Capacity enhancement of aqueous borohydride fuels for hydrogen storage in liquids

David Schubert [a], Doinita Neiner [a], Mark Bowden [b], Sean Whittemore [c], Jamie Holladay [c], Zhenguo Huang [d], Tom Autrey [c],*

[a] U.S. Borax Inc., Rio Tinto, Greenwood Village, CO, USA
[b] Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA, USA
[c] Pacific Northwest National Laboratory, Richland, WA, USA
[d] Institute for Superconducting and Electronic Materials, University of Wollongong, Wollongong, NSW 2500, Australia

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ABSTRACT

In this work we demonstrate enhanced hydrogen storage capacities through increased solubility of sodium borate product species in aqueous media achieved by adjusting the sodium (NaOH) to boron $(B(OH)_3)$ ratio, i.e., M/B, to obtain a distribution of polyborate anions. For a 1:1 mol ratio of NaOH to $B(OH)_3$, M/B = 1, the ratio of the hydrolysis product formed from $NaBH_4$ hydrolysis, the sole borate species formed and observed by ^{11}B NMR is sodium metaborate, $NaB(OH)_4$. When the ratio is 1:3 NaOH to $B(OH)_3$, M/B = 0.33, a mixture of borate anions is formed and observed as a broad peak in the ^{11}B NMR spectrum. The complex polyborate mixture yields a metastable solution that is difficult to crystallize. Given the enhanced solubility of the polyborate mixture formed when M/B = 0.33 it should follow that the hydrolysis of sodium octahydrotriborate, NaB_3H_8, can provide a greater storage capacity of hydrogen for fuel cell applications compared to sodium borohydride while maintaining a single phase. Accordingly, the hydrolysis of a 23 wt.% NaB_3H_8 solution in water yields a solution having the same complex polyborate mixture as formed by mixing a 1:3 M ratio of NaOH and $B(OH)_3$ and releases >8 eq of H_2. By optimizing the M/B ratio a complex mixture of soluble products, including $B_3O_3(OH)_5^{2-}$, $B_4O_5(OH)_4^{2-}$, $B_3O_3(OH)_4^-$, $B_5O_6(OH)_4^-$ and $B(OH)_3$, can be maintained as a single liquid phase throughout the hydrogen release process. Consequently, hydrolysis of NaB_3H_8 can provide a 40% increase in H_2 storage density compared to the hydrolysis of $NaBH_4$ given the decreased solubility of sodium metaborate.

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1. Introduction

The US DoE Fuel Cell Technologies Office recently released a new set of hydrogen storage metrics and targets for non-vehicular applications ranging from materials handling equipment, e.g., fork lifts and airport tugs, to portable power equipment (PPE), e.g., battery chargers and Unmanned Aerial Vehicles [1]. Specifically, the new gravimetric (40 g H_2/kg system) and volumetric (50 g H_2/liter system) hydrogen storage targets for single charge PPE present new opportunities for materials discovery. One approach that has a strong appeal for both PPE and vehicular applications are liquid carriers [2–9]. Liquid hydrogen carriers offer attractive options for hydrogen storage materials given their ease of transfer to and from devices using pumps and pipes in existing infrastructure, as well as ease of transfer within devices (e.g., from a storage tank to a reactor).

Hydrolysis of borohydrides and ammonia borane has been investigated to evaluate the potential of aqueous liquid carriers [10–13]. Aqueous sodium borohydride (SBH) in particular has been researched extensively [14] as a liquid hydrogen carrier because it is highly soluble in water (360 g/L) with a theoretical gravimetric capacity of 7.3 wt.% H_2:

$$NaBH_4 + 4H_2O \rightarrow NaB(OH)_4 + 4H_2 \qquad (1)$$
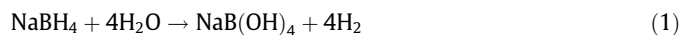
However, a major shortcoming in the $NaBH_4$ approach is the failure to remain liquid *throughout the entire hydrogen release cycle* at high loadings since additional water is required to keep the sodium metaborate hydrolysis product soluble. The Hydrogen-on-Demand, HOD®, system was developed for vehicular applications using 20–30 wt.% solutions of $NaBH_4$ (ca. 4–6.5 wt.% hydrogen on a material basis). Anything greater than 20 wt.% $NaBH_4$, i.e., 4.5 wt.% H_2, presents a challenge to maintain a single liquid phase because of the solubility limit of sodium metaborate (SMB) and led to the DOE curtailing research on aqueous $NaBH_4$ for vehicular applications.
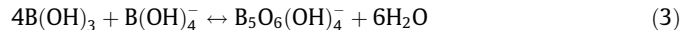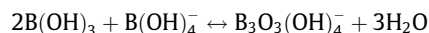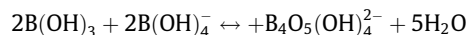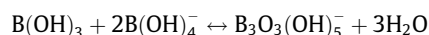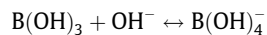
Starting with the known solubility of hydrolysis product: i.e., 590 g (5.8 mol) $NaB(OH)_4$ in a 1 l saturated solution at 60 °C one can work backward to determine the quantity of extra water that is required to maintain a liquid phase starting from SBH and ending with SMB. This approach shows that the aqueous solution needs to 'provide or carry' a minimum 3.5 extra equivalents of water to keep the products in solution at 60 °C, corresponding to a maximum hydrogen capacity of 4.6 wt.% as illustrated in Eq. (2).

