

Supporting Information:

Disentangling the Coupled Origins of Li^+ Ion Transport in LATP through Hierarchical Modeling

Hannes Gustafsson, Fabian Schwarz, Tamme Alex, and Amber Mace*

Department of Chemistry – Ångström, Uppsala University, SE-751 21 Uppsala, Sweden

E-mail: amber.mace@kemi.uu.se

Independent variation of Li and Al concentrations

Detailed plots of the variation among predicted diffusion coefficients with MACE-based Ionic TuTraSt, as functions of Al content and Li^+ content independently, are shown in Figure S1 and Figure S2 respectively. These results show that the Al content had a relatively smaller impact on the diffusion compared to the Li^+ concentration, as well as the observation that lower Li^+ diffusion coefficients were observed for low to intermediate Al concentrations, while a higher Li^+ ion concentration almost monotonically caused a higher diffusion.

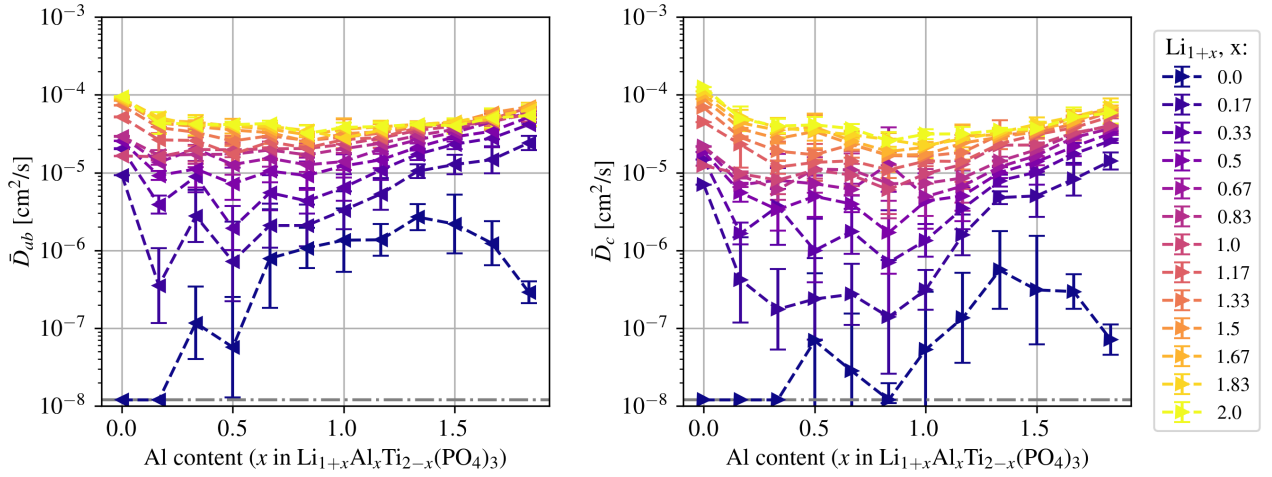


Figure S1: Diffusion coefficients calculated with the MACE-based Ionic TuTraSt workflow, in the ab-directions (left) and c-direction (right) of the unit cell for different LTP/LATP compositions, plotted against the Al content. Results for intermediate Al-concentrations ($0 < x < 2$) are averages over 5 configurations. Each line represents a Li^+ concentration, indicated by the color, which corresponds to the number of Li^+ ions used in the corresponding MMC simulations. Error bars indicate the relative standard deviation. Results on the gray dashed line at the bottom indicate that either no diffusion channels were found below the energy cutoff, or that the MSD did not reach the diffusive regime.

