10^5$ Pa as the samples were heated to 350 °C at 2 °C/min followed with an isotherm at 350 °C for ~3 hours. Before the initial dehydrogenation experiment the sample was heated to 150 °C for one hour under vacuum to remove residual THF present in the sample matrix. Rehydrogenation was conducted at 350 °C starting with a $\sim 1.2 \times 10^7$ Pa $H_2$ gas overpressure for 12 hours.

## ***Results and Discussion***

Based on our initial investigation in to graphitic-metal hydride composites, we explored the $C_{60}$- lithium borohydride composite system in detail. Mixtures containing $LiBH_4$ with $C_{60}$ were made using a ball mill *free* preparation method that prevents the degradation and creation of defect sites in the carbon materials. The results of the hydrogen cycling via temperature programmed desorption (TPD) are shown in Figure 1 below. These results show the first, second, and third desorption cycles (careful measures were undertaken to remove all residual solvent, insuring an accurate first desorption cycle). The fullerene additive clearly aids in desorption and absorption of hydrogen, and as expected, pure $LiBH_4$ yields weak desorption at 350 ºC (ca. 1%) and with no additives does not rehydride from the dehydrogenation products. The hydrogen desorption temperature of the $C_{60}$-$LiBH_4$ composite is lowered to *ca.* 320 ºC by 80 ºC by addition of $C_{60}$ (compared to *ca.* 400 ºC in uncatalyzed $LiBH_4$). These composites also show the remarkable ability for hydride restoration by 4.2 wt% over 12 hour's time with $\sim 1.2 \times 10^7$ Pa $H_2$ pressure. Subsequent hydrogen desorption measurements after composite regeneration show only slightly decreased hydrogen storage capacity, with 4.0 wt% rehydriding. The decrease in capacity can be attributed to the formation of non-reversible lithium borohydride intermediates (e.g. $LiB_xH_y$) and or the formation of diborane $B_2H_6$ during the hydrogenation/dehydrogenation cycles. The formation of non-reversible intermediates will act as inert mass in our measurements leading to lower capacity every time these intermediates form. The formed diborane is expected to react with the pressure vessel walls or is vented into the gas manifold. This will result in losing boron with every cycle and limits the amount of reversed $LiBH_4$.

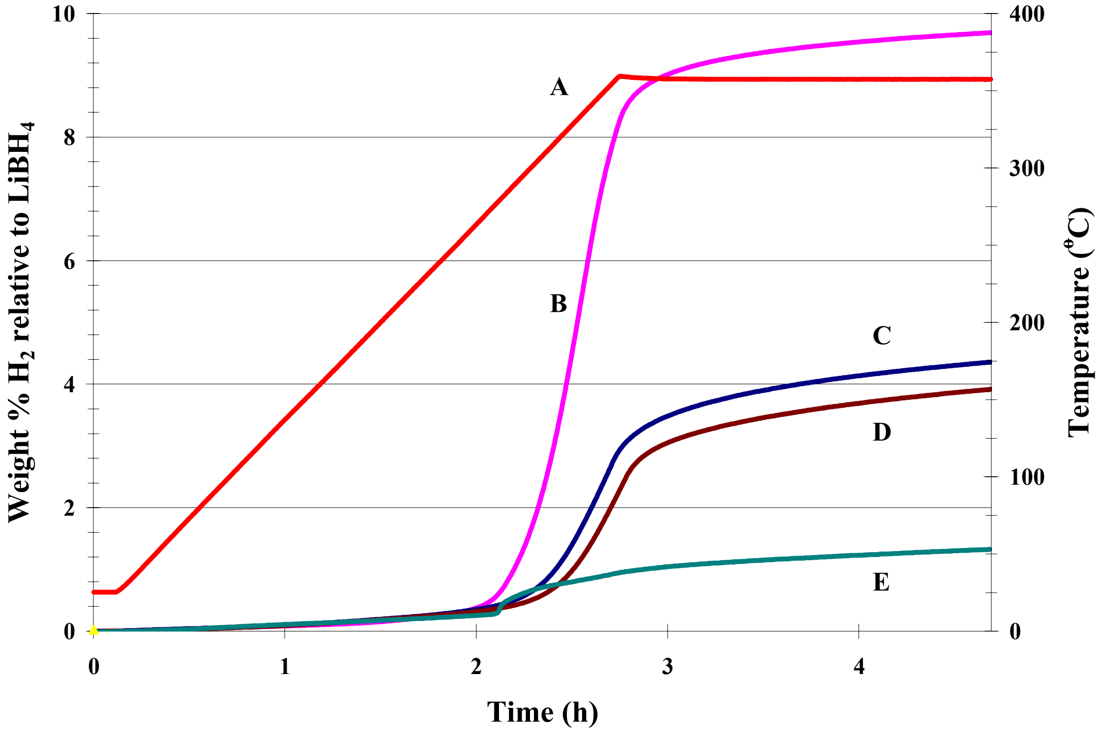

**Figure 1:** TPD curves for the $C_{60}$-$LiBH_4$ composite: first desorption (B), second desorption (C), and third desorption (D). The Temperature gradient (A) increased at 2 ºC/min and held at a 350 ºC isotherm. Hydrogen reabsorption was done with ~1.2 x $10^7$ Pa $H_2$ a 350 ºC for 12 hours. Control TPD of as-received $LiBH_4$ is represented by (E).

