Wet Chemical Synthesis of Non-solvated Rod-Like α'-AlH₃ as a Hydrogen Storage Material

Haizhen Liu[1]*, Hongyu Ma[1], Longfei Zhang[1], Shichao Gao[2], Xinhua Wang[2]*, Li Xu[3], Shuangyu Liu[3], Xiantun Huang[4], Chenglin Lu[1], Hui Luo[1], Hua Ning[1], Zhiqiang Lan[1] and Jin Guo[1]*

[1] Guangxi Colleges and Universities Key Laboratory of Novel Energy Materials and Related Technology, Guangxi Novel Battery Materials Research Center of Engineering Technology, School of Physical Science and Technology, Guangxi University, Nanning, China, [2] State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou, China, [3] State Key Laboratory of Advanced Power Transmission Technology, Global Energy Interconnection Research Institute Co. Ltd., Beijing, China, [4] Department of Materials Science and Engineering, Baise College, Baise, China

Aluminum hydride (AlH₃) is a promising candidate for hydrogen storage due to its high hydrogen density of 10 wt%. Several polymorphs of AlH₃ (e.g., α, β, and γ) have been successfully synthesized by wet chemical reaction of LiAlH₄ and AlCl₃ in ether solution followed by desolvation. However, the synthesis process of α'-AlH₃ from wet chemicals still remains unclear. In the present work, α'-AlH₃ was synthesized first by the formation of the etherate AlH₃ through a reaction of LiAlH₄ and AlCl₃ in ether solution. Then, the etherate AlH₃ was heated at 60°C under an ether gas atmosphere and in the presence of excess LiAlH₄ to remove the ether ligand. Finally, α'-AlH₃ was obtained by ether washing to remove the excess LiAlH₄. It is suggested that the desolvation of the etherate AlH₃ under an ether gas atmosphere is essential for the formation of α'-AlH₃ from the etherate AlH₃. The as-synthesized α'-AlH₃ takes the form of rod-like particles and can release 7.7 wt% hydrogen in the temperature range 120–200°C.
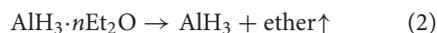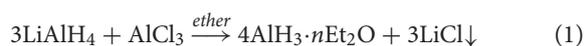
Keywords: hydrogen storage, aluminum hydride, synthesis, desolvation, desorption

INTRODUCTION

Aluminum hydride (AlH₃) is a kinetically stable metal hydride under ambient conditions. It theoretically has a high hydrogen capacity of 10 wt% and can release hydrogen at temperatures below 200°C (Sandrock et al., 2005; Graetz, 2009; Graetz et al., 2011). Therefore, it has long been considered as a promising hydrogen storage media for on-board applications. There are seven known polymorphs of AlH₃: α-, α'-, β-, γ-, δ-, ε-, and ζ-AlH₃ (Brower et al., 1976). These AlH₃ polymorphs have different structures and thermal stabilities and thus have slightly different decomposition properties and mechanisms. α-AlH₃ is the most stable polymorph and will undergo direct decomposition to form Al and H₂ with an increase in temperature (Sandrock et al., 2005; Graetz and Reilly, 2006; Orimo et al., 2006). The other polymorphs, such as β-AlH₃ and γ-AlH₃, will first transform into the more stable α-AlH₃ and then decompose to form Al and H₂ (Graetz and Reilly, 2006). Direct decompositions of γ-AlH₃ and α'-AlH₃ to form Al and H₂ without the first phase transition have also been reported in the literature (Sartori et al., 2008; Liu et al., 2013; Gao et al., 2017).

The synthesis of AlH₃ dates back to 1942 when Stecher and Wiberg (1942) prepared the AlH₃ amine complex in an impure form. The synthesis method of AlH₃ was then modified and improved by other researchers (Finholt et al., 1947; Chizinsky et al., 1955; Ashby, 1964). In 1976, Brower et al. (1976) summarized their findings on the synthesis of non-solvated AlH₃ by

the wet chemical method. They used LiAlH$_4$ and AlCl$_3$ as the starting materials and ether as the solvent. Generally, LiAlH$_4$ was reacted with AlCl$_3$ in the ether solution to form AlH$_3 \cdot n$Et$_2$O and LiCl [reaction (1)]. The precipitate LiCl was then removed by filtration, and the AlH$_3 \cdot n$Et$_2$O precipitated slowly during storage. The obtained solid, AlH$_3 \cdot n$Et$_2$O, was heated under certain conditions to remove the ether ligand [reaction (2)], which was called the desolvation process. Depending on the desolvation conditions used, AlH$_3$ would crystalize in different structures.