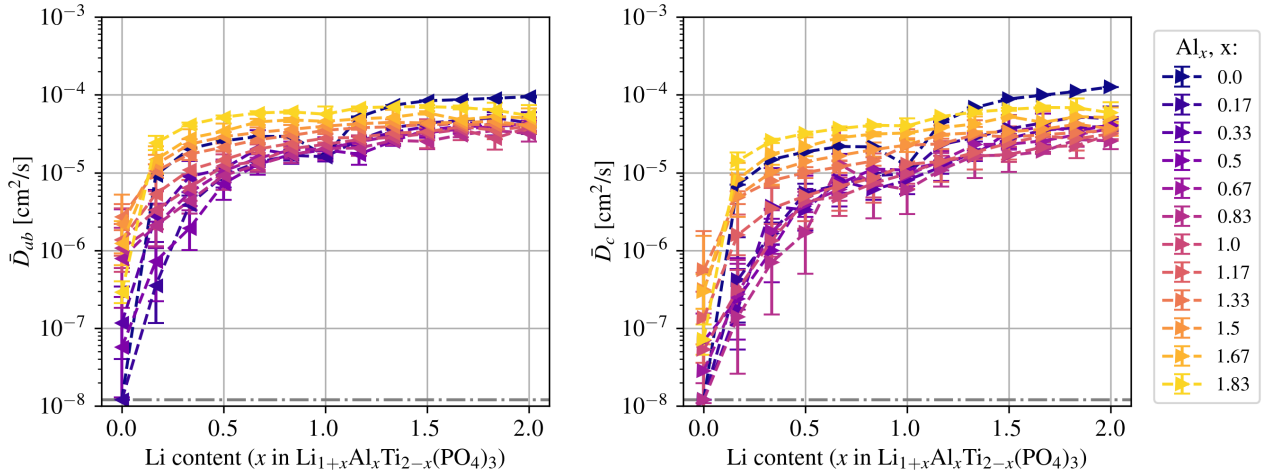


Figure S2: Diffusion coefficients calculated with the MACE-based Ionic TuTraSt workflow, in the ab-directions (left) and c-direction (right) of the unit cell for different LTP/LATP compositions, plotted against the Li^+ -ion content (i. e. corresponding to the number of Li^+ ions present in the MMC simulations). Each line represents a Al concentration, indicated by the color, and results for intermediate Al concentrations ($0 < x < 2$) are averages over 5 configurations. Error bars indicate the relative standard deviation. Results on the gray dashed line at the bottom indicate that either no diffusion channels were found below the energy cutoff, or that the MSD did not reach the diffusive regime.

MACE model validation

The training and test root mean square error for the MD-model on the MD data are 1.0 meV/atom for the energies and 39 meV/Å for the forces. Extrapolation of the models was tested on the grid model, whose performance is shown in Figure S3. The model shows good accuracy in the training interval up to 3 eV and extrapolates well up to 10 eV.

