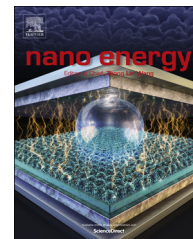




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COMMUNICATION

Reversible Li-insertion in nanoscaffolds: A promising strategy to alter the hydrogen sorption properties of Li-based complex hydrides



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Abstract

Intercalation and de-intercalation of lithium into graphene layers is a well-established phenomenon in Li-ion battery technology. Here we show how this phenomenon can be exploited to destabilize, and alter the hydrogen sorption behaviour of Li-based metal hydrides (LiBH₄ and LiAlH₄), thereby achieving lower hydrogen release temperatures, high hydrogen sorption capacities and enhanced kinetics. Close contact between the hydride and carbon surface facilitates reversible intercalation of Li into graphene layers at moderate temperatures when nanoconfined in turbostratic carbon nanoscaffolds. This leads to the formation of intercalated Li (LiC_x, instead of LiH) during decomposition, resulting in the release of the full hydrogen content at moderate temperatures. For example, LiBH₄ nanoconfined in this graphitic carbon material decomposes into LiC_x+B and 18.5 wt% H₂ (instead of 13.8 wt% H₂ for macrocrystalline LiBH₄) at temperatures as low as 375 °C under Ar flow. Thermodynamic effects were also observed; the decomposition temperature at 1 bar H₂ atmosphere is lowered by ~150 °C compared to the macrocrystalline LiBH₄. These findings present an interesting fundamental insight into interactions between nanoconfined metal hydrides and scaffold materials, and how such interactions can be exploited to generally improve the hydrogen sorption properties of metal hydrides.

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Introduction

The ever increasing global demand for energy and rising concern about anthropogenic global warming is driving the transition towards energy sources that are sustainable and non-polluting. However the use of renewable energy generated from sources like solar, wind, wave, and geothermal will critically depend on efficient energy storage. Due to its high gravimetric energy density, hydrogen is considered an important energy vector for a sustainable future [1]. It can be converted efficiently in a polymer electrolyte membrane (PEM) fuel cell to produce electricity for automobile or stationary applications without producing any toxic or greenhouse gases. Hydrogen can also serve as an energy buffer for renewable energy sources, and thus minimise the problems associated with the intermittent nature of the energy from renewable sources such as solar and wind [2,3]. However the use of hydrogen especially for mobile applications is seriously constrained by its low volumetric energy density which results in the need for compaction [1,4,5]. Conventional hydrogen storage devices such as high-pressure gas containers are used, but limited by safety concerns and energy penalties associated with compressing the gas. Solid state hydrogen storage in light weight metal hydrides has gained considerable attention as an alternative approach due to its advantages in terms of safety and high hydrogen densities. Li-based complex hydrides like LiBH₄, LiAlH₄ and LiNH₂ are among the promising hydrogen storage compounds due to their high hydrogen content. For example, LiBH₄ contains 18.5 wt% H₂, making it one of the highly investigated complex hydrides for reversible hydrogen storage. When heated, it undergoes partial decomposition to LiH, B and H₂ according to Eq. (1).



Unfortunately the compound is thermodynamically very stable, with a standard enthalpy of $-67 \text{ kJ}/(\text{mol of H}_2)$ for reaction (1), implying that an equilibrium pressure of 1 bar H₂ would require temperatures $>400 \text{ }^\circ\text{C}$. Practically, temperatures as high as $450 \text{ }^\circ\text{C}$ in Ar have been reported for the decomposition of bulk LiBH₄, while even harsher conditions (12 h at $600 \text{ }^\circ\text{C}$ and 155 bar H₂) are required for only partial rehydrogenation of the dehydrogenated materials [6,7]. These thermodynamical and kinetical limitations hamper the use of LiBH₄ for practical hydrogen storage. On the other, hand LiAlH₄ is metastable at room temperature therefore its decomposition is not readily reversible at moderate conditions.

