Evaluation of Migration Energy of Lithium Ions in Chalcogenides and Halides by First Principles Calculation

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Migration energies of Li ion in Li3N, Li2X (X = O, S, Se, and Te) and LiX (X = F, Cl, Br, I) via vacancy mechanism have been calculated by first principles pseudopotential method using plane-wave basis. The energy was obtained as the difference in total energies of supercells by two separate calculations; one with a Li+ ion at the normal point and the other with a Li+ ion at the saddle point. Positions of atoms within the second nearest neighbor of the jumping ion were fully relaxed. Two kinds of diffusion paths, i.e., direct and indirect jumps, were considered. Results show rough agreement with available experimental data. The migration energies for the indirect jump in both halides and chalcogenides show a tendency to decrease with the increase in the periodic number in the Periodic table. This is consistent with the widely accepted view. However, the migration energies for the direct jump of chalcogenides do not obey the rule. Comparison of two polymorphs of LiF implies that not only the anionic species but also the crystal structure plays an important role in determining migration energy.

1. Introduction

Lithium-ion batteries are already used massively in our daily life as power sources for cellular phones, portable audio devices, etc. Commercial lithium-ion batteries are composed of lithium transition-metal oxides as a positive electrode material, graphitic carbon as a negative one and liquid organic electrolytes. They show battery voltage of approximately 4 V. There are various kinds of demands for next generation batteries. One is the increase in the battery voltage, which should be very advantageous for applications that require high voltage without increase of weight or volume of the cells. Currently, the use of liquid electrolytes limits the battery voltage at approximately 4.5 V where the liquid electrolytes start to dissociate. The bottleneck can be broken when good solid-state electrolytes become available. Hayashi et al.1,2 reported that some Si–Li-oxysulfide glasses exhibit a wide electrochemical window of more than 10 V. Kanno and Murayama3 reported that some kinds of thio-LISICON crystals show high Li conductivity far exceeding that in oxide crystals. Solid-state batteries using this type of solid-state electrolytes may open the door for the next generation battery-technology.

High Li conductivity is important not only for electrolytes but also electrode materials. Especially in the batteries that require large electric power, electronic and ionic conductivity are very important properties of electrode materials. Despite the experimental efforts to develop new solid-state electrolytes and electrode materials, theoretical investigations to elucidate atomistic or electronic mechanism behind the Li ion conductivity are very limited. First principles calculations of migration energy of Li ions have been reported only in Li2O4 and Li3N.4 However, these works were done in different groups using different computational strategy, which may be difficult to compare. In the present study, systematic first principles calculations on simple compounds such as Li3N, Li2O and LiF were made. In order to see the effect of the crystal structure, two kinds of polytypes of LiF were compared.

2. Computational Procedure

First principles calculations were made using a plane-wave basis pseudopotential (PW-PP) method.5 Ultrasoft pseudopotentials6 were used in order to reduce the size of the plane-wave basis set as represented by the plane-wave cutoff energy. Local density approximation7 (LDA) to density functional theory (DFT) has been employed. Defect calculations were made using supercells composed of 108 atoms for Li3N, 81 atoms for Li2X (X = O, S, Se and Te) with the anti-fluorite (AF)-type structure, and 54 atoms for LiX (X = F, Cl, Br and I) with the rock-salt (RS)-type structure. Plane-wave cut-off energies were chosen to be 450 eV. The error associated with the cut-off was better than 0.05 eV regarding the formation or migration energies. The atomic positions of the first and the second nearest neighbors of the migrating atom and the vacancy were relaxed. The optimization procedure was truncated when the residual forces for the relaxed atoms were smaller than 2.5 eV/Å. Numerical integration over the Brillouin zone was carried out at 2 × 2 × 2 mesh points.

The migration energy of a Li+ ion has been examined using a charged supercell. It corresponds to the case that Li+ ion vacancies are introduced in order to compensate excess charges introduced by impurities or defects. When a divalent impurity, such as Mg2+, occupies a Li position in an ionic crystal, a Li+ vacancy may be introduced to compensate the excess charge. It is also the case when a cation impurity is present at the interstitial position in an ionic crystal. Experi-

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ments on Li$_3$N found that Li$^+$ ion vacancies on Li$_2$N planes play predominant roles for the conduction of Li.$^8$ The Li$^+$ ion vacancies occur to compensate the excess charge of H$^+$ impurities in the Li$_3$N samples. In order to treat the migration of Li$^+$ ion via vacancy that is introduced by the extrinsic reasons, charged supercells have to be employed. The total charge of the supercell was neutralized using jellium background.

