Supporting Information for

Revealing cooperative Li-ion migration in Li_{1+x}Al_xTi_{2-x}(PO_4)_3 solid state electrolyte with high Al doping

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**Computational details**

To evaluate the stability of Al-dopants in LATP, we calculate the defect formation energy of Al-dopants in Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$ (LATP) using a supercell with six LATP units by the following equation:

$$\Delta E_f = E(\text{defected}) + n \cdot \mu_{\text{Al}} - E(\text{bulk}), \quad (1)$$

where $E(\text{defected})$ and $E(\text{bulk})$ represent the total energies of the defected and the pristine LATP supercells, respectively, $\mu_{\text{Al}}$ is the chemical potential of Al, and $n$ is the number of Al removed from the pristine LATP when defects are generated. For Al chemical potential, we define it by the following equation:

$$\mu_{\text{Al}} = \left[ E(\text{Al}_2\text{O}_3) - 3 \cdot E(\text{O}_2)/2 \right]/2, \quad (2)$$

where $E(\text{Al}_2\text{O}_3)$ and $E(\text{O}_2)$ are the total energies of bulk Al$_2$O$_3$ and gas phase O$_2$ molecular. After computing work, the formation energies of Al vacancies are 4.13, 2.98, and 3.10 eV in LATP-0.16, LATP-0.33 and LAPT-0.50, respectively. The more positive the defect formation energy is, the more unfavorably thermodynamical reaction. Moreover, we calculate the decomposition energy with one combination, $\Delta E_f$, which is defined as

$$\Delta E_f (\text{LATP}) = E(\text{LTP}) - E(\text{LiAlPO}_5) - E(\text{LATP}) + E(\text{TiP}_2\text{O}_7). \quad (3)$$

where, the $E(\text{LTP})$, $E(\text{LiAlPO}_5)$, $E(\text{LATP})$, and $E(\text{TiP}_2\text{O}_7)$ is the total energies of LiTi$_2$(PO$_4$)$_3$, LiAlPO$_5$, LATP, and TiP$_2$O$_7$. After calculation, the decomposition energies for LATP-0.16, LATP-0.33 and LATP-0.50 are 262.41, 389.93, and 642.34 meV/atom, respectively. Again, these positive values suggest an unfavorably thermodynamical reaction. We note that the extent of Al defect formation and phase decomposition for LATP-0.33 is even a little higher than that for LATP-0.50. Now many experiments have successfully demonstrated the synthesis of LATP-0.50. Thus, the
stability of Al-dopant in LATP-0.50 is less problematic in practice because the thermodynamically unfavorable reaction and associated kinetic barrier.

The time-evolution of spatial correlations between atoms is described by the van Hove or space-time correlation functions. This function can be decomposed into self:

$$G_s(r, t) = \frac{1}{4\pi r^2 N} \sum_{i=1}^{N} \delta[r - |r(t_0) - r(t + t_0)|] \delta_{t_0}$$

and distinct:

$$G_d(r, t) = \frac{1}{4\pi r^2 N} \sum_{i \neq j}^{N} \delta[r - |r(t_0) - r(t + t_0)|] \delta_{t_0}$$

parts, in which the atom whose position is referred to at time \( t \) is either the same or a different atom from that whose position was specified at time zero. The defined \( G(r, t) \) gives the probability that, at the specified time \( t \), an atom will be located a distance \( r \) away from the location occupied by an atom at an earlier time zero. This method has been widely used to study the diffusion mechanism in other ISEs, such as \( \text{Li}_{4+x}\text{Si}_{1-x}\text{X}_x\text{O}_4 \)\(^{[1]} \) and garnet-type \( \text{Li}_{7-x}\text{La}_{3}\text{Zr}_{2-x}\text{M}_x\text{O}_{12} \)\(^{[2]} \).

To examine the effective migration of Li-ion, we calculate the site displacement function (SDF) of Li-ion as a function of simulation time. The SDF equation is defined \( d(t) = |r(t) - r(0)| \), i.e., the distance between the position of the Li-ion at time \( t \) (\( r(t) \)) and the initial position of the Li-ion atom at time 0).
Fig. S1. Relative energies of 11 possible structures considering different AlO$_6$ arrangement.
Fig. S2. Site displacement function (SDF) plots for one Li-ion trajectory in LATP0.50 taken from 60 ps NVT AIMD simulations at 600 K.
**Fig. S3.** The MSD of O and P atoms in LTP, LATP0.16 and LATP0.50 taken from 30 ps NVT AIMD simulations at 500 K.