$$3\text{LiAlH}_4 + \text{AlCl}_3 \xrightarrow{ether} 4\text{AlH}_3 \cdot n\text{Et}_2\text{O} + 3\text{LiCl}\downarrow \quad (1)$$

$$\text{AlH}_3 \cdot n\text{Et}_2\text{O} \rightarrow \text{AlH}_3 + \text{ether}\uparrow \quad (2)$$

Non-solvated α-, β-, and γ-AlH$_3$ have been successfully synthesized by the wet chemical method (Brinks et al., 2006, 2007a,b; Graetz and Reilly, 2006; Orimo et al., 2006; Liu et al., 2013; Gao et al., 2017). These are the polymorphs of AlH$_3$ that have been intensively studied. However, the intrinsic decomposition properties of α'-AlH$_3$ are still unclear due to the fact that pure and non-solvated α'-AlH$_3$ is hard to synthesyze. As far as we know, the synthesis of pure and non-solvated α'-AlH$_3$ by the wet chemical method has not yet been reported in the open literature. Although Brower et al. (1976) suggested that α'-AlH$_3$ can be synthesized by the slow desolvation of AlH$_3 \cdot n$Et$_2$O, no characterized product of α'-AlH$_3$ was disclosed.

In 2006, Brinks et al. (2006) utilized the cryomilling method to prepare α'-AlD$_3$ from a mixture of 3LiAlD$_4$ + AlCl$_3$. It was shown that cryomilling at a temperature as low as 77 K resulted in the formation of only AlD$_3$ and LiCl. The AlD$_3$ obtained was a mixture of 2/3α-AlD$_3$ + 1/3α'-AlD$_3$ (Brinks et al., 2006). Another work by Sartori et al. (2009) showed that the yield of AlD$_3$ was increased by using 3NaAlH$_4$ + AlCl$_3$ or 3LiAlD$_4$ +AlBr$_3$ as the raw materials. In addition, the relative amount of α'-AlD$_3$ over α-AlD$_3$ was increased from 0.63–0.67 to 1.05 by the addition of FeF$_3$ into the 3LiAlD$_4$ + AlCl$_3$ mixture. Although α'-AlH$_3$ can be obtained by the cryomilling method, the unwanted product of LiCl salt is difficult to remove. Moreover, the α'-AlH$_3$ prepared by this method is usually accompanied by α-AlH$_3$ polymorphs.
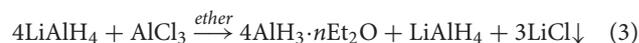
In the present work, the synthesis of non-solvated and pure α'-AlH$_3$ by the wet chemical method is studied. The decomposition properties of α'-AlH$_3$ will also be preliminarily revealed.

EXPERIMENTAL DETAILS

Synthesis of α'-AlH$_3$

The synthesis process of α'-AlH$_3$ employed here is similar to that reported by Brower et al. (1976). However, some conditions needed to be modified. In detail, 1 M ether (Sinopharm Group, Analytical purity) solution of LiAlH$_4$ (TCI, 98% purity) was mixed with 1 M ether solution of AlCl$_3$ (Aldrich, 99.99% purity) at a molar ratio of 4:1. It should be noted that LiAlH$_4$ was used in excess. Brower et al. (1976) found that the etherate AlH$_3$ will decompose to Al if heated under a vacuum, but, in the presence of excess LiAlH$_4$, the ether can be removed without decomposition. LiAlH$_4$ will react with AlCl$_3$ upon mixing in the ether solution to form the etherate AlH$_3$ (AlH$_3 \cdot n$Et$_2$O) and LiCl precipitate based on reaction (3). The mixed solution was stirred for 2 min

to ensure that the reaction was completed. Immediately after that, the LiCl precipitate was removed by filtration and the liquid ether was removed by slowly evacuation at room temperature. The dry and white residue obtained, which was a mixture of 4AlH$_3 \cdot n$Et$_2$O + LiAlH$_4$, was ground to powder with a mortar and pestle for heating treatment. Powder samples were then heated at certain temperatures for various durations under certain atmospheres to remove the ether ligand [reaction (4)]. The conditions used for heat treatment significantly impact the desolvation products of the 4AlH$_3 \cdot n$Et$_2$O + LiAlH$_4$ mixture, as will be shown in the next section. Finally, the desolvated 4AlH$_3 \cdot n$Et$_2$O + LiAlH$_4$ mixture was ether-washed to remove the excess LiAlH$_4$, and AlH$_3$ was obtained.

