Supplementary Information

Systematic Theoretical Investigation of Li_5NbWO_8 as a Novel Solid Electrolyte via First-Principles Calculations

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Table S1. Comparison of thermodynamic stability of different Nb doping concentration configurations

Composition	E_{hull} (meV/atom)
$Li_9NbW_3O_{16}$	22
Li_5NbWO_8	36
$Li_{11}Nb_3WO_{16}$	55

Note1

As shown in Table S1, with increasing Nb doping concentration, the value of E_{hull} increases, indicating a decrease in the structural stability of the material. The E_{hull} of $Li_{11}Nb_3WO_{16}$ exceeds 50 meV/atom, surpassing the threshold typically adopted in high-throughput screening.[1] Therefore, compared with the other two materials, it is more susceptible to decomposition. Consequently, its other properties are not further investigated in this work. Additionally, although $Li_9NbW_3O_{16}$ possesses good thermodynamic stability, its lithium-ion conductivity at room temperature is relatively low (Figure S1). Hence, after balancing thermodynamic stability and lithium-ion conductivity, the main focus of this work is placed on Li_5NbWO_8.

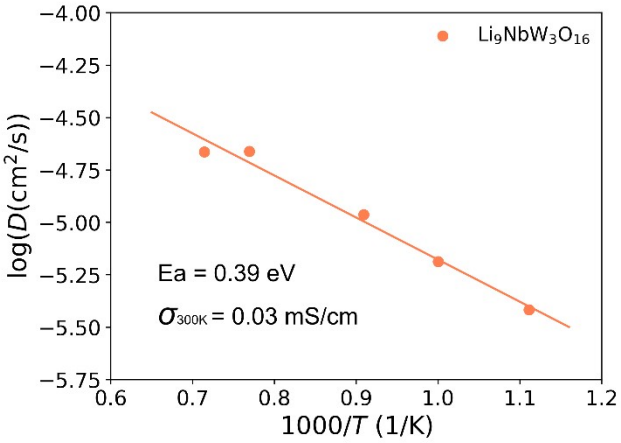

Figure S1. Arrhenius plots of Li ions diffusion in $Li_9NbW_3O_{16}$.

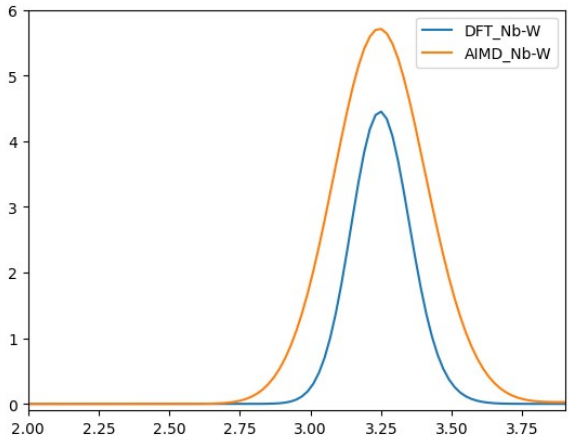

Figure S2. The radial distribution function (RDF) of Nb-W obtained from DFT calculations and AIMD calculations at a temperature of 1400 K.

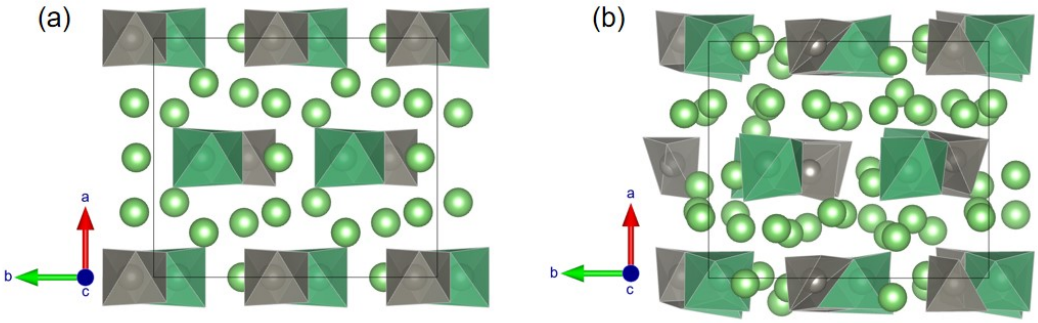

Figure S3. The configuration obtained after (a) DFT calculation and (b) AIMD calculation at a temperature of 1400 K.