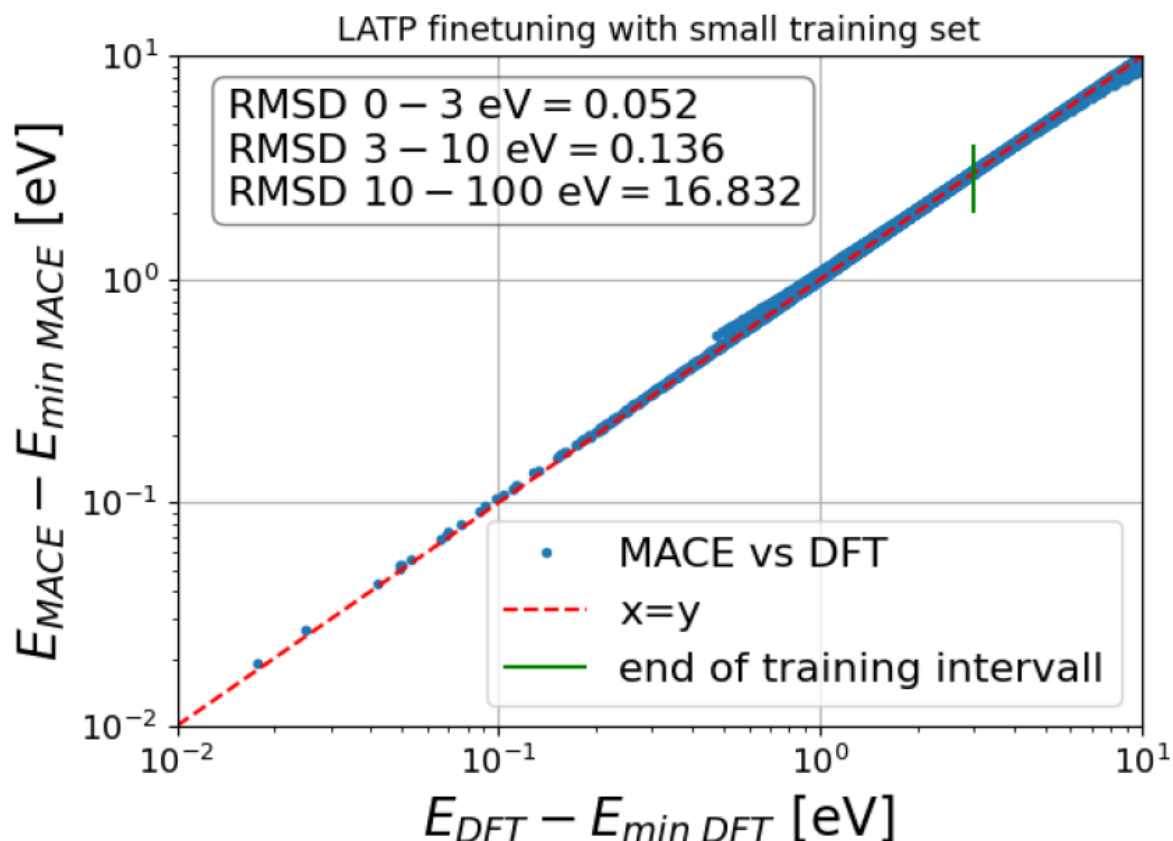


Figure S3: The performance of the finetuned grid model on the combined training- and test-set is evaluated by comparing the energies obtained via the fine-tuned MACE model with DFT energies.

The following sections report the grid model’s extrapolation performance on different substitution concentrations, supercells and geometry optimized structures.

Extrapolation to different substitution concentrations

Starting from the LTP unit cell (containing 12 Ti atoms), six substituted systems were created, where in each system, a random Ti atom was replaced by an Al atom. Single

particle grids were calculated using DFT and MACE and the resulting energies are compared in Figure S4. The results show good agreement up to 3 eV above the minimum energy.

