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A NOVEL AMMINE LITHIUM ALUMINUM BOROHYDRIDE MATERIAL FOR HYDROGEN STORAGE: SYNTHESIS AND REGENERATION

Huynh-Duc NGUYEN^{a*}, Parviz HAJIYEV^a, Umit B. DEMIRCI^b, Gérard GEBEL^a

^a Univ Grenoble Alpes, CEA, Liten, DTNM, 38000 Grenoble, France

^b Institut Européen des Membranes, IEM – UMR 5635, ENSCM, CNRS, Univ Montpellier, Montpellier, France

*E-mail: huynh-duc.nguyen@cea.fr

For both stationary and mobile applications, storing hydrogen in solid form is a big challenge. Ammonia complex of metal borohydrides have sparked considerable interest as a prospective solid hydrogen storage material, and with 17.3 wt.% of theoretical hydrogen capacity, the novel ammine lithium aluminum borohydride $\text{LiAl}(\text{BH}_4)_4(\text{NH}_3)_6$ compound has the potential to be a good one.

This compound is synthesized at room temperature from the LiAlH_4 and $(\text{CH}_3)_2\text{S-BH}_3$ precursors via the solvothermal method in liquid ammonia, which is a one-pot synthesis method that produces no solid byproducts and does not require the synthesis of pyrophoric compounds like $\text{Al}(\text{BH}_4)_3$.

X-ray powder diffraction analysis shows that the structure of $\text{LiAl}(\text{BH}_4)_4(\text{NH}_3)_6$, which has yet to be reported in the literature, does not fit with known compounds, for instance, neither $\text{Li}_2\text{Al}(\text{BH}_4)_5(\text{NH}_3)_6$,¹ nor $\text{Al}(\text{BH}_4)_3(\text{NH}_3)_6$.² Rietveld refinement is thus performed to resolve the crystalline structure of this compound. FTIR, Raman, and MAS NMR spectroscopy are also used to fully characterize $\text{LiAl}(\text{BH}_4)_4(\text{NH}_3)_6$. FTIR and Raman spectra reveal the presence of $[\text{BH}_4]^-$ and NH_3 groups, and the valence vibration of the Al-N bond in the coordination octahedron $[\text{Al}(\text{NH}_3)_6]^{3+}$. These findings are supported by the ¹¹B and ²⁷Al MAS NMR spectra as well.

$\text{LiAl}(\text{BH}_4)_4(\text{NH}_3)_6$ decomposes exothermically with the peak temperature of 154.0°C, releasing 12.5 wt.% H_2 . The purity of H_2 is 96.0 mol% due to the evolution of some NH_3 . An isothermal pretreatment approach can improve the hydrogen purity to >99.0 mol%, while the H_2 capacity reduces to 11.0 wt.%. In addition, the activation energy of dehydrogenation is 143.1 kJ/mol, which is determined by using the Kissinger equation. This energy is comparable to that of similar compounds such as ammonia borane.³

Direct rehydrogenation of the amorphous Li-Al-B-N-H dehydrogenation product is not possible, thereby requiring chemical regeneration. Hence, *in situ* XPS, *in situ* Raman and *ex situ* MAS NMR are utilized to better understand the chemical composition and develop better chemical regeneration routes.

In situ XPS results reveal the evolution of the Li, Al, B and N elements during dehydrogenation, that is comparable to ammonia borane decomposition for B and N elements.⁴ The atomic ratio Li:Al:B:N as a function of temperature is also determined by XPS quantitative analysis. Furthermore, the significance of employing MAS NMR to define the dehydrogenation pathway is that it can investigate all of the nuclei in this material (⁷Li, ²⁷Al, ¹¹B, ¹⁵N, and ¹H). This improves on the results in the literature, which are mostly based on ¹¹B, and gives a fuller picture of the solid phases, from ammonia complex of metal borohydride to amorphous Li-Al-B-N-H dehydrogenation product. Similar investigations are also conducted by *in situ* Raman.

Consequently, the amorphous dehydrogenation product can be processed to separate the mixture of two metals, Li-Al, and to generate the BNH compound. This BNH compound can be regenerated to NH_3 and $(\text{CH}_3)_2\text{S-BH}_3$. Moreover, the mixture of Li and Al can be handled to regenerate LiAlH_4 . As a result, we close the hydrogen cycle with $\text{LiAl}(\text{BH}_4)_4(\text{NH}_3)_6$.

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