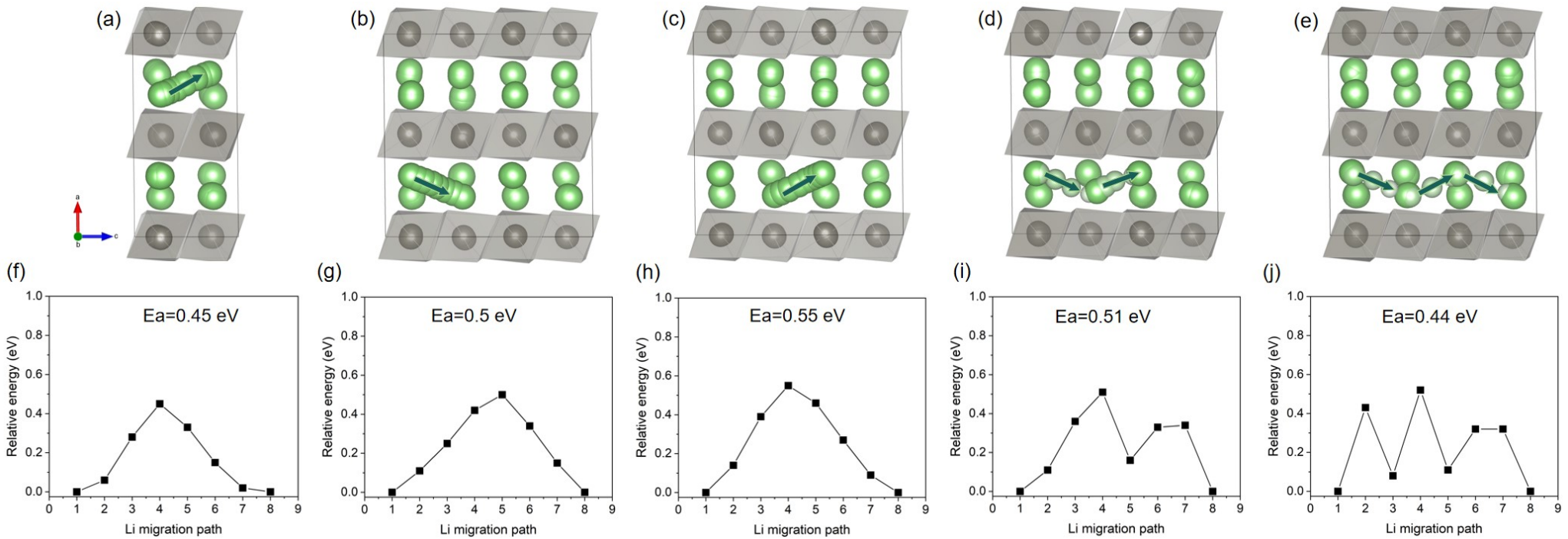

Figure S4. Diffusion pathways and relative energies of lithium ions migrating via different mechanisms in Li_2WO_4, calculated using the NEB method. (a-c) the single-ion hopping manner; (d) the two-ion concerted migration; (e) three-ion concerted migration; (f-j) the corresponding relative energy for the a-e migration mode.