For metal hydride, $MH_n$, destabilization of the M-H bonds results in lowering the hydrogen desorption energy. The stability of the $LiBH_4$ is likely governed by the charge transfer form Li to $BH_4$, transforming the former into a cation and the latter in an anion. Thus, the way to reduce the bond strength between B and H in $LiBH_4$ would be to introduce a competitor for the charge donation from the Li atom. This can be realized in the form of an electronegative substrate on which $LiBH_4$ is supported. In this case, the Li atom could have its electron contributed to the substrate, to the $BH_4$ unit, or have it delocalized and shared by both. Situations involving the electron being transferred elsewhere than the $BH_4$ unit will result in a weakening of the B-H bond and lead to the lowering of the hydrogen desorption energy. The electron affinity of the substrate thus becomes intimately connected with the hydrogen desorption process, since the larger the electron affinity of the substrate, the greater the probability of Li donating its electron to the substrate.

The mechanism for $H_2$ absorption aided by carbon materials is of great interest. Previous work has shown that the catalytic effects are not due to unknown metal contamination but instead are related to the curvature of the graphitic additive.[3] Carbon nanotubes are graphitic carbon sheets rolled into tubes, and it is possible that the accelerated absorption relative to flat graphite particles is due in part to the changes in the $\pi$- and $\sigma$-bonding orbitals that the $H_2$ molecules interact with on the surface of the material. The fullerene material $C_{60}$ is a 7 Å sphere made of graphitic carbon and has increased curvature relative to the 8-50 nm carbon nanotubes, and exhibits the strong catalytic affect on $NaAlH_4$[3] and now $LiBH_4$, suggesting the curvature of the carbon material is important to the function. *Ab initio* modeling has been undertaken to further understand the interactions taking place between metal hydrides and the carbon nanomaterials.

The back donation of electrons from the metal to the carbon can alter the way hydrogen and complex hydrides interact with fullerene. The donation process is hypothesized to be dependent on the carbon configuration and surface curvature. Changes in curvature of graphitic materials can also have unexpected effects due to localization/delocalization of electrons. Theoretical calculations showed that the geometrical parameters deviate from the values obtained from simple wrapping of a perfect hexagonal sheet. The lattice constant along the tube axis exhibits a slight shrinking. The radial breathing mode (RBM) frequency does not follow the usually assumed 1/d behavior and there is a general softening with the increase of curvature; thus the deviation from the expected behavior increases with increasing curvature. The lattice constant along the tube axis also exhibits a slight shrinking[23] when compared to bulk graphite.

## *Conclusion*

Our experimental studies were conducted to examine the interaction of lithium borohydride with fullerene. We have shown that our results support our previous studies into graphitic-metal hydride composites, providing insight into the interaction of these hydrides with nanostructured carbon surfaces. We have shown that carbon nanostructures, traditionally thought of as hydrogen storage materials, can in fact be used as catalysts for hydrogenation/dehydrogenation of lithium borohydride, $LiBH_4$. $C_{60}$ materials were found to be an excellent carbon additive for $LiBH_4$, rehydriding $LiBH_4$ by 4.2 wt% over 12 hour's time. We suspect that a contributing factor to the performance of the $C_{60}$ is its dispersibility. The $C_{60}$ molecules likely have their entire surface available for interaction with $LiBH_4$. When intimately interacted with $LiBH_4$ the $C_{60}$ substrate was found to have a dramatic effect on the hydrogen removal energy. Experimentally we see that the curvature of the nanostructures plays a significant role in this process and $C_{60}$ fullerene is a better catalyst than the nanotubes. We observed degradation of capacity with cycling and we attributed that to the formation of irreversible intermediates and/or diboranes. Further experiments exploring the catalytic effect of carbon nanomaterials on other complex metal hydrides, e.g. borohydrides, are ongoing.

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## *Author contributions*

R.Z. conceived the project. R.Z., P.A.B. and M.S.W. designed the experiments. M.S.W. synthesized the mixtures and performed the experiments. M.S.W., P.A.B., and R.Z. co-wrote the paper.

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