New chemical hydrogen storage materials exploiting the self-sustaining thermal decomposition of guanidinium borohydride†

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Guanidinium borohydride (GBH) was structurally characterized by single-crystal X-ray diffraction and found to release more than 10 wt% H_2 as a fairly pure stream during a self-sustaining thermal decomposition reaction both with and without additives that were identified to reduce the concentration of the main ammonia impurity and control the reaction sustainability.

The ability to store hydrogen at high volumetric and gravimetric density and release it on demand provides enabling technology vital to the widespread implementation of fuel cells as high power density portable systems. One approach is chemical hydrogen storage where hydrogen is generated on demand through a chemical reaction. For small scale PEM fuel cell systems it may be advantageous to employ exothermic self-sustaining reactions to generate hydrogen coupled with a small H_2 storage tank as a buffer. The design of systems based on this approach using a sequentially initiated pellet array can be found in the patent literature.[1] The heat from such reactions may also be used to generate additional hydrogen from storage materials based on endothermic processes.

In our research efforts to develop new manageable chemical hydrogen storage sources we investigated hydrogen generation from the autogenous aminolysis reactions of boron hydrides including guanidinium borohydride (GBH) and ethylenediamine bisborane (EDB). Our results find that these compounds provide a promising, low cost, reliable, and safe high-density chemical hydrogen storage source for applications where fast hydrogen generation on demand is required.

Boron–nitrogen–hydrogen compounds are of general interest for chemical hydrogen storage[2a] providing high weight percent hydrogen materials where the corresponding protic and hydridic character of the hydrogens on the nitrogen and boron, respectively, allows a facile H_2 elimination pathway. In particular, the borohydride ion (BH_4^-) at 27.2 wt% H_2 can provide exceptionally high H_2 density if an appropriate counter-cation is chosen that contributes sufficient protons for hydrogen formation without adding excess dead weight. Unfortunately, the ideal exemplar, ammonium borohydride $[NH_4][BH_4]$, at 24.5 wt% H_2 is thermally unstable. As a result, research on discrete compounds for chemical hydrogen storage has focused on the ammonia borane (AB) adduct,[2] NH_3BH_3, with 19.6 wt% hydrogen.

Few stable borohydride salts are known with a suitable balance of protic and hydridic hydrogens as potential alternatives to AB for chemical hydrogen storage. One example, $[Mg(NH_3)_2][BH_4]_2$ with 16.0 wt% H_2, was successfully demonstrated as a H_2 source for a portable chemical laser application.[3] A Rietveld refinement of the crystal structure and the endothermic decomposition of this compound to yield 13.1 wt% hydrogen as 6 equiv. H_2 along with NH_3 impurity has been reported.[4] A second example, guanidinium borohydride (GBH) $[C(NH_2)_3]^+[BH_4]^-$, with 13.5 wt% H_2 (10.8 wt% H_2 thermally accessible by aminolysis as 4 equivalents of H_2) has not been investigated as a chemical hydrogen storage source. With four hydridic borohydride B–H bonds and six protic N–H bonds, GBH has only a modest dead weight penalty in the guanidinium ion. The higher thermal stability of the borohydride salt of the guanidinium ion, $[C(NH_2)_3]^+$, in comparison to the ammonium salt may be a result of the lower acidity[5] of guanidinium ($pK_a = 13.71$) than ammonium ($pK_a = 9.21$).

The synthesis of GBH was first reported in 1954 by Schechter.[6] Titov and co-workers[7] later published additional synthetic methods, properties (*e.g.* $\Delta H°_f = -111$ kJ mol^{-1}), and studies showing decomposition of GBH begins at 100 °C.

The structure of GBH determined by single-crystal X-ray diffraction in our laboratory[8] is consistent with the results of Custelcean and Jackson[9] where the crystal packing is controlled by dihydrogen bonding interactions and can be described in terms of stacks and layers of one-dimensional GBH tapes (Fig. 1). Within the tapes, four of the six hydrogens on the guanidinium are involved in close dihydrogen bonding to the hydrides of the borohydride providing a low activation energy path for elimination of hydrogen in the solid. The two out of plane borohydride hydrogens are essentially bridging two guanidinium ions in an otherwise planar tape. The calculated density of GBH is 0.905 g cm^{-3},

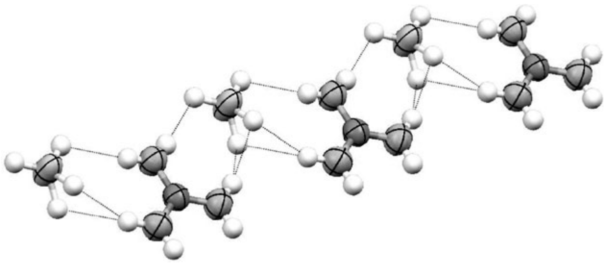

Fig. 1 ORTEP of a one-dimensional GBH tape depicting close hydrogen–hydrogen bonding interactions.