$$4\text{LiAlH}_4 + \text{AlCl}_3 \xrightarrow{ether} 4\text{AlH}_3 \cdot n\text{Et}_2\text{O} + \text{LiAlH}_4 + 3\text{LiCl}\downarrow \quad (3)$$

$$4\text{AlH}_3 \cdot n\text{Et}_2\text{O} + \text{LiAlH}_4 \rightarrow \text{AlH}_3 + \text{LiAlH}_4 + \text{ether}\uparrow \quad (4)$$
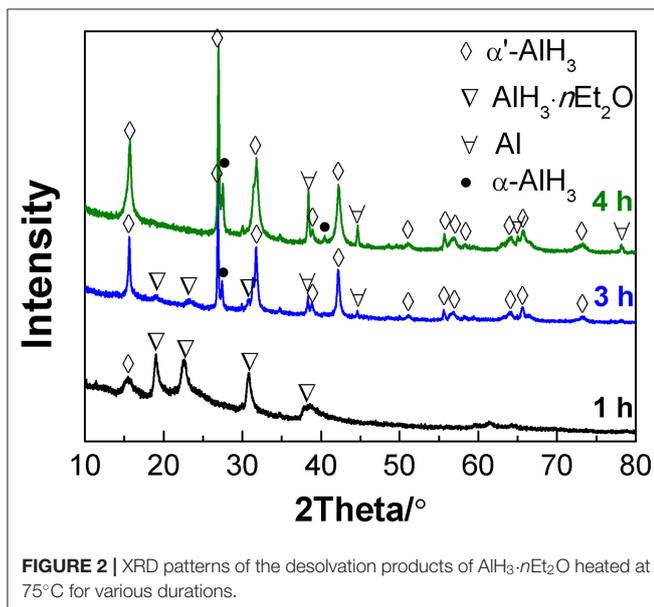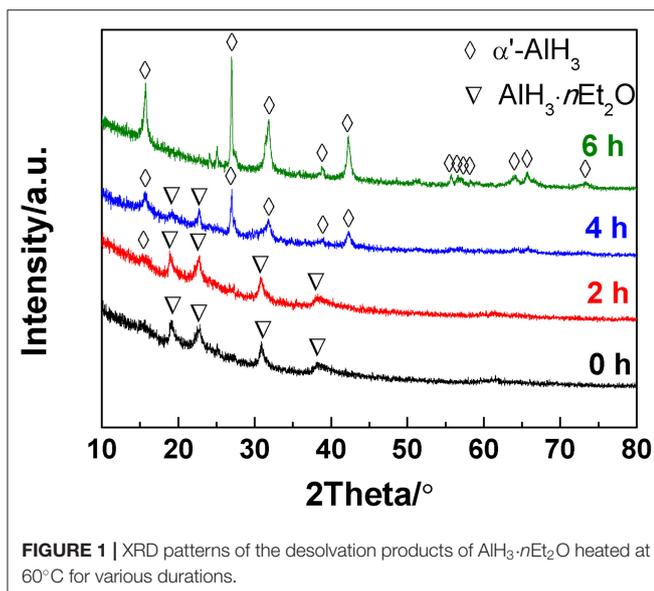
Characterizations of α'-AlH$_3$

Powder X-ray diffraction (XRD, PANalytical X'Pert Pro, Cu Kα, 40 kV, 40 mA) was used to study the phase structures of the samples. The samples for XRD studies were sealed with an amorphous membrane to protect them from oxidation during the sample transformations and measurements. Scanning electronic microscopy (SEM, FEI SIRION-100, 25 kV) was used to study the morphology of the as-synthesized α'-AlH$_3$. The hydrogen desorption property of the as-synthesized α'-AlH$_3$ was studied by using a home-made Sieverts-type hydrogen sorption measurement apparatus based on the volumetric method. Experimentally, the samples were sealed in a reactor and were heated under an initial vacuum gradually from room temperature to the set temperature with a heating rate of 2°C/min.