$$NaBH_4 + 4H_2O + 3.5H_2O^* \rightarrow NaB(OH)_4 + 4H_2 + 3.5H_2O^* \qquad (2)$$
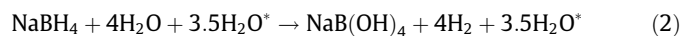
It is notable that 1 l of solution containing 590 g $NaB(OH)_4$ remains a liquid yet only yields 4.6 wt.% H_2. The challenge thus lies in approaches to prepare solutions of borates that will remain soluble on scales >~600 g of a borate salt in a saturated solution.

A survey of the literature shows that the solubility of sodium borates varies dramatically as a function of the Na/B ratio (Fig. 1) [15]. At 60 °C there is a maximum solubility near Na/B = 0.31. The reason for this is that there is not a simple borate anion formed to charge-balance sodium; instead a complex mixture of polyborate anions is formed through a series of condensation equilibria [16]:

$$B(OH)_3 + OH^- \leftrightarrow B(OH)_4^-$$

$$B(OH)_3 + 2B(OH)_4^- \leftrightarrow B_3O_3(OH)_5^- + 3H_2O$$

$$2B(OH)_3 + 2B(OH)_4^- \leftrightarrow +B_4O_5(OH)_4^{2-} + 5H_2O$$

$$2B(OH)_3 + B(OH)_4^- \leftrightarrow B_3O_3(OH)_4^- + 3H_2O$$

$$4B(OH)_3 + B(OH)_4^- \leftrightarrow B_5O_6(OH)_4^- + 6H_2O \qquad (3)$$

Our hypothesis is that this mixture of borate anions will not readily undergo a phase change during the reaction and minimize or delay crystallization through an inverse corollary of the common ion effect. We therefore considered borohydrides where the Na/B ratio is close to the 0.31 maximum in Fig. 1. There are a large
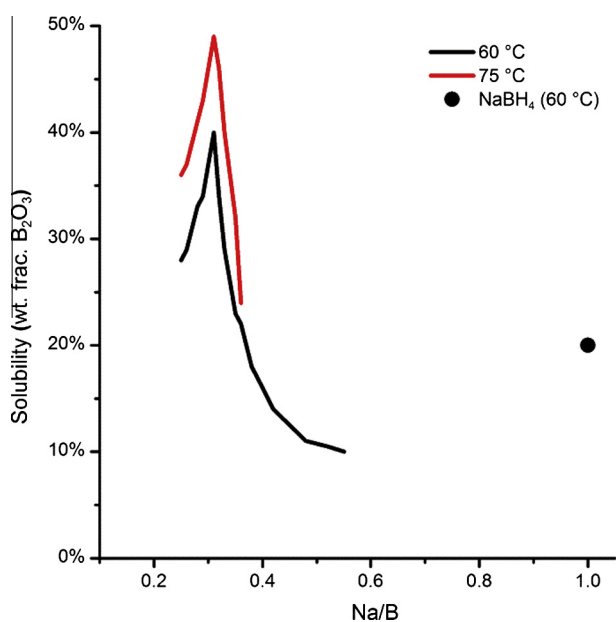
number of boron hydrides species [17,18], however, the candidates with the most potential include $Na[B_4H_9]$ (Na/B = 0.25) and $Na[B_3H_8]$ (Na/B = 0.33).

