Molecular dynamics study on diffusion behavior of Li in $Li_{10}GeP_2S_{12}$

S. Kawano, and S. Iikubo

Abstract—We have investigated anisotropy of Li diffusivity in $Li_{10}GeP_2S_{12}$ by using molecular dynamics method. Although the calculated ion conductivity is slightly small compared with the previous study, our result supports anisotropic Li diffusivity. This result shows that anisotropic Li diffusion is important properties of this material, furthermore one of the possible factors for good ion conductivity. High ion conductivity is also observed in $Li_{10}P_3S_{12}$, this result suggests $Li_{10}P_3S_{12}$ also has a good Li ion conductivity.

Keywords—solid electrolytes, $Li_{10}GeP_2S_{12}$, molecular dynamics simulation

I. INTRODUCTION

Lithium-ion battery is used to electric vehicles, portable devices in modern society. As opposed to their usefulness, they pose a fire risk caused by liquid electrolytes used in them. Therefore, solid electrolytes have been investigated because of their good safety and stability [1]-[4]. Recently, Kamaya *et al.* reported that a new solid electrolyte $Li_{10}GeP_2S_{12}$ shows the highest lithium-ion conductivity [5]. The discovery of this material has led to intensive studies with experimental techniques [6], [7], molecular dynamics simulation [8], and first-principle calculations [9]-[11]. This material gives us the interesting issue that is about anisotropic Li diffusivity, which may relate to its high performance on the conductivity. Several previous studies supported anisotropic Li diffusivity [9-11], on the other hand, Kuhn *et al.* reported nearly isotropic Li hopping process in the bulk lattice of $Li_{10}GeP_2S_{12}$ experimentally [7]. In this study, we have investigated anisotropy of Li diffusivity by using molecular dynamics method. We discuss about the anisotropic ion conductivity by comparing our result to previous reports.

II. METHODOLOGY

Molecular dynamics simulations were performed to investigate Li ion diffusivity. $3 \times 3 \times 2$ super-cell was used in this simulation for $Li_{10}GeP_2S_{12}$ and $Li_{10}P_3S_{12}$. These simulations are carried out from 5 K to 400 K. At each temperature, the system was kept for 1200 ps for structure relaxation, and after that the data were collected. The collected data between 250 and 400 K was used for the estimation of the Li diffusivity. The potential parameters used in this study were

S. Kawano and S. Iikubo are with the Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology, Kitakyushu 808-0196, Japan (corresponding author to provide phone: +81-93-695-6033; e-mail: iikubo@life.kyutech.ac.jp).

determined by Adams *et al* [8]. We note that unit cell of our simulations is orthorhombic, which is different from previous simulations, where they used tetragonal unit cell [8].

From the obtained simulation data, we can derive several physical properties. The diffusion coefficient D is defined as the mean square displacement $<[r(t)]^2>$ over time t:

$$D = (1/2dt)\langle[r(t)]^2\rangle, (1)$$

where d equals to 3, which is the dimension of the lattice in which diffusion takes place. The value of D is obtained by performing a linear fitting to the relationship of mean square displacement *versus* $2dt$. The ion conductivities σ were derived from diffusion coefficients:

$$\sigma = Nq^2D/k_BT, (2)$$

where the number density N of the mobile Li ions of charge q was calculated from crystal structure. The activation energy E for Li-ion diffusion is obtained by fitting the Arrhenius equation to the diffusion coefficient:

$$D = D_0\exp(-E/k_BT), (3)$$

where D_0 is the constant, k_B is Boltzmann's constant and T is temperature.