Significant efforts have been made in the last decade to lower the enthalpy change for hydrogen release from LiBH₄ so that the equilibrium hydrogen release temperatures can be reduced to $100\text{-}150 \text{ }^\circ\text{C}$ which is required for combination with polymer electrolyte membrane (PEM) fuel cell applications. Mixing with other compounds is the main approach that has been intensely investigated. This is based on mixing LiBH₄ with other elements or compound which can either weaken the strong ionic bond between the Li⁺ and (BH₄)⁻¹ [8-12] or result in the formation of more stable dehydrogenation products [13-16], and thereby decrease the enthalpy change for dehydrogenation. A notable one is a mixture of LiBH₄ and MgH₂ which forms MgB₂ (instead

of B), and LiH upon dehydrogenation, and this reduces the enthalpy for the dehydrogenation reaction by $25 \text{ kJ}/(\text{mol of H}_2)$ compared with pure LiBH₄ [14]. However the system still need the addition of TiCl as catalyst to increase the hydrogen sorption kinetics while substantial hydrogen release only occurs around $350 \text{ }^\circ\text{C}$. Other systems based on reactant destabilization especially the double cation borohydrides [8-12] generally suffers from irreversibility due to phase segregation upon dehydrogenation.

Another approach that has been shown to be effective especially for improving hydrogen release kinetics and reversibility is nanoconfinement in carbon based scaffolds [2,17-19]. The improved release and uptake kinetics for nanoconfined LiBH₄ is attributed to the increased surface area to volume ratio at nanoscales, short solid-state diffusion distances (due to confinement of the dehydrogenated phases; B and LiH) and support effects. Although nanosizing is effective in improving hydrogen release kinetics and reversibility in LiBH₄, it does not mitigate the problem of high thermodynamic stability. Berube et al. [20,21] showed that at nanoscales, the contribution of the surface energy term becomes important to the total energy change upon decomposition of the metal hydride. If the surface energy of the metal hydride phase is larger than that of the metal, decreasing the size of the nanoparticles will generally lead to a lower relative stability of the hydride phase. This is the case for ionic or conventional metal hydrides like MgH₂ which show substantial decrease in stability when their sizes are reduced to dimensions between 2-5 nm, as the surface energy of the hydride is much higher than that of the resulting decomposition product (metallic Mg) [20-22]. However complex hydrides like LiBH₄ and NaAlH₄ possess much lower surface energies than their decomposition products. For example the surface energies of LiBH₄ and LiH are $0.12 \text{ J}/\text{m}^2$ and $0.44 \text{ J}/\text{m}^2$ respectively [23,24]. This implies that nanosizing of LiBH₄ will lead to effective stabilization of the hydride phase, hence higher equilibrium decomposition temperatures compared to the macrocrystalline samples, as already demonstrated for NaAlH₄ [24-28]. The significantly lower desorption temperatures reported for nanoconfined LiBH₄ can mostly be attributed to kinetic effects and irreversible reaction with scaffolds and/or impurities in the scaffolds to form oxides [29], carbides (B-C bonds [30] and LiC₂ [31]), titanates [32,33] and silicates [34,35].

In this work we exploits reversible Li insertion into graphitic carbon nanoscaffolds as a means to destabilize, and alter the decomposition pathway of LiBH₄, and thereby achieve low hydrogen release temperatures and high (de)hydrogenation kinetics. Electrochemical intercalation and de-intercalation of metallic Li into graphene layers is a well-established phenomenon in Li-ion battery technology. We show how this phenomenon can be exploited to generally alter the hydrogen sorption properties of Li-based complex hydrides. For LiBH₄ and LiAlH₄ incorporated into the pores of high purity graphitic carbon, the close contact between the compound and carbon surface facilitates reversible Li insertion into the graphene layers during (de)hydrogenation. This alters their dehydrogenation pathway resulting in full decomposition into the metal (B or Al) and intercalated Li (LiC_x, instead of LiH) at relatively low temperatures, while releasing the full hydrogen content of these

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