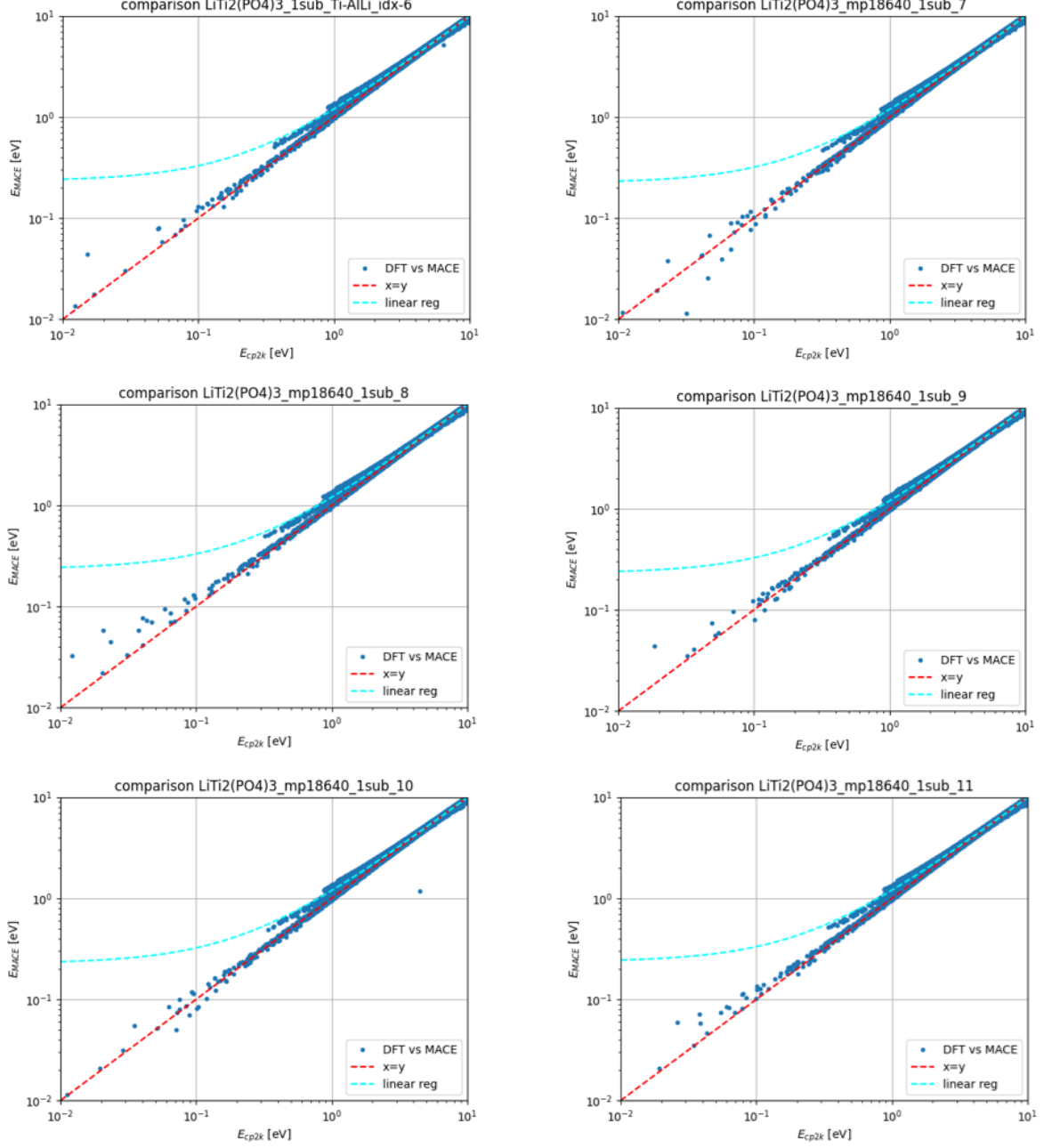


Figure S4: Comparing the energy grids obtained via the fine-tuned MACE model with DFT energies. In every structure, a random Ti was substituted with Al.

The model was trained at $x = 1/3$ and shows good extrapolation to values of $x \leq 0.33$. As discussed in the main manuscript, the model slightly underestimates the energies closer to the minimum energy in fully-substituted LAP. This has to be taken into account

when analyzing the single-particle grid. However, our results show that Li-Li interactions largely dominate the diffusion across all substitution concentrations and especially at higher substitution concentrations.

Extrapolation to supercells

Figure S5 illustrates the extrapolation of the grid model (trained on a $1 \times 1 \times 1$ LATP cell) to LTP supercells of different sizes.

