Alkali Ion Transport in Tavorite-Type ABTO4X (A: Li, Na; B-T: Al-P, Mg-S; X: F)
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ABSTRACT
The promise of high safety and stability in solid-type electrolytes has prompted many battery researchers to find candidate inorganic compounds to replace existing liquid/polymer-based electrolytes. In this report, the alkali ion transport in tavorite-type ABTO4X (A: Li, Na; B-T: Al-P, Mg-S; X: F) is investigated by ab initio calculation, bond valence path approach, and void space analysis in order to explore their viability as solid electrolytes for all-solid state Li/Na ion batteries. Results from nudged elastic band and bond valence pathway methods reveal that the Li analogues are capable of 1D Li ion diffusion (<0.60 eV) characterized by a zigzag pathway along c-axis and passing between BO4F2 pairs at each intersite jumps. However, the Na analogues show poor ionic conduction as evidenced by the relatively higher Na migration energy (>0.80 eV) for the same pathway due the larger size of the Na ion and the unchanged critical size along the conduction channel.

Keywords : Density Functional Theory, Nudged Elastic Band Method, Solid Electrolytes, Tavorite Structure

1. Introduction
Solid electrolytes have been sought to replace conventional liquid or polymer electrolytes in alkali ion batteries due to their advantages such as safety and stability during work operation. However, at present, there is only a limited pool of candidate materials that are identified for such application. Some of the previously reported inorganic compounds are the LISICON, NASICON, beta alumina, garnet, and perovskite. Hence, it would be beneficial if new materials can be discovered in order to fast track the full-scale commercialization of all-solid state alkali ion batteries.

Recently, a class of ABTO4X compounds with a tavorite structure has been confirmed as cathodes with high Li ion insertion rate, suggesting a capability for fast Li ion conduction. The structure is built from chains of two crystallographically independent and slightly distorted BO4X2 octahedra (BO4X2-BO4X2-…) in Fig. 1a) that are vertex-linked together by the X cation in the trans position. The chains are parallel and are bridged by isolated TO4 tetrahedral units to form delimiting cavities which are either empty or occupied by alkali/alkaline A cations. The distortion along the BO4X2 chains directly affects the cavity shape along the tunnels, and this lead to splitting site formation for the A cations (Figs. 1a–1c). So far, only the tavorite-type LiMgSO4F was experimentally characterized for solid electrolyte use but its Li diffusion barrier is measured to be high (0.94 eV). However, our recent ab initio DFT calculation has revealed that the material has a low Li ion migration energy (0.20 eV) which implies that the experimental activation energy is dominated by Li defect formation energy contribution. Therefore, the tavorite structure can indeed provide fast ionic conduction pathways. In this study, we further investigated how the alkali ion transport property in tavorite-type ABTO4X compounds (A: Li, Na; B-T: Al-P, Mg-S; X: F) is affected by structure topology and electronic structure using ab initio DFT calculation, bond valence path method and void space analysis.

Figure 1. a) The atomic structure of tavorite ABTO4X. BO4F2 units: octahedra, TO4 units: tetrahedra, and alkali atoms at half-occupied sites (splitting site): half-colored conjoined spheres. b) ac-plane and c) bc-plane views are also shown.
2. Computational details

All calculations were performed using the Vienna ab initio Simulation Package (VASP)\(^{17}\) within the projected augmented wave (PAW) approach.\(^{18}\) The exchange correlation energy was approximated using the generalized gradient approximation (GGA) with parametrization of Perdew–Burke–Ernzerhof for solids (PBEsol).\(^{19}\)

Two ordered tavorite compositions in the triclinic crystal system \((P\overline{1}, Z = 2)\) taken from the Inorganic Crystal Structure Database (ICSD), LiAlPO\(_4\)F and LiMgSO\(_4\)F, were optimized and evaluated.\(^{20}\) An energy cutoff of 500 eV was employed under spin polarization; a \(5 \times 4 \times 3\) Monkhorst-Pack \(k\)-point grid in a 16-atom unit cell was set for structural optimization. The convergence criteria were set to \(10^{-4}\) eV and \(10^{-3}\) eV for the total energy and ionic step errors, respectively. Density-functional perturbation theory was used for the calculation of the Born effective charge tensors to evaluate bond ionicity/covalency.\(^{21,22}\) For the investigation of Li/Na ion migration, the migration energy (ME) of the alkali ions was calculated via nudged-elastic-band (NEB) approach\(^{23}\) with a \(2 \times 2 \times 2\) supercell and \(\mathcal{J}\)-point sampling of the Brillouin zone. For computational insights, the Na analogues were also calculated using the same atomic configuration.