RESULTS AND DISCUSSION

On the synthesis of AlH$_3$ by the wet chemical reaction in the ether solution, the conditions (desolvation aid, temperature, time, atmosphere) used in the desolvation stage [reaction (4)] significantly affect the desolvation product of AlH$_3 \cdot n$Et$_2$O (Brower et al., 1976). α-AlH$_3$ can be obtained by heating the AlH$_3 \cdot n$Et$_2$O at 60–80°C under a vacuum in the presence of excess LiAlH$_4$ and LiBH$_4$, while γ-AlH$_3$ is formed when the AlH$_3 \cdot n$Et$_2$O is heated at 60–70°C under a vacuum in the presence of only excess LiAlH$_4$ (Brower et al., 1976). It should be noted that the AlH$_3 \cdot n$Et$_2$O should be desolvated in the presence of excess LiAlH$_4$ (and LiBH$_4$), with which AlH$_3 \cdot n$Et$_2$O can easily transform to AlH$_3$ without decomposition (Brower et al., 1976).

In the present work, the AlH$_3 \cdot n$Et$_2$O was heated under a gaseous ether atmosphere, which is the key factor for producing α'-AlH$_3$. The ether atmosphere was generated by injecting a drop of liquid ether into the sample reactor. The liquid ether can easily transform to gaseous ether during heating to 60–80°C since the boiling point of ether is as low as 34.6°C. In this way, the AlH$_3 \cdot n$Et$_2$O can undergo desolvation under a gaseous ether atmosphere. **Figure 1** shows the XRD patterns of the desolvation products of AlH$_3 \cdot n$Et$_2$O heated at 60°C for various durations under an atmosphere of gaseous ether. It can be seen that traces of α'-AlH$_3$ formed after desolvation for 2 h. With an increase in

FIGURE 1 | XRD patterns of the desolation products of $AlH_3 \cdot nEt_2O$ heated at 60°C for various durations.

FIGURE 2 | XRD patterns of the desolation products of $AlH_3 \cdot nEt_2O$ heated at 75°C for various durations.

FIGURE 3 | SEM image of the as-synthesized α'-AlH₃.

FIGURE 4 | Hydrogen desorption curve of the as-synthesized α'-AlH₃ at a heating rate of 2°C/min.

the desolation duration, more and more α'-AlH₃ formed. The $AlH_3 \cdot nEt_2O$ can totally transformed to α'-AlH₃ after desolation for 6 h.

