Lithium Ion Conduction in Tavorite-Type LiMXO_4F (M-X: Al-P, Mg-S) Candidate Solid Electrolyte Materials

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Abstract

Two reported tavorite-type compositions, LiAlPO_4F and LiMgSO_4F , are evaluated by *ab initio* calculation to explore their viability as solid electrolyte materials for the development of solid state Li ion batteries. The two materials are determined to be intrinsically capable of 1D Li ion diffusion along a channels formed by a series of zigzag paths passing in between nearest neighbor trans-position Al (Mg) octahedral pairs. The calculated Li migration energies (ME) (0.55 and 0.20 eV, respectively) are comparable with fast Li ionic conductors currently employed in conventional Li batteries. The covalency of the polyanion group is the dominant factor that directly minimizes the interaction of mobile Li with the lattice, thus leading to ME lowering.

1. Introduction

The portable electronics market and transportation industry have caused a stark increase in the use of Li ion batteries in recent years.[1-5] This has resulted into numerous developments on different Li-containing compounds such as Li_3N [6], garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) and $\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$ (LLTO) [7-8], perovskite-type $(\text{Li},\text{La})\text{TiO}_3$ (LLT) [9], LiPON [10], $\text{Li } \beta\text{-Al}_2\text{O}_3$ [11], $\text{Li}_2\text{S-P}_2\text{S}_5$ glass ceramics [12], LISICON [13], and NASICON [14]. However, varying limiting factors make it difficult for these materials to become ideal solid electrolytes.[7, 9, 12]

Finding new solid electrolytes can lead to a major breakthrough in battery design especially for the solid electrolyte component. Recent studies have reported tavorite-type structures as candidate battery materials [15-16]; most compositions in this

group that have been evaluated so far are those with transition metals that can form redox couples and were intended as cathodes [17-23]. Thermodynamically, many of these favorite-type compositions are predicted to be relatively stable and are most likely to be directly synthesizable.[23] In relation to this, logical solid electrolyte candidates would be those analogs without transition metals such as LiAlPO_4F and LiMgSO_4F . [24,25] However, nontransition metal-based favorites have not yet been intensively explored for possible solid electrolyte use and their Li ionic conduction behavior is still poorly understood. So far, only the Li ion conduction in LiMgSO_4F has been reported, showing poor conductivity with an order of 10^{-3} S/cm (~ 800 K) and activation energy of 0.94 eV.[25] However, experimental activation energy especially for stoichiometric compound includes defect formation energy and Li migration energy. By defect structure design, the former energy can be systematically reduced. Thus, separating the two energy contributions and focusing on the latter energy term is needed to understand the potential for fast Li ion conduction in these compounds. The present work investigates the structure, defect chemistry, and Li ionic diffusion of favorite-type LiAlPO_4F and LiMgSO_4F by *ab initio* calculation.

2. Computational details

Density functional theory (DFT) atomistic modeling was initialized using projected augmented wave (PAW) method [26] as implemented in Vienna *Ab Initio* Simulation Package (VASP) [27]. Standard generalized gradient approximation (GGA) using the parametrization of Perdew–Burke–Ernzerhof for solids (PBEsol) was used for the exchange correlation energy.[28] Published structural information on experimentally synthesized ordered favorite LiAlPO_4F and LiMgSO_4F were taken from the Inorganic Crystal Structure Database (ICSD).[29] Spin-polarized calculation with an energy cutoff of 500 eV was carried out and allowed the total energies to converged within 3 meV per formula unit (f. u.). A $5 \times 4 \times 3$ Monkhorst-Pack kpoint grid in a 16-atom unit cell showed a reasonable convergence and an error of <1 meV/f. u. in the total energy. Berry phase method was used for the Born effective charge calculation in order to evaluate ionicity/covalency of cation bonds.[30] The nudged-elastic-band (NEB) method [31] was used to determine migration pathway and energy; the calculation was done with a $1 \times 2 \times 2$ supercell. Numerical integration was performed over the Brillouin zone by sampling the Γ -point. Convergence was determined to be within 30 meV/f. u.

3. Results and discussion

3.1. Crystal structure and defect formation

Optimization for the structural parameters from present *ab initio* DFT calculation is listed in Table 1. A strong agreement is achieved between theoretical and experimental results with deviations of only at most 0.79%, 0.58%, and 0.75% for lattice parameters, lattice angles, and volume, respectively. It is also apparent that the cell volume is strongly correlated with M cation size, with calculated values of 159.038 and 176.023 Å³ for Al (0.54 Å) and Mg (0.72 Å), respectively. Meanwhile, X cation size, i.e. for P (0.17 Å) and S (0.12 Å), is insensitive of volume size.

Table 1. Structural parameters from DFT calculation and experiment for LiMXO₄F (M-X: Al-P, Mg-S).

