

A H₂ Storage Cycle Based on Alkali Metal Borohydrides

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There is growing concern for the development of nonpolluting energy systems, particularly in the realm of transportation. The oxidation of elemental hydrogen, H₂, to make water represents a chemical energy system that is free of carbon-based emissions. However, because it exists as a gas under standard conditions, its effective specific energy falls well below theory, since one must include the weight of its pressurizing container in the determination. Other means of storing H₂ must be found.

One approach that has received much attention is the storage of H₂ in the solid state in the form of metal hydrides. A fundamental distinction between the various classes of hydrides is whether the H₂ is released via temperature or pressure change (metallic hydrides), or via reaction with another compound, typically water (chemical hydrides). The metallic hydrides are generally considered reversible, as the reuptake of H₂ can be effected by simple pressurization, while the chemical hydrides are considered irreversible, in that they must be regenerated through a series of chemical steps involving an oxo salt.

The alkali metal borohydrides, MBH₄, where M = Li, Na, K, are chemical hydrides that form H₂, boric acid, and alkaline hydroxide when mixed with water:



Borohydrides are nonvolatile, white crystalline solids at ambient temperature, indefinitely stable in dry air, and can also be dissolved into aqueous alkaline solution.^{1,2}

We have been studying mainly the sodium and lithium salts. In particular, LiBH₄ possesses a hydrogen content of 18.5%, impressive among the hydrides in general. In theory, one gram of LiBH₄ liberates 4.11 liters of hydrogen gas at STP. It could be argued that the H-content is only 13.6% when the mass of the water required for reaction is taken into account, but if this water is acquired from the exhaust of the engine or fuel cell, then it need not be included. Volumetrically, LiBH₄ represents 0.119 g H₂/cm³, which is 1.69 times that of liquid hydrogen.

The issue in recovering H₂ from borohydride in water is whether it can be done in a controlled manner, as the rate of reaction can be explosive if not monitored properly. We have found that the rate of H₂ evolution can be rigorously controlled when set values of BH₄⁻ concentration, temperature, and pH are maintained.

Another method of controlling H₂ evolution is through the use of catalysts.³ Our strategy has been to add solid borohydride to an aqueous solution under conditions where the H₂ evolution rate is minimal, and then use the surface area of the exposed catalysts to accelerate the reaction as needed. A schematic of this approach is shown in Figure 1.

Catalysts for this purpose are usually thought to be in the form of metallic powders, such as Co and Ru. We have discovered a new class of borohydride decomposition catalysts based on fused heteroaromatics.⁴ Rates of H₂ evolution for a number of these catalysts are shown in

Figure 2. For the sake of comparison, an equivalent weight of cobalt powder was also tested. It is seen that the organic catalysts are comparable, and in the case of pyranthredione, clearly superior, to the conventional material.

The major technological challenge to the borohydride system is the economic recycling of the spent borate salts back to the starting material. Recent progress in developing such a regeneration scheme will be described.

Acknowledgement

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References

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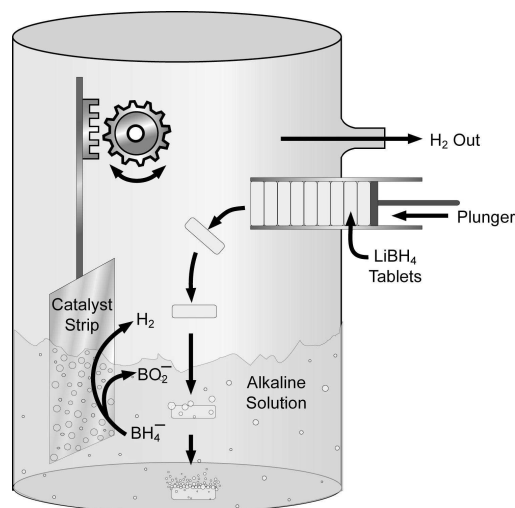


Fig.1 Schematic of a H₂ generation vessel with catalytic control of evolution rate.

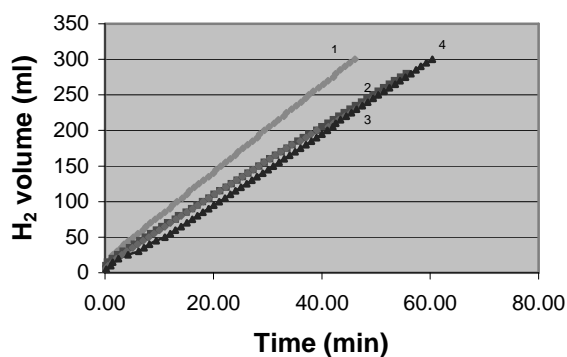


Fig. 2 H₂ evolution curves from borohydride solution for selected organic catalysts. 100 mg catalyst, 0.1 M NaBH₄ solution, pH 11 phosphate buffer; 1) pyranthredione; 2) Vat Orange; 3) ditridecyl perylene tetracarboxylic diimide; 4) metallic cobalt reference.