



Materials Science and Technology Hydrogen Storage

Hydrogen Storage Research in the Metal Hydride Center of Excellence

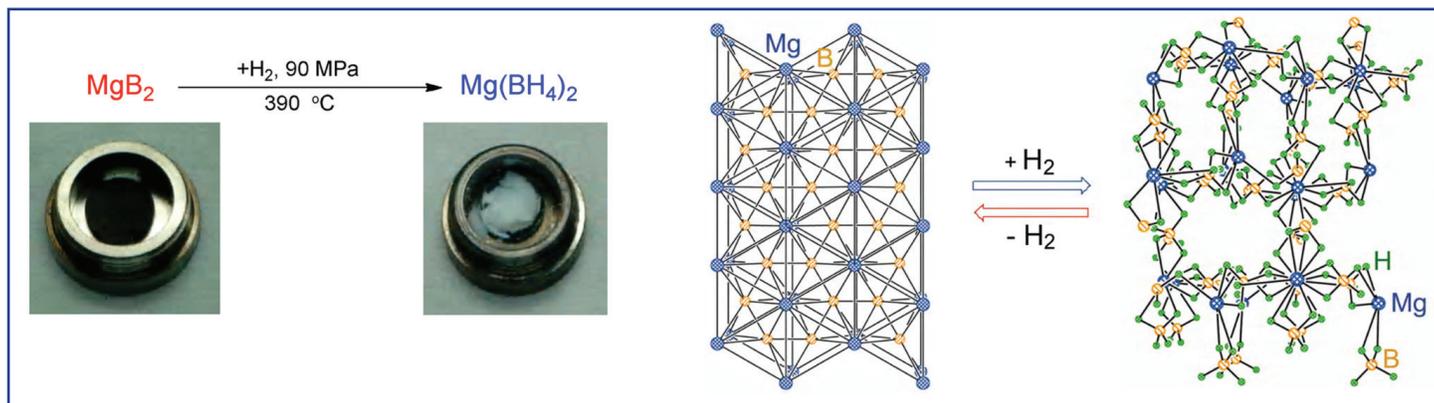


Figure 1: Storing hydrogen in magnesium borohydride.

Significant advances have been made with metal borohydride materials, but reversibility challenges still remain.

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Hydrogen has the potential to be a major alternative to fossil fuels in the effort to reduce global warming. It can be reacted electrochemically with oxygen within a proton exchange membrane fuel cell to produce only water and clean power for electric motors with ~50% efficiency. In addition, hydrogen is abundant and has almost three times the gravimetric energy density of gasoline. Thus, a hydrogen-based economy has been discussed for many years. However, a critical obstacle in the widespread application of hydrogen fuel cell technology, especially for light-duty vehicles, is the lack of a convenient, safe, and efficient method to store hydrogen gas. While the most likely short-term solution to this problem is to store hydrogen as a flammable gas in composite pressure vessels, the development of new solid-state hydrogen storage systems would have a major impact on future automotive uses of hydrogen. Significant efforts are being directed toward finding one material with all the requisite properties for practical hydrogen storage. Many of those efforts have been coordinated by Sandia as the lead laboratory of the Metal Hydride Center of Excellence (MHCoe).

The MHCoe is a 17-institution organization (eight universities, six national laboratories, and three companies) funded out of the Department of Energy's Office of Energy Efficiency and Renewable Energy. The goal of the MHCoe is to find a storage material that can release (desorb) hydrogen when it is needed with very little energy input, and can rapidly adsorb hydrogen during re-fueling. One major area of hydrogen storage research at Sandia for the MHCoe is complex metal hydrides, including metal borohydrides, amides and alanates. Complex metal hydrides have always had exceptional volumetric and gravimetric densities, yet their high thermal stabilities have excluded them from consideration as practical, on-board hydrogen storage materials. Among complex hydrides, metal borohydrides exhibit the highest hydrogen storage capacities (up to 18.5 wt%, 121 kg/m³ for LiBH₄). In particular, magnesium borohydride, Mg(BH₄)₂ is one of the most promising borohydrides that stores an impressive 14.9 wt% hydrogen by weight (References 1,2). The material can be produced by hydrogenation of magnesium diboride pressed into pellets (Figure 1, left),

which involves transformation of hexagonal P_6/mmm MgB_2 into orthorhombic $Fddd$ $Mg(BH_4)_2$ (Figure 1, right).

