

SEARCH FOR A NEW SOLID STATE SODIUM-ION CONDUCTOR

H. Oguchi^{1,2*}, M. Matsuo¹, S. Orimo¹, and H. Kuwano²

¹Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

²Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

*Presenting Author: oguchi@nanosys.mech.tohoku.ac.jp

Abstract: We have studied increase in the sodium-ion conductivity of the complex hydride Na_3AlH_6 by adding NaI . The electrical conductivity of $\text{Na}_3\text{AlH}_6+0.33\text{NaI}$ was studied using ac impedance measurements in the temperature range between room temperature and 363 K. By adding 0.33 molar ration of NaI to Na_3AlH_6 , the conductivity of Na_3AlH_6 increased at any temperature of this study. The largest increase in the conductivity was observed at room temperature form 6.4×10^{-7} S/cm for Na_3AlH_6 to 1.4×10^{-6} S/cm for $\text{Na}_3\text{AlH}_6+0.33\text{NaI}$. This study may give important information to future studies of designing the sodium-ion conductors.

Keywords: Complex hydride, sodium-ion conductor, conductivity increase

INTRODUCTION

Lithium borohydride (LiBH_4) is a complex hydride [1] with ionic bonding between the Li^+ cation and $(\text{BH}_4)^-$ complex anion. In 2007, Matsuo et al. found its fast lithium-ion conduction (more than 1×10^{-3} S/cm above 390 K) accompanied by a structural transition from low-temperature (LT, orthorhombic) to high-temperature (HT, hexagonal) phases by heating to approximately 390 K (see Fig. 1) [2]. This discovery triggered studies of lithium-ion conduction in many complex hydride systems such as $\text{LiBH}_4\text{-LiX}$ ($X = \text{Cl}, \text{Br}, \text{and I}$) [8-10], $\text{LiBH}_4\text{-LiNH}_2$ [11], and $\text{LiNH}_2\text{-LiI}$ [12].

The lithium-ion conduction was also studied in the complex hydrides LiAlH_4 and $\text{Li}_3\text{AlH}_6+x\text{LiI}$ ($x = 0, 0.33$) [13]. LiAlH_4 and Li_3AlH_6 have ionic bonding between the Li^+ cation and $(\text{AlH}_4)^-$ or $(\text{AlH}_6)^{3-}$ complex anions (see Fig. 1). As shown in Fig. 2, temperature dependences of the conductivities of LiAlH_4 and Li_3AlH_6 showed Arrhenius behaviors between room temperature (RT) and 393 K; the conductivities increased almost linearly from 8.7×10^{-9} to 4.6×10^{-6} S/cm for LiAlH_4 , and from 1.4×10^{-7} to 1.6×10^{-5} S/cm for Li_3AlH_6 .

Then, the effect of addition of lithium iodide (LiI) on the conductivity of Li_3AlH_6 was studied by