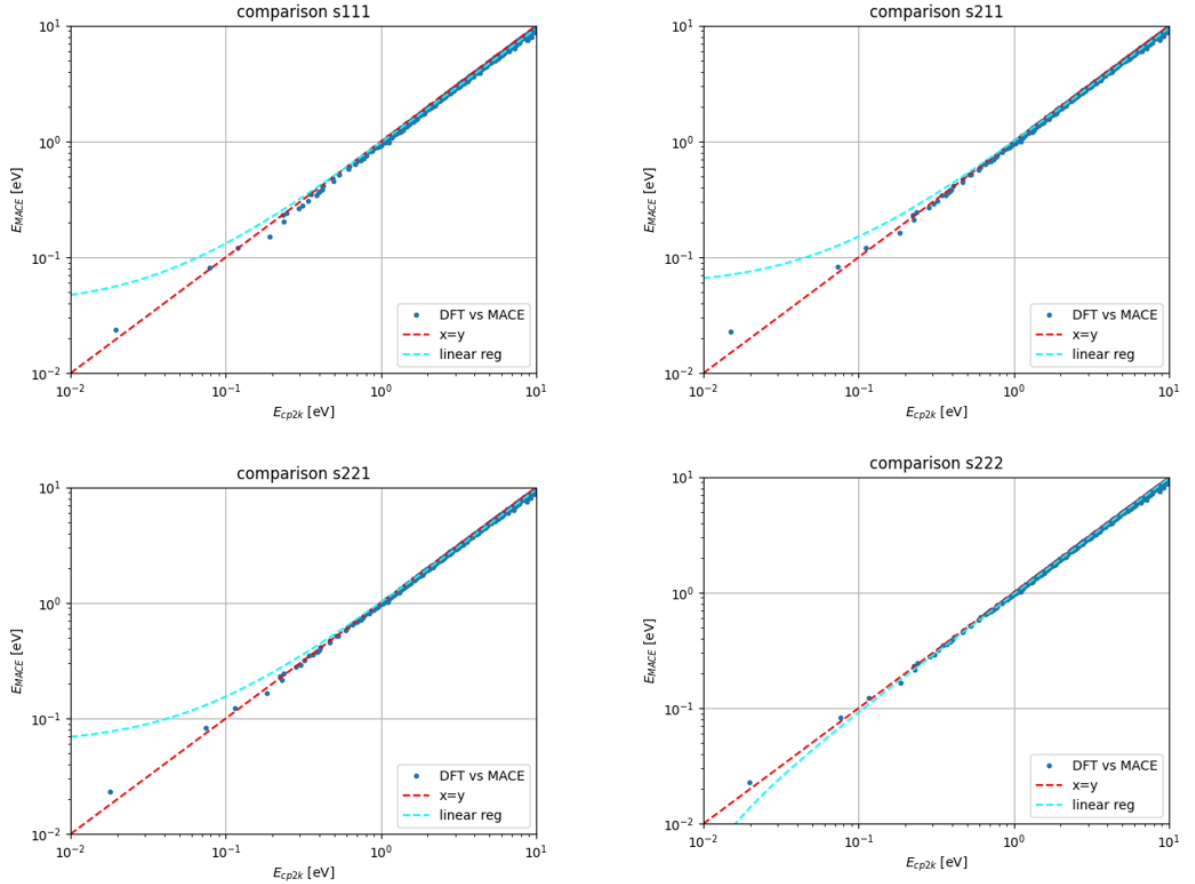


Figure S5: Comparing the energy grids obtained via the fine-tuned MACE model with DFT energies for LTP supercells of different sizes.

Accuracy for cell and geometry optimized structures

Figures S6 and S7 illustrate the extrapolation of the grid model (trained on a $1 \times 1 \times 1$ LATP cell) to $1 \times 1 \times 1$ LATP geometry optimized cells with substitution levels $x = 0.33$ and $x = 1$.

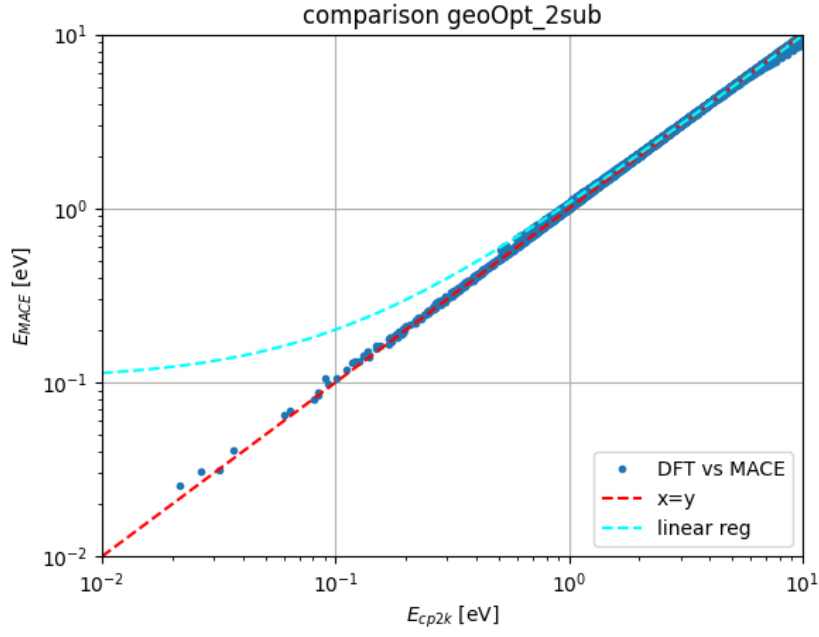


Figure S6: Comparing the energy grids obtained via the fine-tuned MACE model with DFT energies for a geometry-optimized, 2-substituted ($x = 1/3$) LATP structure.