The details for the bond valence path approach are described elsewhere.\(^{24}\) The pathways were visualized inside a \(2 \times 2 \times 2\) supercell as regions enclosed by isosurfaces related to the energy penalty of a mobile Li/Na ion. The energies were calculated for Li/Na positions described in a \(50 \times 50 \times 50\) mesh grid.

The VESTA program\(^{25}\) was used for structural visualization and determination of geometric parameters. For void space analysis, the Zeo++ package\(^{26}\) was employed using the effective ionic radii compiled by Shannon, et al.\(^{27}\)

3. Results and Discussion

3.1 Structural optimization

Table 1 lists the optimized structural information for LiAlPO\(_4\)F, LiMgSO\(_4\)F, NaAlPO\(_4\)F and NaMgSO\(_4\)F. For the Li-based materials, the calculated lattice constants are in very good agreement with the experimental data; the highest difference \(\Delta\) is only 0.79%. Another observation which harmonizes well is the strong positive correlation between cell size and cation size at A and B sites, i.e., Na-based compositions \((r_{\text{Na}} = 1.02 \ang)\) have larger cell sizes than Li-based compositions \((r_{\text{Li}} = 0.76 \ang)\) and Mg-based compositions \((r_{\text{Mg}} = 0.72 \ang)\) have larger cell sizes than Al-based compositions \((r_{\text{Al}} = 0.54 \ang)\).

### Table 1. Structural information for AMTO\(_4\)X (A: Li, Na; M-T: Al-P, Mg-S).

<table>
<thead>
<tr>
<th>Material</th>
<th>(a) ((\ang))</th>
<th>(b) ((\ang))</th>
<th>(c) ((\ang))</th>
<th>(\Delta_{\text{calc-exp}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiAlPO(_4)F</td>
<td>5.074</td>
<td>5.148</td>
<td>7.060</td>
<td>0.014</td>
</tr>
<tr>
<td>LiMgSO(_4)F</td>
<td>5.060</td>
<td>5.160</td>
<td>7.080</td>
<td>0.012</td>
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<tr>
<td>NaAlPO(_4)F</td>
<td>5.203</td>
<td>5.203</td>
<td>7.120</td>
<td>0.020</td>
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<tr>
<td>NaMgSO(_4)F</td>
<td>5.391</td>
<td>5.369</td>
<td>7.427</td>
<td>0.056</td>
</tr>
</tbody>
</table>

3.2 Li/Na ion transport pathways

The alkali ion diffusion considered in this study proceeds through vacancy mechanism. Four distinct paths are required for full connectivity of the tunnels within the tavorite framework as shown in Fig. 2a. The first major path type is for paths 1 and 4 which are relative to \(a\)- and \(b\)-c planes, respectively, and both passing between a TO\(_4\) tetrahedral pair. The second type is for paths 2 and 3 which are relative to \(c\)-axis and both pass between BO\(_4\)X\(_2\) octahedral pairs (Fig. 2a upper left panel). Focusing first on the two reported compositions, LiAlPO\(_4\)F and LiMgSO\(_4\)F, the different conceivable migration pathways were evaluated. As...
mapped out in Figs. 2b and 2c, the ME values based from the saddle-point configuration for paths 1 and 4 are verified to be too high for actual Li/Na ion migration (0.89–1.34 eV). Meanwhile, paths 2 and 3 have relatively lower ME values (<0.55 eV). Also, the intermediate position for path 3 (which is an octahedral site) has been found to be of comparable energy with the initial and final NEB states (within 0.8 meV/atom difference after minimizing this intermediate image using the >10-Å edge cell with 127 atoms (+1 Li vacancy), suggesting that this site is a local minimum. The NEB profile for path 3, when split into two sub-paths (path 3a and 3b), shows <0.2 eV in migration energy barrier (Figs. 2b and 2c). From these, a 1-D alkali ion conduction formed by path 2 and path 3 connections along the c-axis is conceivable for the tavorite framework, with path 2 as the bottleneck path. This is consistent with the result from bond valence method as illustrated in Figs. 3a and 3b. Also, this path dimensionality has been observed in Li-based olivine frameworks although there is a difference in terms of the intermediate position between two adjacent crystallographic sites.\textsuperscript{28–31} In the tavorite structure, the intermediate position it is located at an octahedral site while in the olivine structure, is located at a tetrahedral site. In the next sections, the different factors that affect ME will be discussed.