	LiAlPO ₄ F			LiMgSO ₄ F		
	calc.	exp.	diff.	calc.	exp.	diff.
<i>a</i> (Å)	5.074	5.060	0.014	5.163	5.162	0.001
<i>b</i> (Å)	5.148	5.160	-0.012	5.406	5.388	0.018
<i>c</i> (Å)	7.060	7.080	-0.020	7.129	7.073	0.056
α (°)	109.415	109.870	-0.455	106.935	106.680	0.255
β (°)	107.839	107.500	0.339	107.683	107.400	0.283
γ (°)	98.471	97.900	0.571	97.499	97.500	-0.001
<i>V</i> (Å ³)	159.038	159.780	-0.742	176.023	174.720	1.303

Better understanding of the electrochemical behavior of solid electrolytes requires careful investigation of intrinsic defect formation. In this work, Frenkel-type (Figure 1a-1c), Schottky-type (Fig. 1d), and anti-site defects are evaluated within the favorite structure. Based on Table 2, vacancy-type and site exchange-type defects are unlikely to exist in pure LiAlPO₄F and LiMgSO₄F. As a solid electrolyte material, this implies that there should be no Li trapping on interstitial sites and that conduction pathways should be unimpeded by blocking effects associated with Al cation on Li sites. However, Li vacancy creation by doping is necessary to obtain sufficiently high Li⁺ conductivity in these materials.

Figure 1. Defect structures evaluated within the LiMXO_4F tavorite structure: a) Li Frenkel-type, b) M Frenkel-type, c) F Frenkel-type, and d) Li-F Schottky-type defects, respectively. Gray octahedra are MO_4F_2 units, gray tetrahedra are XO_4 units, and green spheres are Li atoms. Dashed circles are the relevant vacancies while dashed arrow lines indicate direction of movement of relevant species of the defect.

Table 2. DFT-calculated intrinsic defect energies (eV) in LiMXO_4F .

	Li Frenkel	F Frenkel	Li-F Schottky	Li-M Anti-Site
LiAlPO_4F	+1.69	+4.60	+2.13	+2.42
LiMgSO_4F	+1.35	+3.66	+1.36	+1.21

3.2. Li ion jump within the tavorite host framework

As shown in Fig. 2a and 2b, four distinct paths are needed for a complete connectivity and Li long-range diffusion along the open tunnels. One is passing through a XO_4 - XO_4 tetrahedral pair (path 1 and path 4) and another passing through a MO_4F_2 - MO_4F_2 octahedral pair (path 2 and path 3) as illustrated in Fig. 2c and 2d, respectively.

Figure 2. Planar view on a) (100) plane and b) (011) plane for theavorite structure. Possible Li paths are shown as colored dashed lines. The local environment can be categorized as passing through: c) $\text{XO}_4\text{-XO}_4$ tetrahedral pair (path 1 and path 4) or d) $\text{MO}_4\text{F}_2\text{-MO}_4\text{F}_2$ octahedral pair (path 2 and path 3).

In Fig. 3, the migration energies (ME) for each of the path are shown. In both LiAlPO_4F (paths with white markers) and LiMgSO_4F (paths with gray markers), the pathways given by Fig. 2c are found out to be unfavorable for Li migration due to the high ME values (0.89-1.34 eV) while those given by Fig. 2d have lower ME values (<0.55 eV). Thus, Li mobility proceeds predominantly in one dimension (1D) in the two investigated materials, i.e., path 2-path 3-path2-... zigzag in LiAlPO_4F and path 2-path 4-path 2-... zigzag in LiMgSO_4F . Moreover, the bottleneck of this 1D pathway will be primarily governed by path 2 in both compositions, respectively. The difference in the estimated ME in the two sub-paths (path 2 and path 3) comprising the 1D channel can be ascribed to the staggered configuration of MO_4F_2 octahedra that delimits cavities and the Li disordering between two half-occupied sites. Interestingly, this 1D-type diffusion is also observed in olivine-type materials [32-33], particularly the LiFePO_4 composition which is reported to demonstrate ultrafast charging and discharging capabilities [34].

Figure 3. Energy profiles during Li ion jump in tavorite-type LiMXO_4F (path labels are the same as in Figure 2a-2b).

The simple increase in local tunnel size (from AlO_4F_2 pair to MgO_4F_2 pair) should decrease the short-range repulsive interaction arising from electron cloud overlap in the jump vicinity; Al-Al and Mg-Mg distances for the bottleneck path 2 are 5.15 and 5.41 Å, respectively. Another factor is the effect of strong bond directionality in XO_4 tetrahedra (from PO_4 to SO_4). Table 3 highlights the Born effective charge tensor data for the cations in LiAlPO_4F and LiMgSO_4F . Nominal charges of Li, M, and X are +1, +3 (+2), and +5 (+6), respectively. For Li and M cation, Born effective charges (diagonal values) are relatively close to their nominal values which suggest strong ionic character of the Li/M-O bond. For Li cation, the charge is almost isotropic which is reflective of its low polarizability.[35] For M cation, the average effective charge is higher than its nominal charge and this can be owed to the polarizability of M and its partial covalent interaction with the oxide ion.[36-37] However, this is not the case for X cation in which the effective charge is significantly lower than nominal charge; this case indicates strong covalency in the X-O bond.[38-39] Tuning this covalency of the bonds in the polyanion may increase anion electronic polarizability and may reduce Coulombic interaction effect between Li ion and the lattice. With the lower average Born effective charge for S^{6+} cation in $(\text{SO}_4)^{2-}$ than in P^{5+} cation $(\text{PO}_4)^{3-}$ polyanion relative to their nominal charges, the former is expected to have a stronger covalent character than the latter for bonding with oxide ion. Also, this degree of covalency in S-O bond should minimize more the interaction for the migrating Li with the lattice as the electron cloud