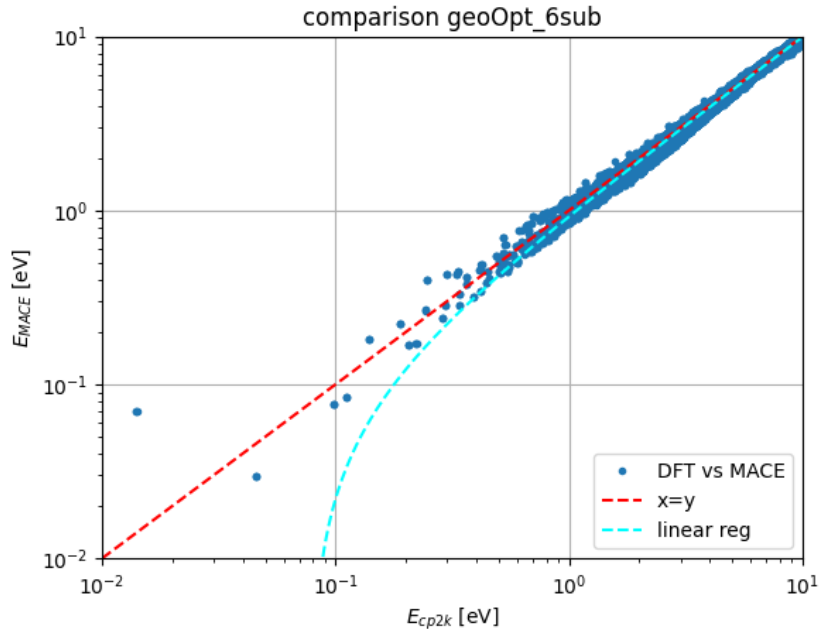


Figure S7: Comparing the energy grids obtained via the fine-tuned MACE model with DFT energies for a geometry-optimized, 6-substituted ($x = 1$) LATP structure.

Additional MD results

In the manuscript, MD simulations were run only for one randomly chosen structure at every substitution level. To illustrate the variability of the diffusion constant across different random realizations of the same substitution concentration, five MD simulations were run at the substitution concentration of $x = 0.33$. The framework atoms were not constrained in the MD simulations. The MSD for the five systems are plotted in Figure S8. The extracted diffusion constant show very small variances within 10% of the average diffusion constant.