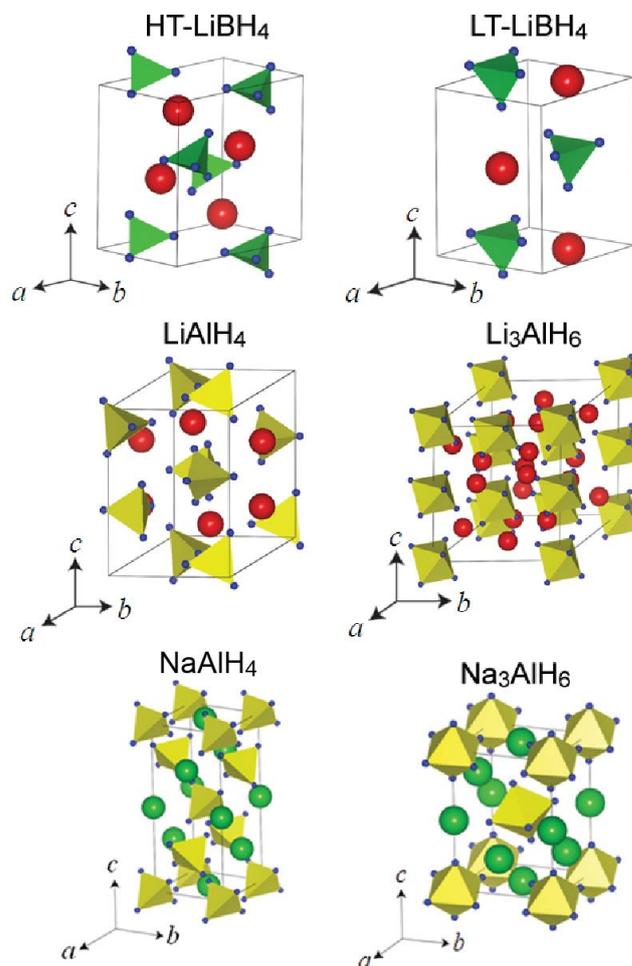


Fig. 1: The schematic crystal structure of HT- and LT- LiBH_4 [3], LiAlH_4 [4], Li_3AlH_6 [5], NaAlH_4 [6] and Na_3AlH_6 [7]. Large and small circles correspond to Li/Na and H atoms, respectively. B/Al atoms are embedded in $(\text{BH}_4)^-$ / $(\text{AlH}_4)^-$ tetrahedra and $(\text{AlH}_6)^{3-}$ octahedra.

comparing the conductivity of $\text{Li}_3\text{AlH}_6+0.33\text{LiI}$ with that of Li_3AlH_6 . As shown in Fig. 2, increase in the conductivity was observed at any temperature between RT and 393 K. At RT, $\text{Li}_3\text{AlH}_6+0.33\text{LiI}$ showed the largest increase of about 35 times higher conductivity than Li_3AlH_6 .

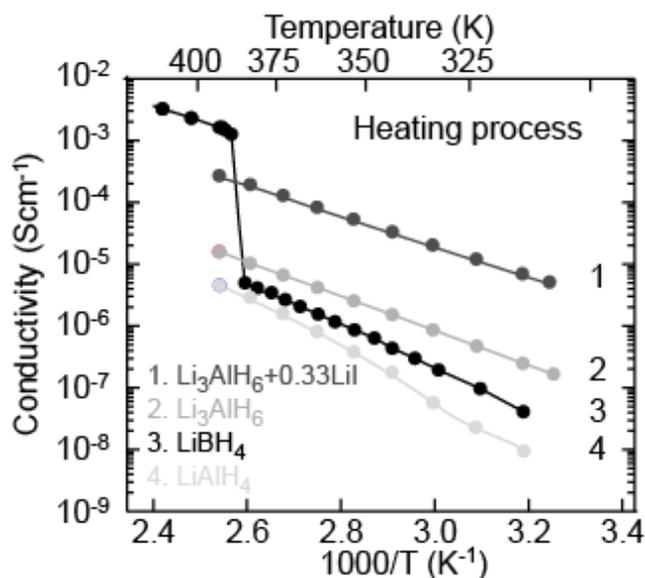


Fig. 2: Temperature dependences of the conductivity of LiBH_4 , LiAlH_4 , and Li_3AlH_6 in heating runs. Li foils were used as non-blocking electrode.

Recently, we noticed that the complex anions $(\text{AlH}_4)^-$ or $(\text{AlH}_6)^{3-}$ can also form ionic bonding between the Na^+ cation to form NaAlH_4 and Na_3AlH_6 (see Fig. 1). Considering the fact that $(\text{AlH}_4)^-$ and $(\text{AlH}_6)^{3-}$ offers lithium-ion conduction in LiAlH_4 and Li_3AlH_6 , there might also be sodium-ion conduction in NaAlH_4 and Na_3AlH_6 , though we knew of no report of sodium-ion conduction in the complex hydrides. Besides, while the sodium-ion conduction has been studied in inorganic materials such as beta-alumina and NASICON, material variety for sodium-ion conduction is not as much as that for lithium-ion conduction. Thus, we studied sodium-ion conduction in the complex hydrides NaAlH_4 and Na_3AlH_6 . [14]

The study above mentioned found the first sodium-ion conduction in these complex hydrides. The conductivity of Na_3AlH_6 was always higher than that of NaAlH_4 between RT and 433 K. The values at RT

were 2.1×10^{-10} S/cm for NaAlH_4 and 6.4×10^{-7} S/cm for Na_3AlH_6 , respectively. Na_3AlH_6 showed the conductivity of 4.1×10^{-4} S/cm at 433 K. This study opened up research of the complex hydrides as solid-state sodium-ion conductors. Next direction of the research may be increasing the sodium-ion conductivity of the complex hydrides.

