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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 (LiNH$_2$)$_x$(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 Li$_3$BN$_2$H$_8$, its true equilibrium composition is Li$_4$BN$_3$H$_{10}$ as determined by single crystal x-ray diffraction (XRD). Li$_4$BN$_3$H$_{10}$ has a body-centered cubic crystal structure, space group I2_13 (# 199) with a = 10.68 Å. 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$_3$BN$_2$. 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 LiNH$_2$: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$_3$BN$_2$. 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.