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significantly less than the pycnometrically measured value of 0.99 g cm^{-3} reported by Titov *et al.*[7a] Based on our crystallographic results, and a theoretical hydrogen yield of 10.8 wt%, GBH potentially provides a material based chemical hydrogen storage density of 97.7 g l^{-1}.

For our studies GBH was synthesized in 65–75% yield from metathesis of either guanidinium carbonate or the sulfate and sodium borohydride in anhydrous isopropanol at room temperature. As previously reported,[7] the product is a slightly hygroscopic, air stable, colorless crystalline solid. A melting point of 102 °C with decomposition was observed while heating the sample at a rate of about 10 °C min^{-1}. For GBH samples maintained at elevated temperature in dry nitrogen no gas evolution was evident after several days at 55 °C. Very slow hydrogen evolution begins at about 60 °C. Less than 0.25% of the available hydrogen evolved after 24 hours at 60 °C (less than 0.025 wt% loss) and 2.1% of available H_2 was generated after 48 hours at 60 °C. The lower temperature (55–60 °C) thermal decomposition appears to be self-catalyzing where the rate of hydrogen evolution slowly increases with time at elevated temperature.

When initiated by a hot point source (greater than 180 °C) samples of neat guanidinium borohydride undergo a self-sustaining thermal decomposition (SSTD) reaction rapidly generating hydrogen gas and producing a low density white residue. It is apparent from examination of the resulting foam that solid GBH generates a transient liquid phase in the SSTD reaction zone which froths as hydrogen is released prior to production of the final infusible solid product. Hydrogen yields above 10 wt% were routinely obtained with greater than 95 mol% purity. A maximum reaction zone temperature of 450 °C was measured using thermocouples positioned in the reacting solid and exit gas. The only volatile products identified from the reaction were hydrogen (95–97%) and ammonia (3–5%).

Gas chromatographic analysis of the evolved gases was negative for the presence of nitrogen reported by Titov *et al.* to have been generated during pyrolysis of an intermediate product at 300 °C in a previous study.[7]

The SSTD reaction was observed for samples of GBH in a vacuum, under a nitrogen atmosphere (from 15 to 4000 psi) and in air on samples as large as 10 g without incident.‡ In the absence of an external ignition source no auto-ignition of the evolved hydrogen was observed when the reaction was conducted unconfined in air. The only other reported example of a borane amine compound exhibiting a self-sustaining thermal decomposition reaction is hydrazine bisborane[10] (HBB). The self-sustaining thermal decomposition of HBB, however, readily transitions from a deflagration to a detonation. This behavior, combined with the toxicity of hydrazine, has discouraged further consideration of HBB for hydrogen storage applications.

The DSC trace of GBH (Fig. 2) heated at a rate of 8 °C min^{-1} exhibits a sharp exotherm at 110 °C followed by another broad exothermic peak extending out to approximately 175 °C. The heat of reaction estimated from the DSC measurements is −60 kJ mol^{-1} (integrated heat flow from 110 °C to 165 °C is 803 J g^{-1}). This provides an estimated average heat of reaction per mole H_2 generated of −15 kJ mol−1, which is less than 30% of the value for the hydrolysis of sodium borohydride (−52 kJ mol^{-1}) and only slightly higher than the value reported for the elimination of the first two equivalents of H_2 from AB (−11 kJ mol^{-1}).[2b] TGA analysis (Fig. 2) shows a stepwise release of products with the expected 15% mass loss (hydrogen and ammonia) reached at approximately 140 °C.

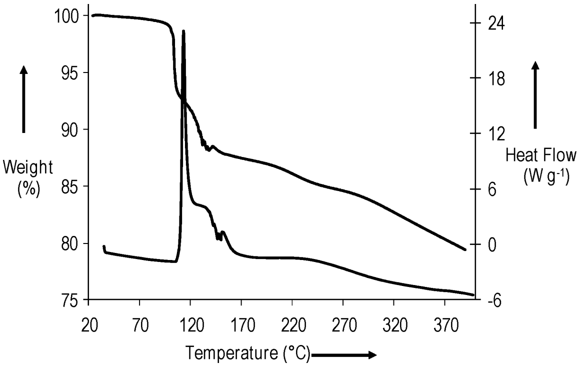

Fig. 2 DSC and TGA traces of GBH (from separate experiments).