Considering the similar chemical formulas of Li_3AlH_6 and Na_3AlH_6 with the same type of the complex hydrides $(\text{AlH}_6)^{3-}$, we hypothesized that adding sodium iodide (NaI) to Na_3AlH_6 may increase its sodium-ion conductivity as was the case for LiI and Li_3AlH_6 .

The purpose of this study is to verify the increase in the sodium-conduction of Na_3AlH_6 by adding NaI . For this purpose, we compared the sodium-ion conductivities of Na_3AlH_6 and $\text{Na}_3\text{AlH}_6+0.33\text{NaI}$.

EXPERIMENTAL

NaAlH_4 , NaH , and NaI were purchased from Aldrich Co. Ltd. Na_3AlH_6 was synthesized by mechanical milling of appropriate amounts of NaAlH_4 and NaH for 5 h under a hydrogen pressure of 1 MPa and subsequent heat treatment at 393 K for 10 h under a hydrogen pressure of 3 MPa. Na_3AlH_6 and NaI with a molar ratio of 0.33 were mechanically milled to obtain $\text{Na}_3\text{AlH}_6+0.33\text{NaI}$. We determined the electrical conductivity by the ac impedance measurements in the temperature range between RT and 363 K in heating runs. The samples were always handled in a glove box filled with purified Ar.

RESULTS & DISCUSSION

Figure 3 shows Nyquist plots of $\text{Na}_3\text{AlH}_6+0.33\text{NaI}$ at various temperatures between RT and 363 K. Na foils were used as non-blocking electrodes. Decreasing radius of the semicircle with increasing temperature indicated decreasing resistivity, thus increasing conductivity, of the bulk component of $\text{Na}_3\text{AlH}_6+0.33\text{NaI}$. A tiny spike in the low-frequency range (on the right) may be caused by the grain boundary contribution.

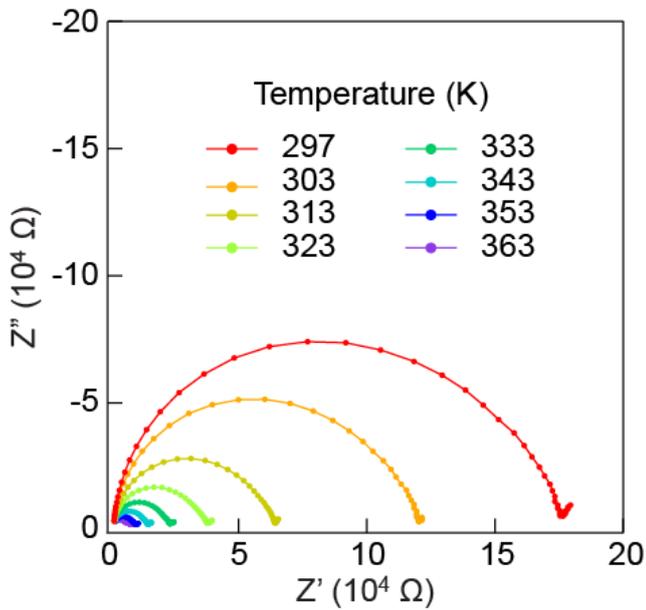


Fig. 3: Nyquist plots of $\text{Na}_3\text{AlH}_6+0.33\text{NaI}$ with Na electrodes.

Figure 4 shows the sodium-ion conductivity of $\text{Na}_3\text{AlH}_6+0.33\text{NaI}$ calculated from the Nyquist plots in Fig. 2. The figure also shows the lithium-ion conductivities of Li_3AlH_6 and $\text{Li}_3\text{AlH}_6+0.33\text{LiI}$ together with sodium-ion conductivity of Na_3AlH_6 as references. Temperature dependences of the conductivity of $\text{Na}_3\text{AlH}_6+0.33\text{NaI}$ showed Arrhenius behaviors in the temperature range between RT and