One factor that may explain ME variation is the structure topology. Table 2 lists the different geometric and void space parameters related to the conduction channels within the tavorite framework. $R_{\text{T-T}, \text{path } 1}$ and $R_{\text{B-B}, \text{path } 2}$ are the TO$_4$-TO$_4$ (for path 1) and BO$_4$F$_2$-BO$_4$F$_2$ (for path 2) separation, respectively, at the intermediate position of the Li/Na ion jump (see Fig. 2a, upper right and lower right subpanels). $D_i$, $D_f$, and $D_{\text{dif}}$ are void space parameters, labeled for the largest included sphere diameter, the largest free sphere diameter and the largest included sphere diameter along the free sphere path, respectively. Figure 4 shows the visual representation of these topology parameters. They were derived from the total void space formed when all A cations are removed from the DFT-optimized structure. For the four compositions, $D_i = D_f$ which implies that the largest pore space exists along the conduction channel (free sphere path) and that the voids are contiguous. $D_i$ is related to the critical size along the conduction channel or the bottleneck between two adjacent sites.

Based from topology analysis, the larger ME in path 1 (and 4) than in path 2 (and 3) may be explained by the smaller separation of the $\text{trans}$ TO$_4$ units than the $\text{trans}$ BO$_4$F$_2$ units for all compositions (i.e., overall, $R_{\text{T-T}, \text{path } 1} < R_{\text{B-B}, \text{path } 2}$ in Table 2). At the intermediate position ($A_{\text{mid}}$ in Figs. 4a and 4b), the mobile A cation occupies an octahedral site. In these environments, the Coulombic interaction of the mobile A cation with the high charge X cations (P$_5^+$, S$_6^+$) is expected to be stronger than with the M cations (Al$^{3+}$, Mg$^{2+}$). The high ME in $\text{trans}$ TO$_4$-bounded paths was also confirmed in a recent DFT study.\textsuperscript{32}

Meanwhile, $R_{\text{B-B}, \text{path } 2}$, $D_p$ and $D_{\text{dif}}$ increase with A ionic size ($r_{\text{Li}} = 0.76$ Å to $r_{\text{Na}} = 1.02$ Å) but these diffusion path-specific parameters negatively correlates with ME. Interestingly, $D_i$ does not increase systematically with A or B size. Hence, the larger size of Na ion coupled with the essentially unchanged critical size along the conduction channel may account for the increase in ME from Li to Na case (i.e., 0.55 eV in LiAlPO$_4$F to 1.62 eV in NaAlPO$_4$F and 0.18 eV in LiMgSO$_4$F to 0.81 eV in NaMgSO$_4$F; both for path 2).

So far, the lower ME in paths 2 and 3 has not been fully resolved by geometric considerations. Although $R_{\text{B-B}, \text{path } 2}$ may account for the difference in ME for Li and Na analogues independently, it

Table 2. Calculated geometric and void space parameters for the optimized tavorite cells.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$R_{\text{T-T}, \text{path } 1}$ (Å)</th>
<th>$R_{\text{B-B}, \text{path } 2}$ (Å)</th>
<th>$D_i$ = $D_f$ (Å)</th>
<th>$D_{\text{dif}}$ (Å)</th>
<th>ME (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiAlPO$_4$F</td>
<td>4.12</td>
<td>5.07</td>
<td>1.71</td>
<td>1.15</td>
<td>0.55</td>
</tr>
<tr>
<td>LiMgSO$_4$F</td>
<td>4.09</td>
<td>5.16</td>
<td>1.77</td>
<td>1.20</td>
<td>0.18</td>
</tr>
<tr>
<td>NaAlPO$_4$F</td>
<td>4.54</td>
<td>5.22</td>
<td>1.99</td>
<td>1.19</td>
<td>1.62</td>
</tr>
<tr>
<td>NaMgSO$_4$F</td>
<td>4.57</td>
<td>5.39</td>
<td>2.09</td>
<td>1.11</td>
<td>0.81</td>
</tr>
</tbody>
</table>

Figure 3. a) Projection view and b) $b$-$c$ plane view of the bond valence-based model (probe radius = 0.8 Å) showing the 1D alkali ion transport pathways along c-axis (in dark gray) for LiAlPO$_4$F. PO$_4$ units and Li cations are removed for clarity.