from oxide ion in MO_4F_2 (c.f. path 2) are drawn more towards $(\text{SO}_4)^{2-}$ polyanion. This bond directionality should then as well directly affect sterically the MO_4F_2 octahedra via displacement of common and corner-shared oxide ions. Hence, weighing among the two factors mentioned, polyanion covalency is suggested to contribute more towards ME variation.

Table 3. DFT-calculated Born effective (dynamic) charge (a. u.) tensors for cations in tavorite-type LiAlPO_4F and LiMgSO_4F .

LiAlPO_4F				LiMgSO_4F			
Li	1.24	-0.04	0.04	Li	1.28	-0.02	-0.03
	-0.07	1.12	0.06		-0.08	1.03	-0.07
	0.04	0.09	1.06		-0.10	-0.07	1.07
Al1	3.60	0.05	0.15	Mg1	2.51	-0.02	-0.14
	0.11	2.84	-0.06		0.10	1.99	0.07
	-0.11	-0.46	3.04		0.14	0.41	2.17
Al2	2.64	-0.18	-0.03	Mg2	1.84	-0.14	0.04
	-0.02	3.70	-0.11		-0.03	2.64	0.13
	-0.37	0.12	3.17		0.31	-0.05	2.08
P	3.36	-0.04	-0.32	S	3.33	-0.02	0.26
	-0.12	3.24	-0.07		-0.08	3.08	0.04
	-0.08	-0.02	3.33		0.07	-0.01	3.27

For comparison of the diffusion coefficient for Li ion jump, the relevant equation is [40-41]:

$$D = g v^* d^2 \exp(-ME/kT) \quad (1)$$

where g is a geometric factor which is assumed to be unity, v^* is the Li ion jump pre-exponential factor which can be estimated by analyzing the potential profile curvature, d is the specific jump distance, k is the Boltzmann's constant, and T is the temperature of the system. Assuming $T = 300$ K, diffusion coefficient values for path 2 is around 10^{-12} and 10^{-5} cm^2/s for LiAlPO_4F and LiMgSO_4F , respectively. These are also comparable with experimental measurements for a typical LiCoO_2 cathode which is in the range $10^{-11} - 10^{-13}$ cm^2/s . [42-43] A similar tendency is reported as well in previous studies conducted for transition metal-based tavorites. [22,23] However, ME by impedance spectroscopy for LiMgSO_4F was reported to be about 0.94 eV [25] which is sufficiently larger than the calculated bulk ME of 0.20 eV. This may be due to the following factors: i) some intrinsic defects which may cause blocking effects on the

conduction path such as Li-M anti-site pair, or ii) penalty arising from Li vacancy creation which may be a prerequisite before the actual Li ion conduction process could occur. As a whole, the conduction mechanism should be close to the predicted one and ME should be dominated by contribution from Li vacancy creation in conductivity measurements.[44] It may be beneficial to dope with aliovalent cations, targeting the M octahedral site in order to increase Li vacancies. Candidate dopants would be similar sized cations (≤ 1.15 factor of radius) such as Si^{4+} (0.4 Å), and Ge^{4+} (0.53 Å) for Al^{3+} (0.54 Å) and Sc^{3+} (0.75 Å), Al^{3+} (0.54 Å), Ga^{3+} (0.62 Å), and In^{3+} (0.8 Å) for Mg^{2+} (0.72 Å). We intend to carry out this doping strategy in order to eliminate the defect formation energy contribution to the activation energy,[25] thus activating the predicted bulk Li conductivity in these materials.

4. Conclusions

The Li ion conduction in tavorite-type LiAlPO_4F and LiMgSO_4F was successfully investigated by *ab initio* calculations. Li mobility occurs predominantly along 1D channel formed by a series of MO_3F_2 - MO_4F_2 octahedral pair path linkages. The bottleneck pathway of this channel has ME values of 0.55 and 0.20 eV for LiAlPO_4F and LiMgSO_4F , respectively. The strong covalency in XO_4 polyanion is suggested as the main factor for ME variation. It is unlikely in pure LiAlPO_4F and LiMgSO_4F to have significant intrinsic defect concentration. Doping of aliovalent cations at the M octahedral site is a viable approach for the activation and control of the intrinsic Li ionic conductivity in this group of materials.

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6. References

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