Shore and co-workers have recently shown that hydrolysis of sodium octahydrotriborate, NaB_3H_8 provides 9 equivalents of H_2 [19,20]. Furthermore they note that aqueous solutions of NaB_3H_8 are more stable than aqueous solutions of $NaBH_4$, a desirable feature for practical hydrogen storage carriers. Based on our analysis of sodium polyborate solubility, we suggest that the hydrolysis of NaB_3H_8 can be carried out under concentrated conditions; i.e., only 2 extra equivalents of water are required:

$$NaB_3H_8 + 10H_2O + 2H_2O^* \rightarrow Na^+ + 3BO_2^- + 2H^+ + 9H_2 \\ + 2H_2O^* \qquad (4)$$
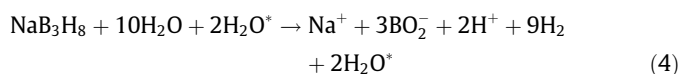
This corresponds to a 23 wt.% solution of NaB_3H_8 in water and a hydrogen capacity of 6.5 wt.%. Hypothetical BO_2^- and H^+ are shown in this equation for simplicity, but in practice the hydrolysis products will contain the polyborate anions shown in Eq. (3) and further water will be generated in condensation reactions to aid solubility. Thus we anticipate increased solubility of both the polyborate hydrolysis products and the NaB_3H_8, which has a reported aqueous solubility of 74 wt.%.

In this report we test the hypothesis of the 'reverse engineering' approach by confirming the solubility of the corresponding polyborate hydrolysis products for a ratio of Na/B = 1/3 by preparing surrogate products from 1 to 3 stoichiometric mixtures of NaOH and $B(OH)_3$ and measuring hydrogen release from aqueous solutions of NaB_3H_8 at concentrations necessary to deliver 6.5 wt.% H_2 from a liquid fuel.

2. Materials and methods

2.1. Synthesis of NaB_3H_8

Solvent-free NaB_3H_8 was synthesized according to a published literature procedure [21]. A Na/Hg amalgam was reacted with $THF \cdot BH_3$ under nitrogen to form $NaBH_4$ and NaB_3H_8. After removal of THF and redissolution in diethyl ether, $NaBH_4$ was removed by filtration. The filtrate was concentrated under vacuum to an oil from which NaB_3H_8 precipitated upon addition of dichloromethane. Approximately 4.5 g of the white powder was recovered by filtration and vacuum drying. It is notable that Titov has reported the preparation of a variety of cationic octohydrotriborates, i.e., lithium, potassium, magnesium, calcium and strontium, as solvates of dioxane or diglyme [22], while Chong et al. have prepared the unsolvated $Mg(B_3H_8)_2$ by a diborane-free pathway by thermal decomposition of $Mg(BH_4)_2$ [23].

2.2. Solubility measurements

A surrogate solution of the corresponding polyborate solution expected to be formed in the hydrolytic decomposition of NaB_3H_8 were prepared from 1 to 3 stoichiometric mixtures of NaOH and $B(OH)_3$ in various amounts of 'excess' water. For example to simulate the product solution from the reaction of 7.50 g NaB_3H_8 (0.118 mol) with 21.28 g reactant H_2O (1.18 mol) with 4.12 g excess water that would yield 6.5 wt.% H_2, 4.12 g H_2O, 4.73 g NaOH, and 21.9 g $B(OH)_3$ were added in the order listed to a 3-neck flask with magnetic stirrer and temperature controller set at 60 °C. The mixture readily formed a clear mobile solution. [Caution: the reaction of NaOH with $B(OH)_3$ is rather exothermic]. This solution was maintained with stirring at 60 °C for 24 h and remained crystal clear.

2.3. Hydrogen measurements from catalytic hydrolysis of NaB_3H_8

Under an atmosphere of N_2, a 5 mL round bottom flask was charged with sodium triborane (56.2 mg, 0.885 mmol), equipped with a Schlenk adapter, and capped with a rubber septum. The reaction vessel was then connected to a gas burette which included a condenser to prevent moisture contributing to the measurement of gas released. An aqueous solution of 0.253 M $CoCl_2$, prepared under ambient conditions, was then added (180 µL, 0.0455 mmol, 5.1 mol%) to the reaction vessel. The mixture rapidly released hydrogen and precipitated cobalt nanoparticles. The amount of hydrogen released was found to be 8.7 equivalents in 2 min. After no more hydrogen evolved, the mixture was analyzed by ^{11}B NMR spectroscopy. All of the sodium triborane had been consumed, and the remaining material was a mixture of borates. ^{11}B NMR (H_2O, 160 MHz): 17–11 (br), 0.97 (s) ppm.

Fig. 1. Plot of solubility of sodium polyborate solutions (B_2O_3) as a function of Q = Na/B ratio. The highest solubility of borates is between Q = 0.25 and 0.33). At Q = 1, e.g., hydrolysis of $NaBH_4$ to yield $NaB(OH)_4$ solubility limit at 60 °C is ca. 20 wt.% B_2O_3 compare to Q = 0.31 where solubility is ca. 40 wt.% B_2O_3.