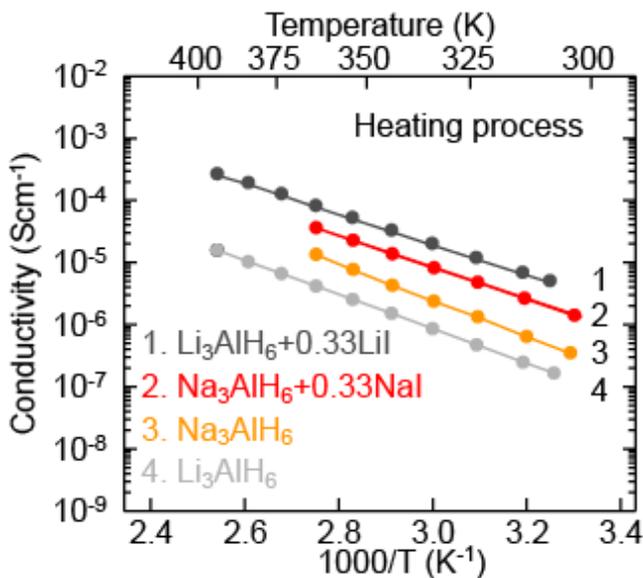


Fig. 4: Temperature dependences of the conductivity of $\text{Na}_3\text{AlH}_6+0.33\text{NaI}$ in heating runs. Na foils were used as non-blocking electrodes. Those of Li_3AlH_6 , $\text{Li}_3\text{AlH}_6+0.33\text{LiI}$, and Na_3AlH_6 are also shown as references.

363 K. Comparison between the sodium-ion conductivities of Na_3AlH_6 and $\text{Na}_3\text{AlH}_6+0.33\text{NaI}$ verified increase in the sodium-ion conductivity of Na_3AlH_6 by adding NaI at any time of this study, though the increase was not as much as in case of adding LiI to Li_3AlH_6 . The largest increase was twice the higher conductivity of $\text{Na}_3\text{AlH}_6+0.33\text{NaI}$ than that of Na_3AlH_6 at RT Figure 5 shows the XRD patterns of $\text{Na}_3\text{AlH}_6+0.33\text{NaI}$ together with those of Na_3AlH_6 and NaI as references. The XRD patterns of $\text{Na}_3\text{AlH}_6+0.33\text{NaI}$ were composed of Na_3AlH_6 and NaI, and nothing else. The remaining diffraction peaks of NaI indicate that the origin of the increase in the conductivity of Na_3AlH_6 by adding NaI may be the increase in the carrier concentration caused by a dispersion of remaining NaI [15]. Decomposition, hydration, and compounds formation were not likely to have been responsible for the increase in the conductivity, because no XRD diffraction peaks were observed except for those of Na_3AlH_6 and NaI.

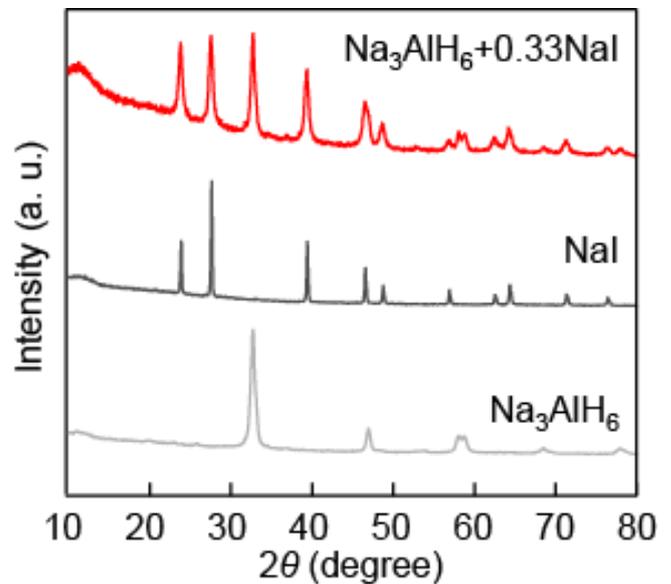


Fig. 5: XRD patterns of Na_3AlH_6 , NaI, and $\text{Na}_3\text{AlH}_6+0.33\text{NaI}$.