Sandia has been studying several metal borohydride materials including lithium, magnesium and calcium borohydrides; however, full reversibility in these materials is problematic. A key to their successful use for hydrogen storage is the ability to tailor their composition, structure and morphology, as well as to control their size-dispersion and surface functionality. One such strategy is to improve the sorption/desorption reversibility properties with additives. As shown in Figure 2, addition of small amounts of scandium trichloride/titanium trifluoride to $Mg(BH_4)_2$ results in a dramatic improvement in the kinetics of hydrogen desorption with ~ 10 wt% H_2 released at 300 °C (Reference 1).

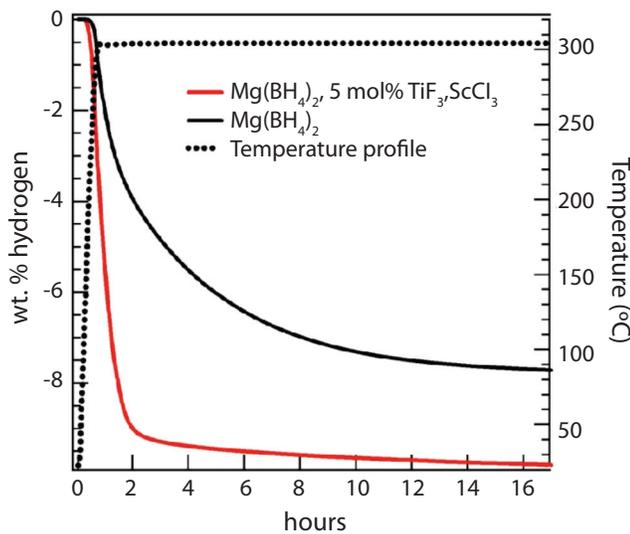


Figure 2: Temperature-programmed hydrogen desorption data for $Mg(BH_4)_2$ with 5 mol% TiF_3 and $ScCl_3$ (red curve) and pure $Mg(BH_4)_2$ (black curve) heated to 300 °C.

The decomposition of metal borohydrides during desorption is a complex process. One important limitation in using borohydride materials is the formation of stable intermediates such as dodecahydro-closo-dodecaborates ($MgB_{12}H_{12}$). Sandia has developed two strategies to mitigate this problem. One solution is to destabilize the intermediates thermodynamically, for instance CaH_2 decreases the decomposition temperature of $CaB_{12}H_{12}$ by more than 200 °C (Reference 3). Another strategy is to hydrogenate the intermediates, forming starting metal borohydrides. Almost full conversion of $Li_2B_{12}H_{12}$ into $LiBH_4$ can be achieved at high hydrogen pressures in the presence of stoichiometric amounts of lithium hydride (Figure 3).

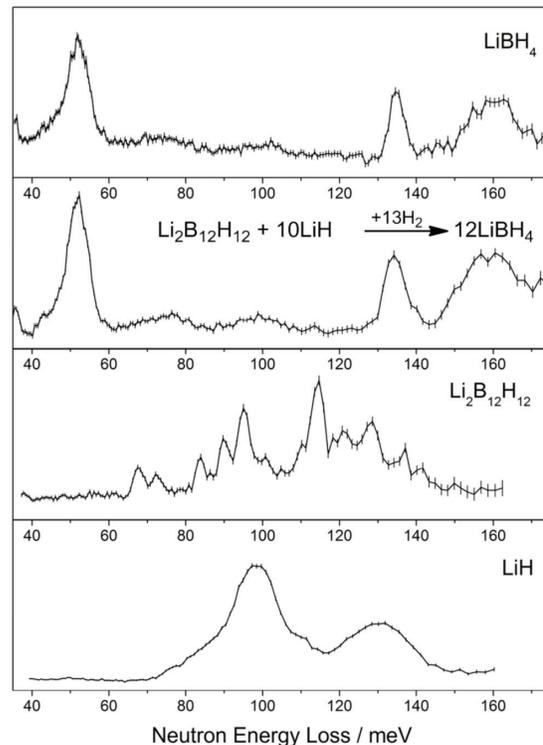


Figure 3: Neutron vibrational spectroscopy data showing full conversion of ball-milled $Li_2B_{12}H_{12} + 10LiH$ composite into $LiBH_4$.

Significant advances have been made at the MHCoe to improve the hydrogen storage characteristics of metal borohydrides. Several materials from this class of compounds have higher volumetric densities than gaseous or liquid hydrogen. The key to enable effective hydrogen storage in these materials is to improve the reversibility using destabilization, catalysis and nanoengineering approaches.

References

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