Pertanika J. Sci. & Technol. 25 (1): 247 - 254 (2017)

SCIENCE & TECHNOLOGY

Journal homepage: http://www.pertanika.upm.edu.my/

Molecular dynamics study of the diffusion behaviour of Li in $Li_{10}GeP_2S_{12}$

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ABSTRACT

In this study, we investigated the anisotropic Li diffusion in $Li_{10}GeP_2S_{12}$ using a molecular dynamics method. Although the calculated ion conductivity is slightly lower in comparison to the calculated and experimental ion conductivity of previous studies, our results support anisotropic Li diffusion. These findings show that the anisotropic Li diffusion estimated from the activation energy is an important property of $Li_{10}GeP_2S_{12}$, and a potential factor for good ion conductivity. Further, a high diffusion coefficient was observed in $Li_{10}P_3S_{12}$, which is a good Li-ion conductor.

Keywords: Solid electrolytes, $Li_{10}GeP_2S_{12}$, molecular dynamics simulation, Li-ion battery, activation energy, ion conductivity

INTRODUCTION

A Li-ion battery is nowadays widely used in electric vehicles and portable devices. Despite their usefulness, the liquid electrolytes used in them are potentially a fire risk. Therefore, solid electrolytes have been studied with regards to their safety and stability (Hayashi et al., 2001; Kanno et al., 2001; Homma et al., 2010; Holzwarth et al., 2011; Homma et al., 2011; Bron et al., 2013; Lepley et al., 2013; Hori et al., 2015). In recent studies, Kamaya et al. (2012) reported a new solid electrolyte, $Li_{10}GeP_2S_{12}$, which shows the highest Li-ion conductivity. The discovery of this material has led to intensive studies based on experimental techniques (Kuhn et al., 2013; Kuhn et al., 2014), molecular dynamics simulation (Adams et al., 2012), and first-principles calculations (Mo et al., 2012; Ong et al., 2013; Du et al., 2014). The anisotropic nature of Li diffusion is an interesting property of this material, and may explain its high conductivity. A number of previous studies supported the anisotropic Li diffusion (Mo et al., 2012; Ong et al., 2013; Du et al., 2014). On the other hand, Kuhn et

Article history:
Received: 08 January 2016
Accepted: 11 November 2016

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ISSN: 0128-7680

al. (2013) reported the nearly isotropic Li hopping process in the bulk lattice of $Li_{10}GeP_2S_{12}$. In this study, the anisotropy of Li diffusivity has been investigated using a molecular dynamics method. Our results support the anisotropic ion conductivity in the $Li_{10}GeP_2S_{12}$.

METHODOLOGY

Molecular dynamics simulations were conducted in order to investigate the Li-ion diffusivity. A 3 × 3 × 2 supercell was used in this simulation for $Li_{10}GeP_2S_{12}$ and $Li_{10}P_3S_{12}$. These simulations were carried out at 5, 50, 100, 150, 200, 250, 300, 350, and 400 K; at each temperature, the system was kept for 400 ps for structure relaxation, and then, the data were collected. The collected data between 250 K and 400 K were used for the estimation of Li diffusivity. The potential parameters that control interaction between atoms are the values determined by Adams et al. (2012). In our simulations, we used an orthorhombic unit cell, which is different from that used in Adams et al. which used a tetragonal unit cell.

From the simulation data a number of physical properties were derived. The diffusion coefficient D is defined as,

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

where $<[r(t)]^2>$ and t denote the mean square displacement and time, respectively. Here, $d = 3$, 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 against $2dt$. The ion conductivity σ was derived from diffusion coefficient according to the following relation:

$$\sigma = Nq^2D/k_BT \tag{2}$$

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

$$D = D_0\exp(-E/k_BT) \tag{3}$$

where, D_0, k_B, and T denote a constant, the Boltzmann's constant, and the temperature, respectively.

RESULTS AND DISCUSSION

The potential parameters used in this study were confirmed to reproduce a number of experimental results. Figure 1 shows the dependence of the unit cell volume of $Li_{10}GeP_2S_{12}$on the temperature. The experimental data at room temperature, which is reported by Kamaya et al. (2012), is also denoted by filled square in Figure 1. The calculated values in this study are 1.7% larger than the results obtained by Kamaya et al. (2012); however, the difference between the calculated and experimental values is in a permissible range. Further, the calculated data are compared with the work of Adams et al. (2012). Our values are lower than that obtained by Adams et al. (2012), but both follow similar trends.