III. RESULT AND DISCUSSION

First we confirmed that the potential parameters used in this study are relevant to reproduce some experimental results. Fig. 1 shows temperature dependence of unit cell volume of $Li_{10}GeP_2S_{12}$. Experimental value at room temperature, which is reported by Kamaya *et al.* is also denoted by filled square. Our calculated result is 1.7 percent larger than Kamaya *et al.*,
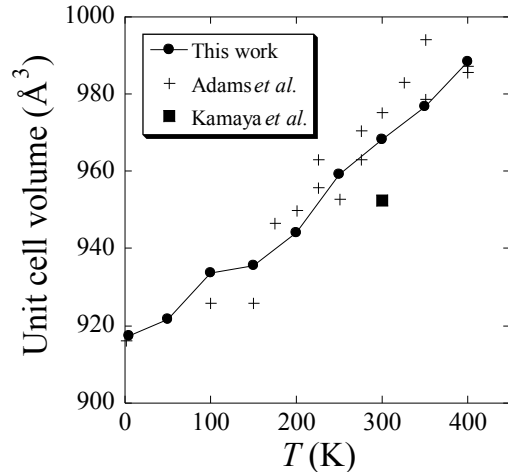

Fig. 1 Temperature dependence of unit cell volume

but we can consider that agreement between the calculated data and experimental value is in a permissible range. Our

calculated data is also compared with the previous studies of Adams *et al*. Our result is smaller than Adams *et al*., but they follows the same trend as previous work. Figure 2 shows temperature dependence of lattice parameters of $Li_{10}GeP_2S_{12}$. Our calculated data is also compared with studies of Adams *et al*. and Kamaya *et al*. Our result along *a* and *b* axis follows the same trend as Adams *et al*. For *c* axis, we can see a little difference between our results and Adams *et al*. This may be caused by difference of constrain condition of unit cell. As mentioned above, Adams *et al*. used tetragonal unit cell, on the other hand, we performed our simulation with orthorhombic unit cell, because we think that the lower symmetry condition seems to be suitable to reveal realistic Li diffusivity. Regardless of small quantitative difference between our result and previous reports, these show roughly same temperature dependence. Therefore our simulation is reliable to discuss about microscopic Li diffusivity.
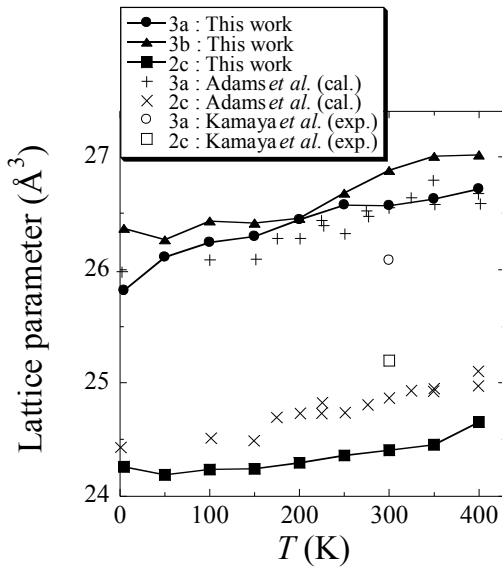

Fig. 2 Temperature dependence of lattice parameters

  Here we are ready for estimating several physical properties from the molecular dynamics simulation. Figure 3 shows temperature dependence of Li ion diffusion coefficient in $Li_{10}GeP_2S_{12}$. This graph also shows result of Adams *et al*., Kamaya *et al*. and Mo *et al*. As decreasing temperature, calculated diffusion coefficient decrease monotonically. This behavior follows the same trend as previous studies. Our calculated values are slightly smaller than other previous reports. We thought that the origin of the small difference of the diffusion coefficient may be caused by difference of constrain condition of unit cell shape. We can see same feature in ion conductivity σ. Figure 4 shows temperature dependence of Li ion conductivity in $Li_{10}GeP_2S_{12}$ which is compared with Adams *et al*., Kamaya *et al*. and Mo *et al*. As for the slightly small diffusion constant and Li ion conductivity, similar behavior is observed in previous study. Ong *et al*. pointed out the relationship between lattice parameters and activation energy or ion conductivity [9]. As increasing lattice parameters, activation energy decreases and ion conductivity increases. Therefore small value of ion conductivity in our