3. Results and Discussion

3.1 Atomic jumps in Li$_3$N, Li$_2$O and LiF

The migration energy of Li$^+$ ion via the vacancy mechanism can be calculated using the following equation:

$$ E_{Li^+}^M = E_T[Li^+ \text{at saddle point}] - E_T[Li^+ \text{at normal point}], $$

(1)

where $E_T$ is the total energy of the supercell. Generally speaking, the total energy of the charged supercell is dependent on the Fermi energy of the system. For example, the formation energy of the Li$^+$ vacancy varies with the Fermi energy. As for the migration energy, however, the term that is dependent on the Fermi energy can be cancelled in eq. (1) assuming that the Fermi energy of the whole system is unchanged during the atomic jump.

The saddle point should be determined from the hypersurface of the total energy for the atomic jump. However, it is not easy to find out the saddle point in an arbitrary structure. In the present study, two kinds of diffusion paths as shown in Fig. 1 were examined and the saddle point was set a priori. The “direct jump” means that the saddle point is located on the line that connects the initial and final position. It may be most pertinent to assume that the saddle point is located at the exact midway between two positions. The other kind of the route is called “indirect jump”. Many ionic crystals are composed of a close-packed sublattice of anions with cations located at either tetrahedral (T) or octahedral (O) interstitial positions of the anions. In the RS-type structure, cations occupy all octahedral positions in anion-sublattice making the cubic close packed (CCP) structure. All tetrahedral positions for cations are empty. In the AF-type structure, cations occupy all tetrahedral positions in anion-sublattice of the CCP structure. All octahedral positions are empty. In such structures, an indirect jump via the inherently empty cation position may occur. It can be expressed by O $\rightarrow$ T $\rightarrow$ O and T $\rightarrow$ O $\rightarrow$ T jumps for RS and AF type structures, respectively. The saddle points for such indirect jumps were set on the line connecting octahedral and tetrahedral positions. As shown in Fig. 1, they are set at the center of a triangle composed of three anions, since this may be the narrowest along the diffusion path.

Lithium nitride, Li$_3$N, does not include such a close-packed sublattice of nitrogen. It consists of consecutive Li$_2$N planes sandwiched by Li planes as shown in Fig. 2. Since Li$^+$ ions are known to diffuse predominantly on the Li$_2$N plane, only the migration energy of the “direct jump” on the Li$_2$N plane was calculated. The value obtained by eq. (1) is $-0.02$ eV. This means that the migrating Li ion prefers to stay at the “saddle point” of the present calculation rather than the “normal point”. It is necessary to search the real saddle point in order to calculate the real migration energy. From the examination of atomic geometry, however, much energy gain associated with the change in the location of the saddle point cannot be anticipated. The migration energy should therefore be slightly greater than 0.02 eV, which is consistent to the experimental value, i.e., 0.04 eV. Starnthein et al.$^4$ made similar calculation to the present study using the projector augmented wave (PAW) method and a supercell of 32 atoms. They have
Table 1 Migration energies of Li ion through the two kinds of diffusion path in anti-fluorite type Li$_2$X (X=O, S, Se and Te) and in rock-salt type LiX (X=F, Cl, Br and I).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Migration energy, $E_{Li^+}^{M}$/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Direct path</td>
</tr>
<tr>
<td>Li$_2$O</td>
<td>0.24</td>
</tr>
<tr>
<td>Li$_2$S</td>
<td>0.38</td>
</tr>
<tr>
<td>Li$_2$Se</td>
<td>0.39</td>
</tr>
<tr>
<td>Li$_2$Te</td>
<td>0.42</td>
</tr>
<tr>
<td>LiF</td>
<td>0.80</td>
</tr>
<tr>
<td>LiCl</td>
<td>0.70</td>
</tr>
<tr>
<td>LiBr</td>
<td>0.65</td>
</tr>
<tr>
<td>LiI</td>
<td>0.61</td>
</tr>
</tbody>
</table>

...also set the saddle point as the center of the path. Their value, 0.004 eV agree with the present result within the computational accuracy.

Computational results for Li$_2$O and LiF can be found in Table 1. Experimental data have been obtained by various kinds of techniques including NMR (nuclear magnetic resonance) method and conductivity measurements, using either polycrystalline pellets or single crystals. Some scattering in experimental data can be recognized among the measurements. The experimental $E_{Li^+}^{M}$ in Li$_2$O ranges from 0.38 to 0.7 eV. It ranges from 0.65 to 0.73 eV for LiF. Theoretical $E_{Li^+}^{M}$ in the present study is smaller than these values for Li$_2$O and greater for LiF. However, the rough agreement may be satisfactory since any temperature effects for the atomic jump is ignored. First principles calculation of the migration energy for the direct jump in Li$_2$O by the PW-PP method was reported by De Vita et al. They used a 48-atoms supercell to obtain the energy of 0.34 eV. Our extra calculation using the 48-atoms supercell found 0.30 eV for the direct jump. The use of a large supercell to include wide area for structural relaxation may be important if we are interested in the second decimal of the migration energy.