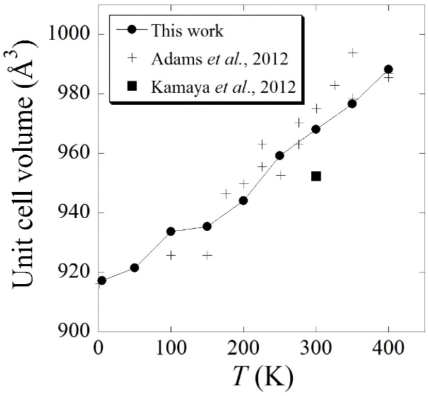

Figure 1. Temperature dependence of unit cell volume

Figure 2 shows the temperature dependence of the lattice parameters of $Li_{10}GeP_2S_{12}$. The calculated data is also compared with the studies of Adams et al. (2012) and Kamaya et al. (2012). Our results along the *a*- and *b*- axes is similar to that of Adams et al. (2012). For the *c*-axis, a minor difference is observed between our results and that of Adams et al. (2012). This can be due to the difference in the constrain condition of the unit cell. As mentioned above, Adams et al. (2012) has used a tetragonal unit cell while our simulations were performed using an orthorhombic unit cell. We think that the Li ions in this material are distributed inhomogeneously. The inhomogeneous distribution causes local lattice distortion, which derives low symmetry structure, such as orthorhombic or monoclinic structure. Therefore, it is unreasonable to impose tetragonal symmetry on this system. Instead, the lower symmetry orthorhombic condition seems to be suitable to reveal realistic Li diffusivity. Regardless of a minor quantitative difference between our results and previous reports, they show an almost similar temperature dependence. Therefore, the simulations in the present study are reliable to discuss about microscopic Li diffusivity.

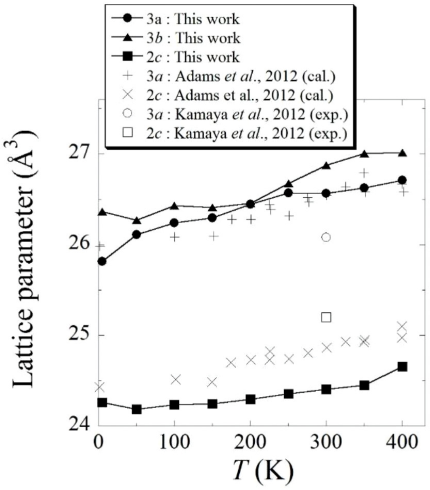

Figure 2. Temperature dependence of lattice parameters

Moreover, an estimation of several physical properties was presented from the molecular dynamics simulation. Figure 3 shows the temperature dependence of the Li-ion diffusion coefficient in $Li_{10}GeP_2S_{12}$. This graph also illustrates the results of Adams et al. (2012), Kamaya et al. (2012), and Mo et al. (2012). It was found that when the temperature decreases, the diffusion coefficient decreases monotonically. The calculated values are slightly smaller than the previous reports; however, they follow a similar trend towards temperature variation. The difference in the values of the diffusion coefficient is due to the difference in the constrain condition of unit cell shape. Similar feature can be seen in ion conductivity.

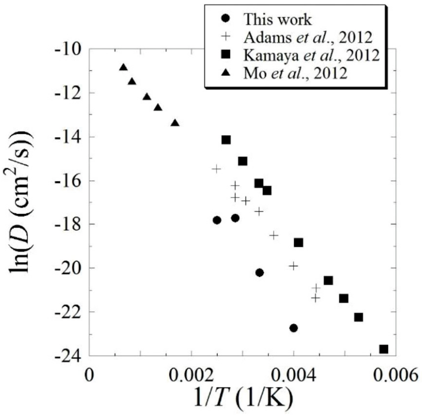

Figure 3. Temperature dependence of the Li-ion diffusion coefficient in $Li_{10}GeP_2S_{12}$

Figure 4 shows the temperature dependence of Li-ion conductivity in $Li_{10}GeP_2S_{12}$ which is compared with Adams et al. (2012) Kamaya et al. (2012) and Mo et al. (2012) Calculated diffusion constant of Li ion and Li-ion conductivity are slightly smaller than experimental values. A similar underestimation is observed in Adams et al. (2012) and Mo et al. (2012). Ong et al. (2013) has pointed out the relationship between lattice parameters and activation energy or ion conductivity. As the lattice parameters increase, the activation energy decreases and the ion conductivity increases. Compared to the previous work, we have obtained a smaller value for ion conductivity, which is mostly because of the short lattice parameter of the *c*-axis, as shown in Figure 2.

