Electronic state of sulfide-based alkali-ion conducting solid-state electrolytes applied to all-solid-state secondary batteries

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Abstract. All-solid-state batteries are expected as the next generation secondary batteries for their higher energy density, in-flammable properties, and so on. In order to develop these batteries, there are several problems to improve. One of them is the lower ionic conductivities of the solid-state electrolyte. In order to improve the ionic conductivity, electronic states of the sulfide-based alkali-ion conducting solid-state electrolyte were calculated by the DV-Xα cluster method. The cluster models were constructed by the coordination number reported by experimental methods and the bond length estimated from the ionic radii of each ion. The movement of the cation was simulated by several model clusters with different positions of the moving ion. The relationship between ionic conductivity and the differential total bond overlap population (DBOP) of the moving ion was discussed for the sulfide-based solid-state electrolytes in the several different systems. In any cases, the smaller change of DBOP of the moving cations played an important role for the fast ion movement in the solid-state electrolytes. This bonding state of the moving cations is one of the characteristics of the electronic state in the sulfide-based solid-state electrolytes.

1. Introduction

Recently, solid-state electrolytes are very attractive because of their application for all-solid-state batteries. Those batteries are expected as the next generation secondary batteries for their higher energy density, in-flammable properties, and so on. There are, however, several serious problems in developing commercially available battery cells. One of the importants to improve is the ionic conductivities of the solid-state electrolyte. In the case of the lithium ion secondary batteries, there were significant improvement of the ionic conductivity in the sulfide-based lithium ion solid-state electrolytes. That is, LGPS (Li₁₀GeP₂S₁₂) series of superionic conductors were developed and showed incredibly high ionic conductivity (25 mS cm⁻¹ at R.T.).[1,2] Therefore, the all-solid-state lithium ion batteries will be appeared in the next several years. On the other hand, there are the other problems in the lithium ion secondary batteries, that is, their high-cost, high-environmental impact and the low abundance ratio of its natural resources. Thus, the sodium all-solid-state batteries would be expected alternatives for the next generation low-cost secondary batteries. In the sodium ion batteries, the lower ionic conductivity of the solid-state electrolytes is still a serious problem to apply to the all-solid-state secondary batteries. In this study, electronic states of the sulfide-based alkali ion conducting solid-state
electrolytes were calculated by the DV-Xα cluster method, which is one of the first-principle density functional method.
The relationship between the ionic conductivity and the bonding nature of the mobile ions in the alkali ion solid-state electrolytes was discussed.

2. Calculation Methods
In this study, the DV-Xα cluster method was used to obtain the electronic state of the solid-state electrolytes. This method is one of the first principles density functional methods and is a linear combination of atomic orbital (LCAO) molecular orbital method, in which the exchange potential, $V_{XC}$, is described by:

$$V_{xc}(r) = \begin{bmatrix} -3 & \frac{1}{3} \\ -3\alpha & \rho \uparrow \downarrow (r) \end{bmatrix}$$

where $\rho$ is the electron density of the cluster and $\alpha$ is a constant. [3] $\alpha$ was fixed at 0.7 in the present work. The numerical basis functions were used in the method. As the results, $H$ and $S$ matrices were evaluated by the weighted sum of each value on the sample points distributed in the three-dimensional space.

$$S_{\#} = \sum \omega(r) \phi_i^*(r) \phi_j(r)$$

$$H_{\#} = \sum \omega(r) \phi_i^*(r) h(r) \phi_j(r)$$

where $\phi_i$ is the basis functions, $h$ is the Hamiltonian, $\omega$ is the weight of each sample point. This method has several characteristics, such as the same accuracy for all elements in the periodic table, the shorter calculation time by using numerical integration than the common Hartree-Fock method, the accurate energy and transition intensity of the electronic transition spectrum obtained by the slater transition method.

We have used Mulliken population analysis to obtain the bonding state of the moving alkali ion. The ionicity and covalency of the chemical bonding of the alkali ion are discussed by using net charge and bond overlap population. The net charge is the measure of the ionic interaction between mobile alkali ion and the surrounding ions. The bond overlap population is the measure of the covalent interaction between the mobile alkali ion and the other ions.