When the desolation of the $AlH_3 \cdot nEt_2O$ was conducted at 75°C, the transformation to α'-AlH₃ proceeded more rapidly. **Figure 2** shows the XRD patterns of the desolation products of $AlH_3 \cdot nEt_2O$ after heating at 75°C for various durations under an atmosphere of gaseous ether. It was observed that some traces of α'-AlH₃ formed after desolation for only 1 h. After 4 h of desolation, the $AlH_3 \cdot nEt_2O$ had completely transformed to AlH₃, which was a mixture of α'-AlH₃ and α-AlH₃. This means that some of the α'-AlH₃ may have transformed into more stable α-AlH₃ during heat treatment at 75°C. Therefore,
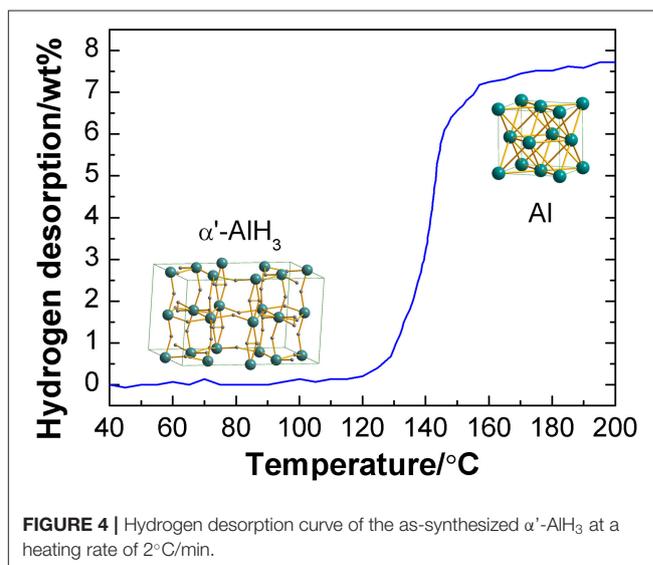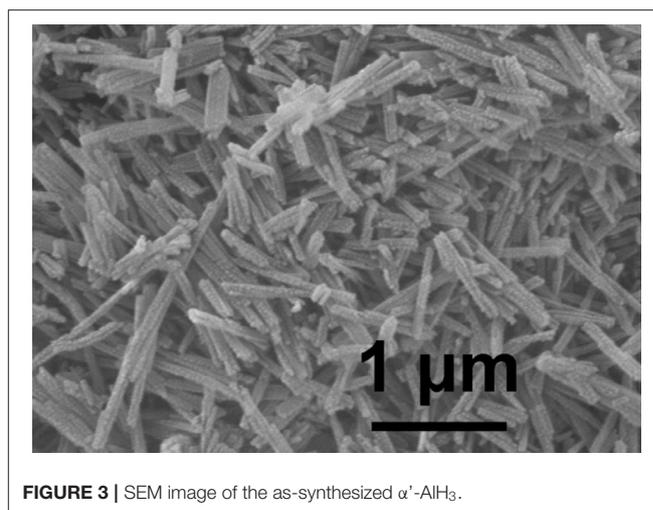
a lower desolation temperature (e.g., 60°C) is preferred in order to produce pure α'-AlH₃.

The morphology of the as-synthesized α'-AlH₃ was studied by SEM techniques, as shown in **Figure 3**. It can be seen that the as-synthesized α'-AlH₃ takes the form of rod-like particles with lengths of about 1 μm and widths of about 100 nm. This unique particle morphology may benefit the hydrogen desorption process of α'-AlH₃ because it possesses more surface area than other morphologies such as spheres of similar dimensions.

The hydrogen desorption curve of the as-synthesized α'-AlH₃ with a heating rate of 2°C/min is shown in **Figure 4**. As can be seen that it starts to release hydrogen at 120°C and reaches a hydrogen desorption capacity of 7.7 wt% when the temperature is increased to 200°C. After hydrogen desorption, Al is formed. It should be noted that the practical capacity is somewhat lower than the theoretical value, which may be due to the impurity of the sample. This decomposition temperature range is similar to that of α-AlH₃ and γ-AlH₃ (Graetz and Reilly, 2006; Liu et al., 2013).

CONCLUSION

Non-solvated α'-AlH$_3$ was successfully synthesized by the wet chemical reaction of LiAlH$_4$ and AlCl$_3$ in ether solution followed by desolvation. The conditions used in the desolvation stage are the essential factors in producing α'-AlH$_3$. Desolvation under a gaseous ether atmosphere is the key to the transformation of AlH$_3 \cdot n$Et$_2$O into non-solvated α'-AlH$_3$. The as-synthesized α'-AlH$_3$ particles are rod-like and can release 7.7 wt% hydrogen in the temperature range 120–200°C. The purity of the α'-AlH$_3$ needs to be improved in future work.

DATA AVAILABILITY STATEMENT

All datasets generated for this study are included in the article/supplementary material.

REFERENCES

Ashby, E. C. (1964). The direct synthesis of amine alanes. *J. Am. Chem. Soc.* 86, 1882–1883. doi: 10.1021/ja01063a066

Brinks, H. W., Brown, C., Jensen, C. M., Graetz, J., Reilly, J. J., and Hauback, B. C. (2007a). The crystal structure of γ-AlD$_3$. *J. Alloy. Compd.* 441, 364–367. doi: 10.1016/j.jallcom.2006.09.139

Brinks, H. W., Istad-Lem, A., and Hauback, B. C. (2006). Mechanochemical synthesis and crystal structure of α'-AlD$_3$ and α-AlD$_3$. *J. Phys. Chem. B* 110, 25833–25837. doi: 10.1021/jp0630774