CONCLUSION

In summary, we demonstrated that adding NaI to Na_3AlH_6 is an effective means to increase the sodium-ion conductivity of the Na_3AlH_6 . The conductivity of Na_3AlH_6 was increased more than twice at RT by adding 0.33 molar ratio of NaI. This study may give important information to future studies of designing sodium-ion fast conductors

ACKNOWLEDGEMENTS

This work was partially supported by; KAKENHI (No. 18GS0203 and No. 22760529), NEXT program (No. GR008), and cooperative program of the ARCMG-IMR, Tohoku University.

REFERENCES

- [1] S. Orimo, Y. Nakamori, J. R. Eliseo, A. Zuttel, and C. M. Jensen, 2007, Complex Hydrides for Hydrogen Storage, *Chem. Rev.* **107**, 4111.
- [2] M. Matsuo, Y. Nakamori, S. Orimo, H. Maekawa, and H. Takamura, 2007, Lithium superionic conduction in lithium borohydride accompanied by structural transition, *Appl. Phys. Lett.* **91** 224103.
- [3] J-Ph. Soulié, G. Renaudin, R. Černý, and K. Yvon, 2002, L Lithium boro-hydride LiBH_4 I. Crystal structure, *J. Alloys Compd.* **346**, 200.
- [4] B. C. Hauback, H. W. Brinks, and H. Fjellvåg, 2002, Accurate structure of LiAlD_4 studied by combined powder neutron and X-ray diffraction, *J. Alloys Compd.* **346**, 184.
- [5] H. W. Brinks, and B. C. Hauback, 2003, The structure of Li_3AlD_6 , *J. Alloys Compd.* **354**, 143.
- [6] B. C. Hauback, H. W. Brinks, C. M. Jensen, K. Murphy, and A. J. Maeland, 2003, Neutron diffraction structure determination of NaAlD_4 , *J. Alloys Compd.* **358**, 142.
- [7] V. Ozolins, E. H. Majzoub, and T. J. Udovic, 2004, Electronic structure and Rietveld refinement parameters of Ti-doped sodium alanates, *J. Alloys Compd.* **375**, 1.
- [8] H. Maekawa, M. Matsuo, H. Takamura, M. Ando, Y. Noda, T. Karahashi, and S. Orimo, 2009, *J. Am. Chem. Soc.* **131**, 894.
- [9] H. Maekawa, M. Matsuo, H. Takamura, M. Ando, Y. Noda, T. Karahashi, and S. Orimo, 2009, Halide-Stabilized LiBH_4 , a Room-Temperature Lithium Fast-Ion Conductor, *J. Am. Chem. Soc.* **131**, 894.
- [10] M. Matsuo, H. Takamura, H. Maekawa, H. W. Li, and S. Orimo, 2009, Stabilization of lithium superionic conduction phase and enhancement of conductivity of LiBH_4 by LiCl addition, *Appl. Phys. Lett.* **94**, 084103.
- [11] H. Oguchi, M. Matsuo, J. Hummelshoj, T. Vegge, J. Norskov, T. Sato, Y. Miura, H. Takamura, H. Maekawa, and S. Orimo, 2009, Experimental and computational studies on structural transitions in the LiBH_4 -LiI pseudobinary system, *Appl. Phys. Lett.* **94**, 141912.
- [12] M. Matsuo, A. Remhof, P. Martelli, R. Caputo, M. Ernst, Y. Miura, T. Sato, H. Oguchi, H. Maekawa, H. Takamura, A. Borgschulte, A. Zuttel, and S. Orimo, 2009, Complex Hydrides with $(\text{BH}_4)^-$ and $(\text{NH}_2)^-$ Anions as New Lithium Fast-Ion Conductors, *J. Am. Chem. Soc.* **131**, 16389.
- [13] H. Oguchi, M. Matsuo, T. Sato, H. Takamura, H. Maekawa, H. Kuwano, and S. Orimo, 2010, Lithium-ion conduction in complex hydrides LiAlH_4 and Li_3AlH_6 , *J. Appl. Phys.* **107**, 096104.
- [14] H. Oguchi, M. Matsuo, S. Kuromoto, H. Kuwano, and S. Orimo: submitted to *J. Appl. Phys.*
- [15] H. Maekawa, T. Iwatani, H. Shen, T. Yamamura, and J. Kawamura, 2008, Enhanced lithium ion conduction and the size effect on interfacial phase in Li_2ZnI_4 -mesoporous alumina composite electrolyte, *Solid State Ionics* **178**, 1637.