Fig. 1 shows the schematic diagram of the model cluster for the sulfide-based solid-state electrolyte. This figure shows the M$_{16}$X$_4$S$_{16}$ (M=Li, Na; X=B, Si, P, Sn, Sb etc.) cluster, that is one of the simplest models of M$_2$S-XS$_2$ solid-state electrolytes. This model cluster was constructed from the structure of the Li ion superionic conducting glasses. The coordination number of sulfide ions to the alkali ion and the distances between the alkali ion and the first neighbor ions were reported about several kinds of the sulfide materials. [4-6] As based on these studies, we have adapted tetrahedral structure and estimated the bond length from the ionic radius of each ion reported by Shannon, [7] to calculate electronic state near alkali ions. In this model, a M ion (M=Li, Na) is located in the center and four sulfide ions are coordinated. Each sulfide ion is included in a XS$_4$ unit (X=B, Si, P, Sn, Sb etc.), which has regular tetrahedron structure. The outside sulfide ions of XS$_2$ units are terminated by M ions. Near the center tetrahedral unit, three M ions are located on the outside to keep the cluster neutral. The movement of the center M ion was simulated by five clusters with different position of the ion. The XS$_2$ content was changed with exchange X in XS$_4$ units with the other elements. In this case, the neutrality of the model clusters was adjusted by the number of the outside M ions. Then the contents of XS$_2$ in the clusters could become 25, 50, 75, and 100 mol% in the present work. To compare the theoretical results with the experimental ones, the bond overlap population of the composition corresponding to the experimental samples was obtained by interpolation of the results of these four compositions.

As previously reported, the covalency of bonding nature between the moving cations and surrounding ions were very important to realize the fast movement of the ions.[9-14] We investigated the total bond overlap population to estimate total of covalent interactions of moving cations and it was suggested that
the cations, which could move easily, had small change of the total bond overlap population with the movement. In the present work we would like to introduce differential total bond overlap population (DBOP), to evaluate the relationship between the covalent interaction and the fast movement of the moving Li ions. That is obtained by subtracting the minimum from the maximum of the total bond overlap population with the movement of the lithium ion through the path. In this study the electronic state of the moving lithium ions were calculated in the many kinds of the sulfide-based solid-state electrolytes to compare with the ionic conductivity.

3. Results and discussion

We have already reported about the electronic state of the sulfide-based Li ion superionic conducting glasses in the several systems [15], and suggested that the covalent interaction between the mobile Li ion and the surrounding ions near conduction path was very important to understand the incredibly high ionic conductivity. In previous reports, the change of the covalent interaction between the mobile Li ion and the surrounding ions showed clear relationship with the ionic conductivities in the systems Li$_2$S-SiS$_4$-Al$_2$S$_3$ and Li$_2$S-SiS$_4$-P$_2$S$_5$.

![Figure 2](image)

Figure 2 (a) The composition dependence of ionic conductivity and DBOP, (b) The composition dependence of the $E_a$ of the ionic conductivity and DBOP in the 60Li$_2$S・40(xPS$_{2.5}$・(100-x)BS$_{1.5}$) glasses

that is, the smaller change of the covalent bonding of the mobile Li ion made the higher ionic conductivity of the superionic conducting glasses. This tendency of the superionic conductivity is also observed in the other systems, like Li$_2$S-B$_2$S$_3$-P$_2$S$_5$ shown in Fig. 2. In this system, there is a maximum in the ionic conductivity and a minimum in the activation energy of the ionic conductivity with the content of P$_2$S$_5$. The composition dependence of the ionic conductivity is much complicated than the previous reported systems. However, the composition dependence of the DBOP is corresponding to that of the activation energy of the ionic conductivity and has the opposite tendency toward the ionic conductivity. Thus, the result suggested that the covalent interaction of the mobile Li ion is very important to understand the high ionic conductivity in many kinds of the sulfide-based superionic conducting glasses. Fig. 3 shows the ionic conductivity at 25°C and activation energy for conduction as a function of the DBOP in the 60Li$_2$S・40(xPS$_{2.5}$・(100-x)BS$_{1.5}$) glasses. The evaluated correlation coefficient