Brinks, H. W., Langley, W., Jensen, C. M., Graetz, J., Reilly, J. J., and Hauback, B. C. (2007b). Synthesis and crystal structure of β-AlD$_3$. *J. Alloy. Compd.* 433, 180–183. doi: 10.1016/j.jallcom.2006.06.072

Brower, F. M., Matzek, N. E., Reigler, P. F., Rinn, H. W., Roberts, C. B., Schmidt, D. L., et al. (1976). Preparation and properties of aluminum hydride. *J. Am. Chem. Soc.* 98, 2450–2453. doi: 10.1021/ja00425a011

Chizinsky, G., Evans, G. G., T., Gibb, R. P., and Rice, M. J. (1955). Non-solvated aluminum hydride. *J. Am. Chem. Soc.* 77, 3164–3165. doi: 10.1021/ja01616a092

Finholt, A. E., Bond, A. C., and Schlesinger, H. I. (1947). Lithium aluminum hydride, aluminum hydride and lithium gallium hydride, and some of their applications in organic and inorganic chemistry. *J. Am. Chem. Soc.* 69, 1199–1203. doi: 10.1021/ja01197a061

Gao, S., Liu, H., Wang, X., Xu, L., Liu, S., Sheng, P., et al. (2017). Hydrogen desorption behaviors of γ-AlH$_3$: diverse decomposition mechanisms for the outer layer and the inner part of γ-AlH$_3$ particle. *Int. J. Hydrogen Energy* 42, 25310–25315. doi: 10.1016/j.ijhydene.2017.08.074

Graetz, J. (2009). New approaches to hydrogen storage. *Chem. Soc. Rev.* 38, 73–82. doi: 10.1039/B718842K

Graetz, J., and Reilly, J. J. (2006). Thermodynamics of the α, β and γ polymorphs of AlH$_3$. *J. Alloy. Compd.* 424, 262–265. doi: 10.1016/j.jallcom.2005.11.086

Graetz, J., Reilly, J. J., Yartys, V. A., Maehlen, J. P., Bulychev, B. M., Antonov, V. E., et al. (2011). Aluminum hydride as a hydrogen and energy storage material: past, present and future. *J. Alloy. Compd.* 509, S517–S528. doi: 10.1016/j.jallcom.2010.11.115

Liu, H., Wang, X., Dong, Z., Cao, G., Liu, Y., Chen, L., et al. (2013). Dehydriding properties of γ-AlH$_3$. *Int. J. Hydrogen Energy* 38, 10851–10856. doi: 10.1016/j.ijhydene.2013.02.095

Orimo, S., Nakamori, Y., Kato, T., Brown, C., and Jensen, C. M. (2006). Intrinsic and mechanically modified thermal stabilities of α-, β- and γ-aluminum trihydrides AlH$_3$. *Appl. Phys. A* 83, 5–8. doi: 10.1007/s00339-005-3468-x

Sandrock, G., Reilly, J., Graetz, J., Zhou, W. M., Johnson, J., and Wegrzyn, J. (2005). Accelerated thermal decomposition of AlH$_3$ for hydrogen-fueled vehicles. *Appl. Phys. A* 80, 687–690. doi: 10.1007/s00339-004-3105-0

Sartori, S., Istad-Lem, A., Brinks, H. W., and Hauback, B. C. (2009). Mechanochemical synthesis of alane. *Int. J. Hydrogen Energy* 34, 6350–6356. doi: 10.1016/j.ijhydene.2009.06.019

Sartori, S., Opalka, S. M., Løvvik, O. M., Guzik, M. N., Tang, X., and Hauback, B. C. (2008). Experimental studies of α-AlD$_3$ and α′-AlD$_3$ versus first-principles modelling of the alane isomorphs. *J. Mater. Chem.* 18, 2361–2370. doi: 10.1039/b718896j

Stecher, O., and Wiberg, E. (1942). Über einen nichtflüchtigen, polymeren Aluminiumwasserstoff (AlH$_3$)x und einige flüchtige Verbindungen des monomeren AlH$_3$. *Berichte der deutschen chemischen Gesellschaft* 75, 2003–2012. doi: 10.1002/cber.19420751280

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct and intellectual contribution to the work, and approved it for publication.

FUNDING

ACKNOWLEDGMENTS