Figure 4. Different topology parameters describing the Li/Na ion migration pathway within the tavorite structure: a) TO$_4$-TO$_4$ separation along path 1 ($R_{\text{T-T}, \text{path } 1}$, see Fig. 2a), b) BO$_4$F$_2$-BO$_4$F$_2$ separation along path 2 ($R_{\text{B-B}, \text{path } 2}$, see Fig. 2a), and c) void space descriptors for the largest included sphere diameter in the structure ($D_i$), the largest free sphere diameter ($D_f$), and the largest included sphere diameter along the free sphere path ($D_{\text{dif}}$). $A_{\text{mid}}$ is the mobile A cation when at the intermediate position along the migration pathway.
cannot explain the ME variation between A cation types, i.e., the larger \( R_{B_{D1}} \) for the Na analogues does not lead to lower ME values relative to the Li analogues. Therefore, there should be another factor that explains this relationship. Looking at the BO\(_4\)F\(_2\) and TO\(_4\) units, it is evident that the bonding nature of the B and T cations are different. Consequently, the local electronic structure of these two polyhedral units may impose different influences on a migrating A cation. To prove this, the average Born effective cation charges for LiAlPO\(_4\)F, LiMgSO\(_4\)F, NaAlPO\(_4\)F, and NaMgSO\(_4\)F were calculated and are tabulated in Table 3. The nominal charges of A, B, and T cations are assigned as +1, +3 (+2), and +5 (+6), respectively. Results show that the A/B-O bond is predominantly ionic as evidenced by the comparable values between Born and nominal charges for both Li and Na case. However, T-O bonding is determined to be strongly covalent as indicated by the relatively lower values of the Born charges than the nominal ones.28 This T-O covalency should allow for a reduced interaction between the mobile A cation and the lattice along paths 2 and 3, and should lead to a lower ME; the electron cloud from the oxide ion in BO\(_4\)F\(_2\) is drawn away towards TO\(_4\) (Figs. 2b–2d), thus effectively minimizing the energy penalty for electron cloud overlap at the transition site for paths 2 and 3. Furthermore, the larger difference charge\(\text{nominal} - \text{charge}_\text{Born}\) for S\(^{6+}\) than in P\(^{5+}\) (\(-2.78\) vs \(-1.70\), respectively, for both Li and Na case) suggests that (SO\(_4\))\(^{2-}\) is more covalent than (PO\(_4\))\(^{3-}\). This can account for the smaller ME in S-based compositions than in P-based compositions. This could also partly explain why paths 1 and 4 are energetically unfavorable because the electron cloud from the oxide ion in BO\(_4\)F\(_2\) is drawn away towards (PO\(_4\))\(^{3-}\) and more towards (SO\(_4\))\(^{2-}\), causing a stronger short-range repulsion from electron cloud overlap when Li/Na is at the transition site located between two TO\(_4\) units. This repulsion effect should also be stronger for the Na case along 1D conduction channel since the \(D_1\) parameter does not vary significantly against A cation size.

Overall, it was determined that the strength of the covalency in the TO\(_4\) units is crucial in lowering the migration barrier for A cations along the 1D diffusion channel bounded by trans BO\(_4\)F\(_2\) units. Also, the pathway size (described by \(R_{B_{D1}}\), \(D_1\), \(D_6\), and \(D_{14}\)) is found out to be negatively correlated with Li ion migration energy barrier for Li-based favorities. However, no strong correlation exists for the pathway size in Na-based favorities due to the large size of Na cation.

4. Conclusions

We successfully evaluated the Li/Na ion transport property in favority-type ABTO\(_X\) (A: Li, Na; B-T: Al-P, Mg-S; X: F) by ab initio DFT calculation, bond valence path method and void space analysis. Alkali ion migration proceeds in 1D along c-axis-oriented channels bounded by trans BO\(_4\)F\(_2\) units. The Li analogues are determined to be capable of fast ionic conduction along these channels (i.e., 0.55 eV in LiAlPO\(_4\)F and 0.18 eV in LiMgSO\(_4\)F for path 2). However, poor ionic conduction is noted for the Na analogues for the same pathway. While the degree of covalency in TO\(_4\) polyanions aids in ME lowering, Na ion migration is not aided significantly due larger ionic size of Na and the essentially unchanged critical size along the conduction channel (\(D_1\)).

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References


| Table 3. | DFT-calculated average Born effective (dynamic) cation charges (e) in favority-type ABTO\(_X\). |
|---|---|---|---|---|
| Composition | A | B1 | B2 | T |
| LiAlPO\(_4\)F | +1.14 | +3.16 | +3.17 | +3.31 |
| LiMgSO\(_4\)F | +1.12 | +2.22 | +2.19 | +3.22 |
| NaAlPO\(_4\)F | +1.09 | +3.16 | +3.16 | +3.29 |
| NaMgSO\(_4\)F | +1.11 | +2.18 | +2.18 | +3.23 |