calculation compared with previous study seems due to short lattice parameter of *c*-axis, which is shown in Fig.2.
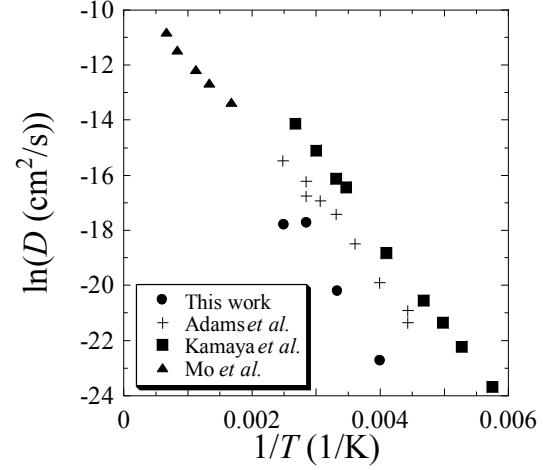

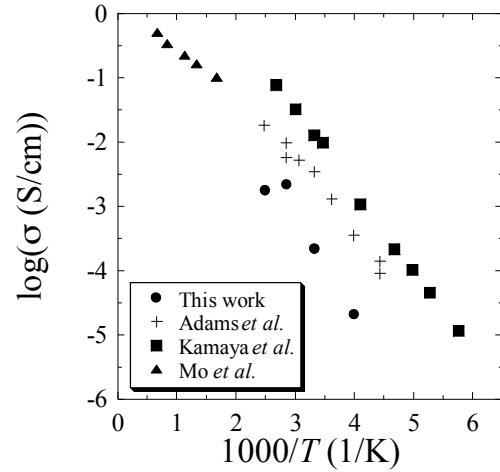Fig. 3 Temperature dependence of Li ion diffusion coefficient in $Li_{10}GeP_2S_{12}$

Fig.4 Temperature dependence of Li ion conductivity in $Li_{10}GeP_2S_{12}$

  To investigate the anisotropy of Li ion conductivity, it is better to examine the direction decomposed diffusion coefficients D_a, D_b, and D_c. We decomposed the mean square displacement $<[r(t)]^2>$ along *a*, *b*, *c*-axis, then the direction D_a, D_b, and D_c were estimated by the procedure identical to estimate total diffusion constant D. After that we obtained activation energy for Li diffusivity by fitting equation (3) to temperature dependence of D_x (*x=a, b, c*). Table. 1 shows activation energy of Li diffusion which was calculated on the three crystalline axis. Obtained value in our study is 0.29 and 0.13 eV for *a* and *c* direction, respectively. Our data supports anisotropic Li diffusivity, which is consistent to previous reports of Adams *et al*. and Mo *et al*., although the previous reports used tetragonal condition. Therefore, we can consider that anisotropic Li diffusion is important properties of this material, suggesting one of the possible factors for good ion conductivity.

However, it is also interesting to consider discrepancy between experimental results and calculation. For the simulation, we have to deal with ideal crystal structures, therefore we may leave some important characteristics out. It is important to understand the difference between experimental results and calculation, in the future work.

TABLE I
ACTIVATION ENERGY OF LI DIFFUSION

Activation energy of Li (eV)			
a direction	b direction	c direction	References
0.29	0.29	0.13	This work
0.30		0.19	Adams *et al*. (cal.)
0.28		0.17	Mo *et al*. (cal.)
0.22		0.22	Kuhn *et al*. (exp.)