LiF with a zinc-blend (ZB)-type structure is a hypothetical negative pressure phase. Although the phase has not been reported by experiment, the structure can be optimized by first principles calculations. Comparison between RS and ZB structures is interesting since both of them have a CCP sublattice of anions in common (see Fig. 3). Li ions occupy all octahedral interstitial positions of the anion-sublattice in the RS structure, whereas they occupy a half of tetrahedral interstitial positions in the ZB structure. The calculated atomic density of the ZB-type is smaller by a factor of 0.82 than the RS-type reflecting the stability at negative pressures. The Li-F bond length in the optimized structure is 0.194 nm in the RS-type and 0.180 nm in ZB-type, which can be explained by the difference in the coordination number of Li. The migration energy in ZB-type structure with the direct route is 0.85 eV which is almost the same as that in the RS-type. On the other hand, the migration energy of the indirect jump in the ZB-type structure is 0.25 eV, which is remarkably lower than that of the RS-type. Difference in the crystal structure can change the migration energy by such a significant amount. It can be concluded that not only the composition or constituent atoms but also structure modifies significantly the migration energy of a Li ion.

### 3.2 Comparison in other chalcogenides and halides

It is very interesting that the direct route gave smaller $E_{Li^+}^{M}$ than the indirect one for Li$_2$O (AF) and LiF (RS). It is contrary to the naive idea that the direct jump is more difficult because of the narrower path. In order to see the trend in other compounds having the same crystal structures, series of other halides and chalcogenides with RS and AF type structures are examined. Results are shown in Table 1 and Fig. 4. As for the indirect jump, the migration energy shows monotonous decrease with the increase in the periodic number in the Periodic table in both of chalcogenides and halides. On the other hand, different dependency can be noted for the direct jump. It increases with the increase of the periodic number in chalcogenides. The dependency on the periodic number is much smaller for the direct jump in halides, although it decreases with the increase of the periodic number.

West proposed criteria for good ionic conductors. According to them, the anion framework of highly polarizable should have higher conductivity when compounds of the same crystal structure are compared. Since atomic polarizability is greater in later chalcogens and halogens, better conductivity can be expected for anions with greater periodic number. From geometrical viewpoints, ions with greater radius may have smaller barrier for the atomic jump because of the greater open channel. This is also suggestive of better conductivity for anions with greater periodic number. The trends as found for indirect jumps by the present calculations are
Fig. 4 Migration energies of Li\textsuperscript{+} ion through two kinds of diffusion path in anti-fluorite type Li\textsubscript{2}X (X = O, S, Se and Te) and rock-salt type LiX (X = F, Cl, Br and I).

Fig. 5 Relaxation of interatomic distance, \(\xi\), given by eq. (2) for lithium chalcogenides and halides.

therefore quite natural.

Regarding the direct jump, there is little open space at the saddle point if a rigid sphere model of an original anion sublattice is taken (cf. Fig. 1). A large structural relaxation should therefore be mandatory for the direct jump. When the anion sublattice is close-packed, the AF-type structure accommodates more cations than the RS-type. In other words, atomic density is greater in the AF-type, which make the structural relaxation more difficult. The magnitude of the structural relaxation can be evaluated by

\[
\xi = (d_{\text{saddle}} - d_{\text{normal}})/d_{\text{normal}},
\]

where \(d_{\text{normal}}\) and \(d_{\text{saddle}}\) denote the interatomic distances between two neighboring anions when the migration Li ion is located at the normal and saddle point, respectively. Figure 5 shows \(\xi\) for the two structures. The relaxation is much smaller in the series of chalcogenides as expected by the inspection of the structure. This should be a part of the reasons why the theoretical migration energies of the direct jump in the chalcogenides do not obey the simple rule. Within chalcogenides, however, Li\textsubscript{2}O exhibits smallest migration energy although the magnitude of the structural relaxation is smallest among chalcogenides. The reason is still unclear at the present moment.

4. Conclusion

First principles calculations using the PW-PP method have been made to evaluate the migration energies of Li\textsuperscript{+} ion vacancy in Li\textsubscript{3}N, Li\textsubscript{2}X (X = O, S, Se and Te) and LiX (X = F, Cl, Br and I). Results show rough agreement to available experimental data. Two kinds of diffusion paths, i.e., “direct” and “indirect” jumps were considered. The migration energies of the indirect jump in both chalcogenides and halides show a tendency to decrease with the increase in the periodic number in the Periodic table. This is consistent to the widely accepted view. However, the migration energies of the direct jump of chalcogenides do not obey the rule. Comparison of two polymorphs of LiF implies that not only the anion species but also the crystal structures play important roles on the migration energy.

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