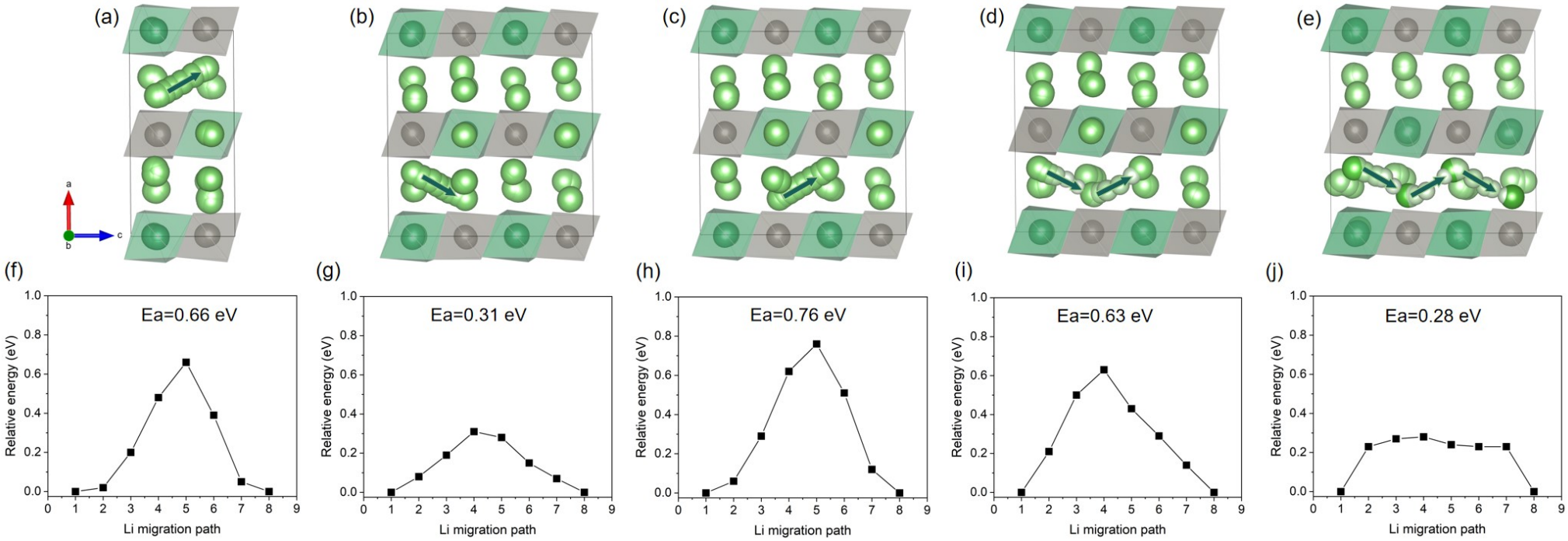

Figure S5. Diffusion pathways and relative energies of lithium ions migrating via different mechanisms in Li_5NbWO_8, calculated using the NEB method. (a-c) the single-ion hopping manner; (d) the two-ion concerted migration; (e) three-ion concerted migration; (f-j) the corresponding relative energy for the a-e migration mode.