Finally, calculated results for Ge-free $Li_{10}P_3S_{12}$ are presented. For the practical use of this solid electrolyte as a battery, the amount of Ge is expected to be reduced as low as possible. We constructed Ge free crystal structure by substitution of Ge to P, and performed molecular dynamics simulation with the same procedure. Fig. 5 shows temperature dependence of Li ion diffusion coefficient in $Li_{10}P_3S_{12}$, which is compared to result of $Li_{10}GeP_2S_{12}$, and first-principle molecular dynamics study of $Li_9P_3S_{12}$ reported by Ong *et al*. Note that we also tried calculation on $Li_9P_3S_{12}$, but crystal structure of this composition is not kept during the simulation. Therefore here we compare our result in $Li_{10}P_3S_{12}$ with previous report in $Li_9P_3S_{12}$. The result of $Li_{10}P_3S_{12}$ follows similar behavior to $Li_{10}GeP_2S_{12}$ and $Li_9P_3S_{12}$ calculated by Ong *et al*.. The result confirms that this material also has a good Li ion conductivity. To the best of our knowledge, $Li_{10}P_3S_{12}$ has not been synthesized experimentally, but this result suggests $Li_{10}P_3S_{12}$ has good conductivity for solid electrolyte used Li ion battery.
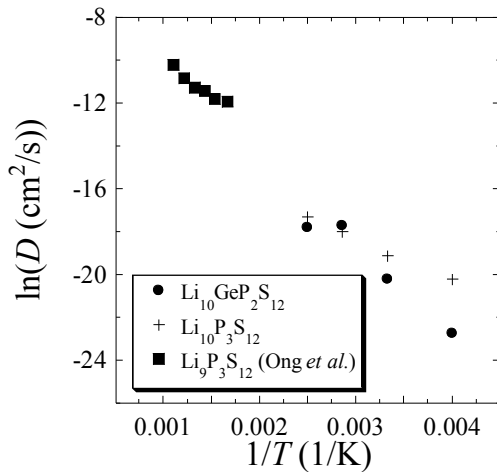

Fig. 5 Temperature dependence of Li ion diffusion coefficient in $Li_9P_3S_{12}$

IV. SUMMARY

We have investigated anisotropy of Li diffusivity in $Li_{10}GeP_2S_{12}$ by using molecular dynamics method. Although

Our result supports anisotropic Li diffusivity. This results show that anisotropic Li diffusion is important properties of this material, suggesting one of the possible factors for good ion conductivity. Furthermore, Ge-free $Li_{10}P_3S_{12}$ is expected to have high Li ion conductivity.

REFERENCES

[1] N. D. Lepley, N. A. W. Holzwarth, and Y. A. Du, Phys. Rev. B, 2013, 88, 104103.
[2] N. A. W. Holzwarth, N. D. Lepley, and Y. A. Du, J. Power Sources, 2011, 196, 6870-6876.
[3] K. Homma, M. Yonemura, M. Nagao, M. Hirayama, and R. Kanno, J. Phys. Soc. Jpn. 2010, 79 Suppl. A, 90-93.
[4] K. Homma, M. Yonemura, T. Kobayashi, M Nagao, M. Hirayama, and R. Kanno, Solid State Ionics, 2011, 182, 53-58.
[5] N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kato, S. Hama, K. Kawamoto, and A. Mitsui, Nat. Mater., 2011, 10, 682-686.
[6] A. Kuhn, O. Gerbig, C. Zhu, F. Falkenberg, J. Maier, and B. V. Lotsch, Phys. Chem. Chem. Phys., 2014, 16, 14669-14674.
[7] A. Kuhn, V. Duppel, and B. V. Lotsch, Energy Environ. Sci., 2013, 6, 3548-3552.
[8] S. Adams and R. P. Rao, J. Mater. Chem., 2012, 22, 7687-7691.
[9] S. P. Ong, Y. Mo, W. D. Richards, L. Miara, H. S. Lee, and G. Ceder, Energy Environ. Sci., 2013, 6, 148-156.
[10] Y. Mo, S. P. Ong, and G. Ceder, Chem. Mater. 2012, 24, 15-17.
[11] F. Du, X. Ren, J. Yang, J. Liu, and W. Zhang, J. Phys. Chem. C, 2014, 118, 10590-10595.