![Figure 3](image)

Fig. 3 Relationship between the ionic conductivity, $E_a$ and DBOP in the 60Li$_2$S・40(xPS$_{2.5}$・(100-x)BS$_{1.5}$) glasses
between the ionic conductivity and DBOP is -0.717 and that between the activation energy and DBOP is 0.656. They are slightly smaller compared with the previously reported other systems. However, we can say that there is a good correlation between the DBOP and the ionic conductivity, though the variations of the ionic conductivity and the activation energy are very complex in this system.

The variation of DBOP in the cluster models of the Li ion superionic conducting glasses showed the good agreement with that of the activation energy of the ionic conductivities. The next, we would try to calculate DBOP in the Na ion solid-state electrolytes. Table 1 shows the DBOP and the change of

| Li$_{12}$P$_4$S$_{16}$ | DBOP | Differential of NC |
|----------------------|------|--------------------|
| 0.023                | 0.015|

| Na$_{12}$P$_4$S$_{16}$ | DBOP | Differential of NC |
|------------------------|------|--------------------|
| 0.072                  | 0.029|

The net charge of the mobile cations between the initial and final positions in the M$_{12}$P$_4$S$_{16}$ cluster model. In the case of the Li$_{12}$P$_4$S$_{16}$, which is the model for the typical Li ion conductor, the DBOP was 0.023, that is very small value described previously. In the Na$_{12}$P$_4$S$_{16}$ cluster, the DBOP was 0.072 with the movement of the Na ion from initial to final positions. This value was somewhat larger than that in the Li$_{12}$P$_4$S$_{16}$ but it still small compared with the other Li ion conductors. This result suggests that the M$_{12}$P$_4$S$_{16}$ model cluster is useful to discuss the ionic conductivity of the Na ion solid-state electrolytes. Table 2 shows the experimentally obtained ionic conductivities in the several kinds of the typical Na ion conductors and the DBOP of the corresponding model clusters. In the Na ion conductors which shows the higher ionic conductivity than 3.0 mScm$^{-1}$, the DBOP also became small like the Li ion superionic conducting glasses.

DBOP had good correlations with experimental ionic conductivity and activation energy of sulfide-based solid-state electrolytes. We could expect to design new solid-state electrolytes by using this analysis method. These figures show calculated DBOP in the other combination of many kinds of elements, for example, fig. 4 (a) shows the results of 4th periodic elements, and fig. 4 (b) shows those
of 5th periodic elements. DBOP becomes small and the minimums are observed in the several systems, such as Germanium, Gallium in 4th periodic elements, Tin, Antimony, Indium in 5th periodic elements. In the fact, the new solid-state electrolyte, Li₄SnS₄ was reported in 2012, that is corresponding to our calculation results. That is, it could be expected that new solid-state electrolytes would be found by using the chemical bonding analysis of the mobile alkali ions.

4. Conclusion

Electronic states of moving alkali ions in the sulfide-based solid-state electrolytes were calculated by the DV-Xα cluster method. The differential of the total bond overlap population (DBOP) was obtained from the model clusters constructed with no strict structural parameters by experimental measurements. The DBOP had good correlations with the ionic conductivity and activation energy in the system \( \text{Li}_2\text{S}-\text{P}_2\text{S}_5\text{B}_2\text{S}_3 \). In addition, DBOP of the Na ion in the model clusters for the Na ion solid-state electrolytes had the similar tendency as the Li ion conductors. That is, DBOP showed relatively small values in the model clusters for the typical Na ion conducting solid-state electrolytes. This result suggests that the covalent interaction of the moving alkali ions is very important to understand the fast movement of the ions in the sulfide-based solid-state electrolytes. Furthermore, composition dependence of DBOP in the many kinds of systems \( \text{Li}_2\text{S}-\text{P}_2\text{S}_5\text{M}_x\text{S}_y \) was calculated and the results suggested that the DBOP estimated by the DV-Xα cluster method could be applied to design new sulfide-based superionic conducting glasses.

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