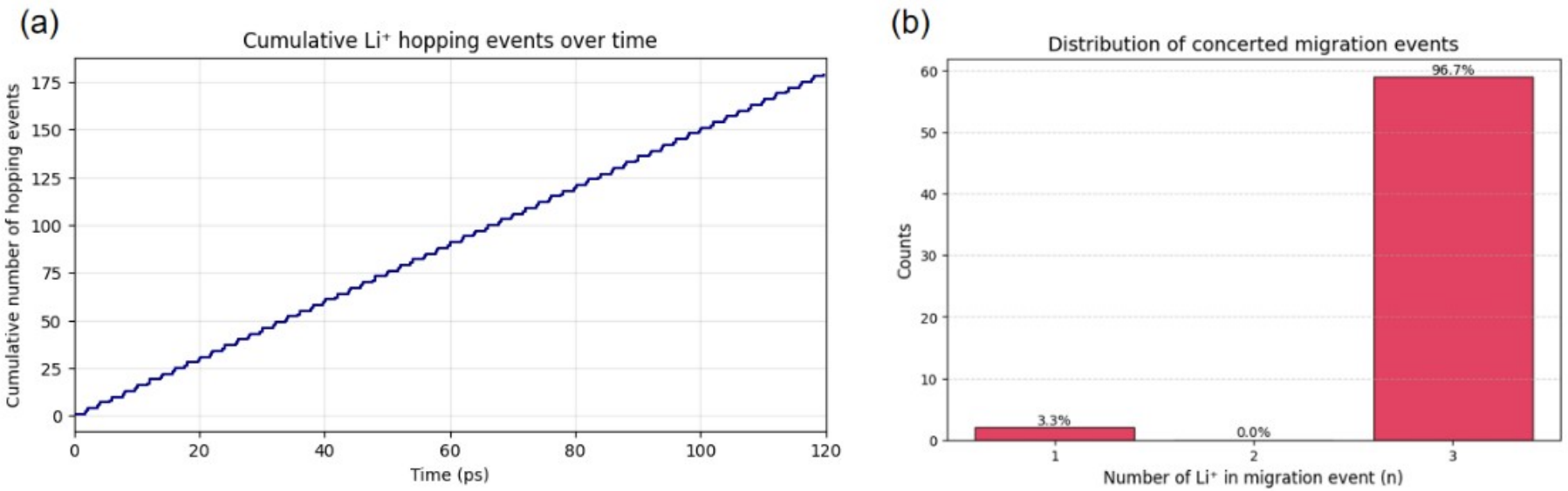

Figure S6. Statistical analysis of hopping events. (a) cumulative hopping events over time and (b) the histograms of the number n of Li^+ hopping from AIMD simulations.

Note2

We selected several typical pathways and compared the energy barriers for single-ion hops and multi-ion concerted migration. We calculated and compared the energy barriers for lithium-ion diffusion in Li_2WO_4 and Li_5NbWO_8 under different migration modes (Figure S4 and S5). The calculation results show that when lithium ions move via single-ion hopping, the energy barrier in Li_2WO_4 falls within the range of 0.45-0.55 eV. After Nb doping, however, the barrier range for single-ion hopping broadens to 0.31-0.76 eV. These results indicate that with Nb doping, lithium ions are prone to short-range diffusion through single-ion hopping, making long-range diffusion via this mechanism unlikely. For concerted diffusion of two lithium ions, the barrier is 0.51 eV in Li_2WO_4, whereas in Li_5NbWO_8 it rises to 0.63 eV. Interestingly, in the case of three-ion concerted migration, the barrier in Li_2WO_4 slightly decreases to approximately 0.44 eV, while in Li_5NbWO_8 it drops significantly to 0.28 eV, and the energy landscape becomes notably flattened. In summary, Nb doping significantly reduces the lithium-ion diffusion barriers, and the diffusion is dominated by the concerted migration of three lithium ions. Moreover, the energy barriers calculated based on the NEB method are very close to the results obtained from the AIMD calculation (0.26 eV).

Additionally, we have collected the probabilities of different hopping mechanisms among lithium-ion jump events in Li_5NbWO_8 (Figure S6).[2] The

probability of single-ion hopping is only 3.3%, whereas three-ion concerted migration accounts for 96.7% of the events; no two-ion concerted migration events are observed. Based on the above computational results, lithium-ion diffusion in Li_5NbWO_8 proceeds predominantly via the concerted migration of three lithium ions.

References

1. X. He, Q. Bai, Y. Liu, A. M. Nolan, C. Ling and Y. Mo, Crystal structural framework of lithium super-ionic conductors, *Adv. Energy Mater.*, 2019, **9**, 1902078.
2. X. He, Y. Zhu and Y. Mo, Origin of fast ion diffusion in super-ionic conductors, *Nat. Commun.*, 2017, **8**, 15893.