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Quaternary Li-B-N-H Hydrides: New Hydrogen-Rich Storage Materials

FREDERICK PINKERTON, General Motors Research and Development Center

We have synthesized light metal Li-B-N-H quaternary hydrides by ball milling mixtures of LiNH_2 and LiBH_4 for a series of compositions $(\text{LiNH}_2)_x(\text{LiBH}_4)_{1-x}$ ($x = 0.33$ to 0.8). We discovered a new quaternary hydride phase, referred to here as α Li-B-N-H, as the primary constituent for amide-rich ($x > 0.6$) compositions. Although previously tentatively identified as $\text{Li}_3\text{BN}_2\text{H}_8$, its true equilibrium composition is $\text{Li}_4\text{BN}_3\text{H}_{10}$ as determined by single crystal x-ray diffraction (XRD). $\text{Li}_4\text{BN}_3\text{H}_{10}$ has a body-centered cubic crystal structure, space group $\text{I}2_13$ (# 199) with $a = 10.68 \text{ \AA}$. In situ XRD data demonstrate that the α -phase also forms without ball milling by reacting mixed LiNH_2 and LiBH_4 powders at temperatures above about 95°C . The α phase melts at about 190°C and releases hydrogen from the liquid above 250°C , forming solid Li_3BN_2 . Using mass spectrometry residual gas analysis (RGA) we observe that NH_3 is released concurrently, and the quantity of NH_3 released is strongly dependent on the composition x . Maximum hydrogen release, exceeding 10 wt%, with minimum NH_3 release (1-3 mole % of the evolved gas) occurs for compositions near $\text{LiNH}_2:\text{LiBH}_4 = 2:1$ ($x = 0.667$). Small additions of Ni, Pt, or Pd as powder or metal chloride reduce the dehydrogenation temperature by as much as 112°C , and also reduce the quantity of NH_3 released by about an order of magnitude. Differential scanning calorimetry shows an endothermic melting peak above 190°C , followed by substantial exothermic heat flow above 250°C associated with hydrogen release and solidification of Li_3BN_2 . The exothermic hydrogen release suggests that the reverse reaction is not thermodynamically favored. This new quaternary compound and its derivatives nonetheless represent promising research candidates in the search for practical on-board hydrogen storage materials.