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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 $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP) using a supercell with six LATP units by the following equation:

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

where E(defected) and E(bulk) represent the total energies of the defected and the pristine LATP supercells, respectively, μ_{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:

$$\mu_{Al} = [E(Al_2O_3) - 3 \cdot E(O_2)/2]/2, \quad (2)$$

where $E(Al_2O_3)$ and $E(O_2)$ are the total energies of bulk Al_2O_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, ΔE_f, which is defined as

$$\Delta E_f\,(\text{LATP}) = E(\text{LTP}) - E(LiAlPO_5) - E(\text{LATP}) + E(TiP_2O_7). \quad (3)$$

where, the E(LTP), $E(LiAlPO_5)$, E(LATP), and $E(TiP_2O_7)$ is the total energies of $LiTi_2(PO_4)_3$, $LiAlPO_5$, LATP, and TiP_2O_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:

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

and distinct:

$$G_d(r, t) = \frac{1}{4\pi r^2 N}\langle \sum_{i\neq j}^{N} \delta[r - |r_i(t_0) - r_j(t + t_0)|]\rangle_{t_0} \quad (5)$$

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 $Li_{4\pm x}Si_{1-x}X_xO_4$[1] and garnet-type $Li_{7-x}La_3Zr_{2-x}M_xO_{12}$[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)).

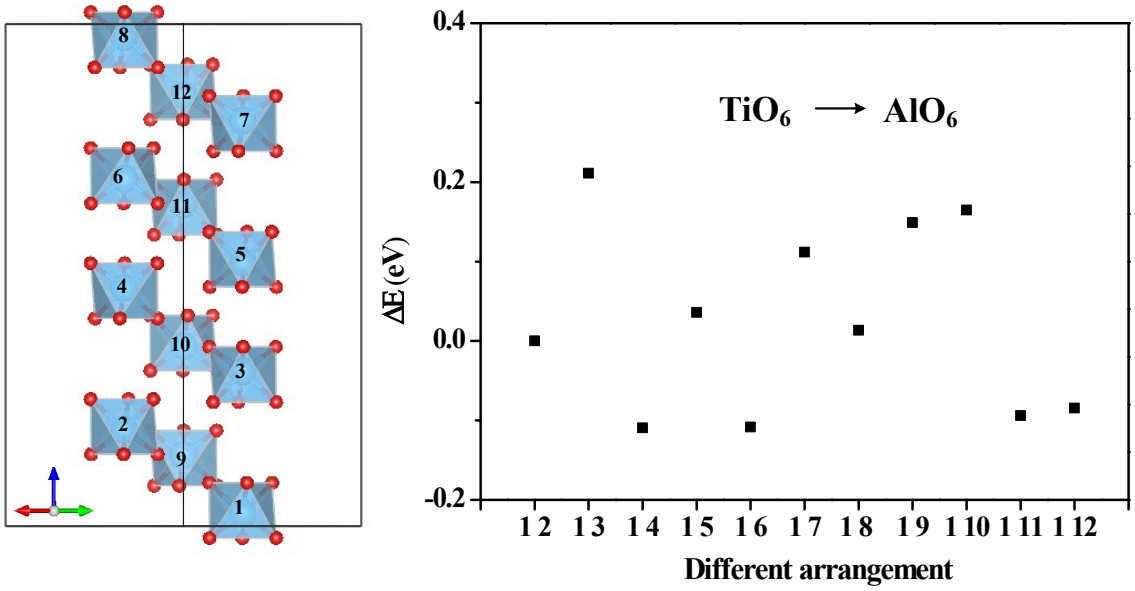

Fig. S1. Relative energies of 11 possible structures considering different AlO_6 arrangement.

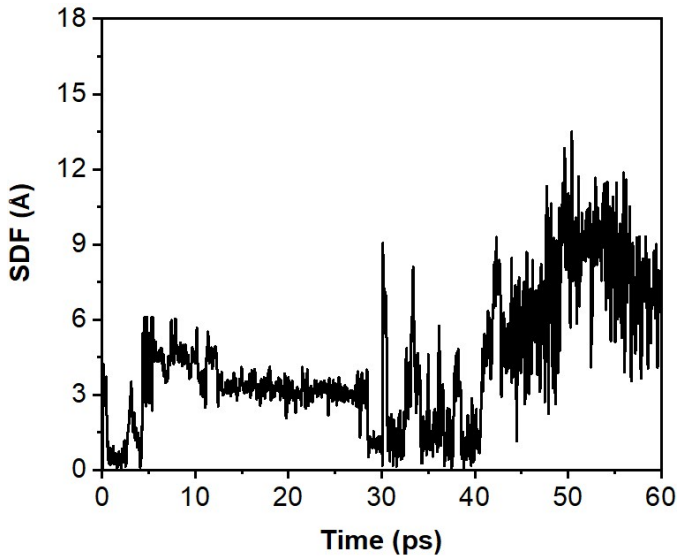

Fig. S2. Site displacement function (SDF) plots for one Li-ion trajectory in LATP0.50 taken from 60 ps NVT AIMD simulations at 600 K.

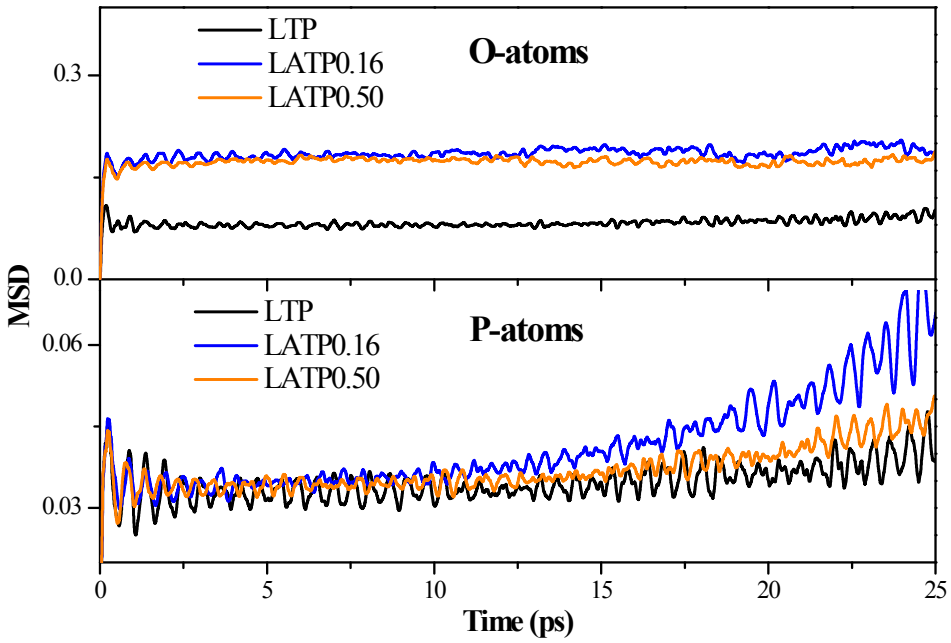

Fig. S3. The MSD of O and P atoms in LTP, LATP0.16 and LATP0.50 taken from 30 ps NVT AIMD simulations at 500 K.

[1] Y. Deng, C. Eames, B. Fleutot, R. David, J.-N. Chotard, E. Suard, C. Masquelier, M. S. Islam, *ACS Applied Materials & Interfaces* **2017**, *9*, 7050-7058.

[2] S. Adams, R. P. Rao, *Journal of Materials Chemistry* **2012**, *22*, 1426-1434.