While the results of our investigation on the use of GBH as a chemical hydrogen storage material are promising, the amount of ammonia in the product stream is problematic for PEM fuel cell applications. Therefore, to improve the yield and purity of the hydrogen product as well as control the reaction rate and thermal characteristics, preliminary screening studies were conducted on mixtures of GBH with other hydride additives. In general, addition of up to 25 wt% of active hydrides (MgH_2, $NaBH_4$, $LiAlH_4$, Me_4NBH_4) had little or no effect on the amount of ammonia produced and did not influence the hydrogen production. With the addition of as little as 1 wt% tetra-*n*-butylammonium borohydride (*n*-Bu_4NBH_4), however, the mixture failed to sustain a thermal decomposition reaction.

A remarkable improvement in the purity of the hydrogen product was observed from mixtures of GBH and ethylenediamine bisborane[11] (EDB). The rather high hydrogen generating capacity of EDB alone, with 9.2 wt% H_2 thermally available by aminolysis to produce 4 equivalents of H_2, makes it a useful chemical hydrogen source. The compound is a white crystalline solid (density of 0.82 g cm^{-3}) that is stable in dry air and decomposes rapidly above approximately 90 °C. The addition of EDB to GBH resulted in a decrease in the ammonia production without significantly affecting the overall gravimetric hydrogen yield of the mixture. The observed reaction zone temperature of the 40% EDB mixture was 430 °C, not significantly changed from the neat GBH reaction.

Since GBH contributes excess N–H bonds in the mix and EDB excess B–H bonds, a stoichiometric mixture of 46 wt% GBH and 54 wt% EDB provides an equivalent number of protic and hydridic hydrogens for complete reaction of all thermally accessible hydrogens (12.4 wt% hydrogen at 5 equivalents of H_2 per mole of reactant). The hydrogen yields obtained in our studies amounted to just slightly less than to slightly above 4 equivalents H_2 per mole of GBH and EDB (Table 1).

Preliminary NMR and X-ray structural investigations of the products obtained from hydrolysis of the reaction residue

Table 1 GBH–EDB SSTD reaction products[a]

wt% GBH	wt% EDB	wt% H_2 yield	mol% NH_3[b]	$\frac{\text{mol } H_2 \text{ generated}}{\text{mol (GBH+EDB)}}$
100	0	10.6	4.1	3.94
89.5	11.5	10.4	2.7	3.89
60.0	40.0	10.4	0.10	4.11
46.0	54.0[c]	9.60	0.069	3.87
40.0	60.0[d]	10.1	0.026	4.12

[a] For pellets compressed to approximately 60% TMD. [b] NH_3 concentration in gas stream. [c] Stoichiometric mix. [d] Mixture is not self-sustaining, external heat supplied (reaction initiated by a 120 °C oil bath).

identified guanidinium and ethylenediammonium salts as the major products indicating that the C–N skeletal structure of the cations remains mostly intact during the hydrogen elimination reaction.

While no special precautions were taken in the storage of GBH during our investigation, and only a slight odor was noted after a year, mixtures of GBH–EDB stored unprotected in air underwent a slow reaction and became inactive after several months. Samples of the mixture stored under dry nitrogen for the same period, however, were still reactive.

In conclusion, GBH was found to reliably undergo a tractable SSTD reaction when initiated by a heated bridge wire providing a chemical hydrogen storage material with a lower adiabatic reaction temperature (~450 °C) and a higher gravimetric storage density than previous borohydride compositions that used, for example, mixtures of sodium borohydride with an oxidizer.[1] The only gaseous products identified from the SSTD reaction of GBH were H_2 and NH_3 where the hydrogen yield was nearly quantitative (above 10 wt%). The SSTD reaction of mixtures of GBH and EDB rapidly produces a H_2 gas stream suitable for PEM fuel cell applications with minimal NH_3 scrubbing required.

Notes and references

‡ **Caution!** The decomposition reaction of GBH is rapid, producing heat and large amounts of combustible gas. The reaction is capable of generating sufficiently high pressure to burst vessels if confined. Our safety tests show GBH powder is insensitive to impact and friction initiation but was found to be sensitive to initiation by electrostatic discharge. At high wt% EDB, the reaction of GBH–EDB mixtures in air will consistently ignite the mixture and hydrogen product and should be avoided.

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8 Crystal data for GBH. $CH_{10}BN_3$: M = 74.93, tetragonal,: $I4(1)/amd$, a = 6.7433(8) Å, b = 6.7433(8) Å, c = 24.195(3) Å, α = 90°, β = 90°, γ = 90°, V = 1100.2(2) Å^3, Z = 8, absorption coefficient: 0.060 mm^{-1}, wavelength: 0.71073 Å, T: 296(2) K, $F(000)$: 336, reflections collected: 4900, independent reflections: 287 [R(int) = 0.0179, GOF on F^2: 1.180, final R indices: [235 data; $I > 2\sigma(I)$] R_1 = 0.0545, wR_2 = 0.1461; [all data] R_1 = 0.0597, wR_2 = 0.1559.

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