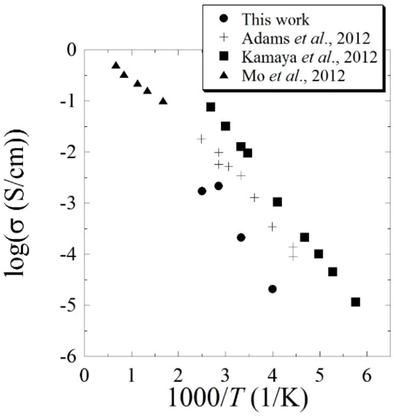

Figure 4. Temperature dependence of Li-ion conductivity in $Li_{10}GeP_2S_{12}$

To investigate the anisotropy of Li-ion conductivity, it is better to examine the direction of decomposed diffusion coefficients D_a, D_b, and D_c. First, the mean square displacement was decomposed along the *a*-, *b*-, and *c*-axes, and then D_a, D_b, and D_c were estimated by performing a linear fitting using Equation (1). Then, the activation energy for Li diffusivity was obtained by fitting Equation (3) to the temperature dependence of D_x ($x = a, b, c$). Table 1 lists the activation energy of Li diffusion, which was calculated on the three crystalline axes. The values we obtained for activation energy are 0.29 eV, 0.29 eV, and 0.13 eV along the *a*-, *b*-, and *c*-directions, respectively. These data support the anisotropic Li diffusion, which is in better agreement with the reports of Adams et al. (2012) and Mo et al. (2012), although they have used the tetragonal unit cell. Therefore, the anisotropic Li diffusion is one of the important properties of this material, suggesting potential factors for better ion conductivity.

Table 1
Activation energy of Li diffusion for three crystalline axes

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., 2012 (cal.)
0.28		0.17	Mo et al., 2012 (cal.)
0.22		0.22	Kuhn et al., 2013 (exp.)

Finally, the calculated results for Ge-free $Li_{10}P_3S_{12}$ are presented in Figure 5. For the practical use of this solid electrolyte in batteries the Ge content needs to be as low as possible. The Ge free crystal structure was constructed by the substitution of Ge with P, and the molecular dynamics simulation was performed using the same procedure as we use for $Li_{10}GeP_2S_{12}$. Figure 5 depicts the temperature dependence of the Li-ion diffusion coefficient in $Li_{10}P_3S_{12}$, and the values are compared to the results of $Li_{10}GeP_2S_{12}$ and the first-principle molecular dynamics study of $Li_9P_3S_{12}$ reported by Ong et al. (2013). Note that the calculation on $Li_9P_3S_{12}$ was performed, but the crystal structure of this atomic composition was not recorded during the simulation. The result obtained in $Li_{10}P_3S_{12}$ is compared with the previous report of $Li_9P_3S_{12}$ by Ong et al. (2013). Accordingly, the results of $Li_{10}P_3S_{12}$ follow a similar behaviour to that of $Li_{10}GeP_2S_{12}$ and $Li_9P_3S_{12}$ calculated by Ong et al. (2013). Note that diffusion constant is dependent on the temperature, and the difference between Ong et al. (2013) and our calculation can be attributed to the effect of temperature. This confirms that $Li_{10}P_3S_{12}$ also demonstrates a good Li-ion conductivity. To the best of our knowledge, $Li_{10}P_3S_{12}$ has not been synthesized experimentally, but our study suggests that it has a good conductivity for solid electrolytes used in Li-ion battery.

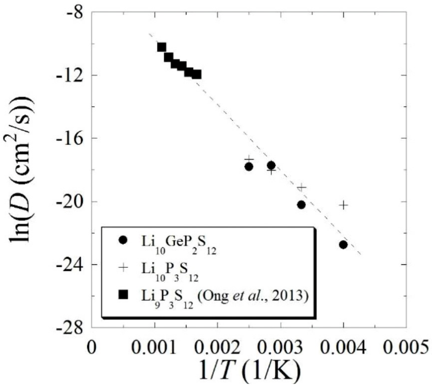

Figure 5. Temperature dependence of the Li ion diffusion coefficient in $Li_{10}P_3S_{12}$

CONCLUSION

We have investigated the anisotropy of Li diffusivity in $Li_{10}GeP_2S_{12}$ using the molecular dynamics method. The results obtained in our study support anisotropic Li diffusion. These findings confirm that anisotropic Li diffusion as an important property of this material, suggesting one of the potential factors for good ion conductivity. Furthermore, our calculations showed that Ge-free $Li_{10}P_3S_{12}$ is expected to have high Li-ion conductivity.

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