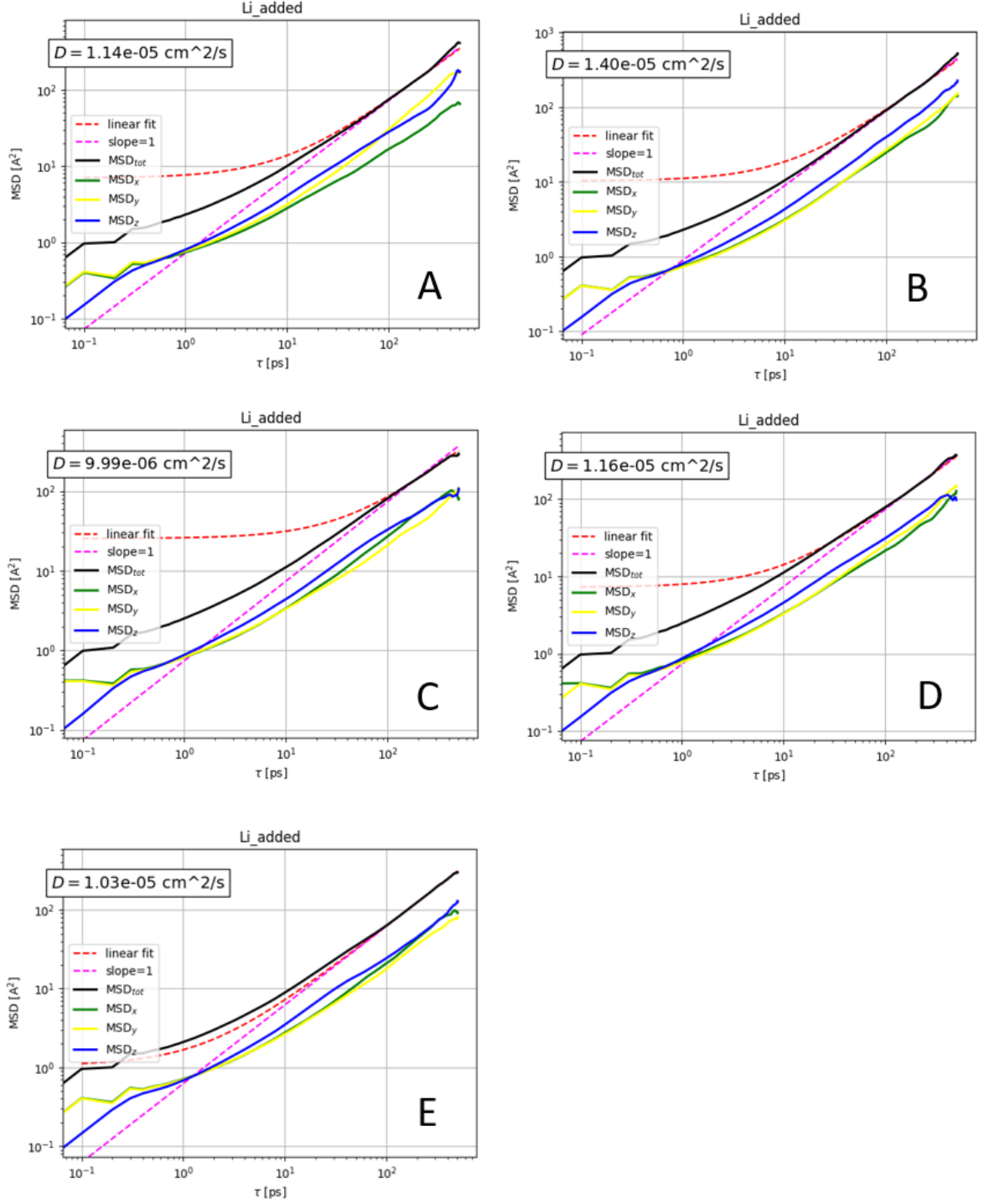


Figure S8: MSD plots for five different realizations of the 8-substituted ($x = 0.33$) simulation supercells.

To judge the change in electronic structure after geometry optimization, single-point DFT calculations were run for the initial and geometry optimized structures to extract effective REPEAT charges. Figure S9 shows that oxygen atoms have a significantly more negative charge after geometry optimization. Furthermore Figure S10 shows the cell

volume of the geometry and cell-optimized structures. The general trend is a decrease in cell volume with an increasing substitution concentration.

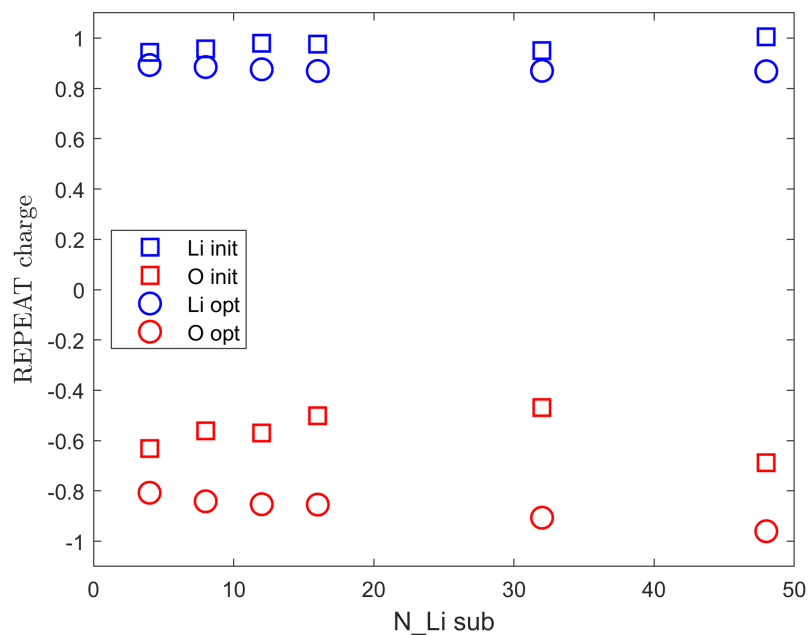


Figure S9: Showing effective REPEAT charges for Li and O for the initial and geometry optimized structures.

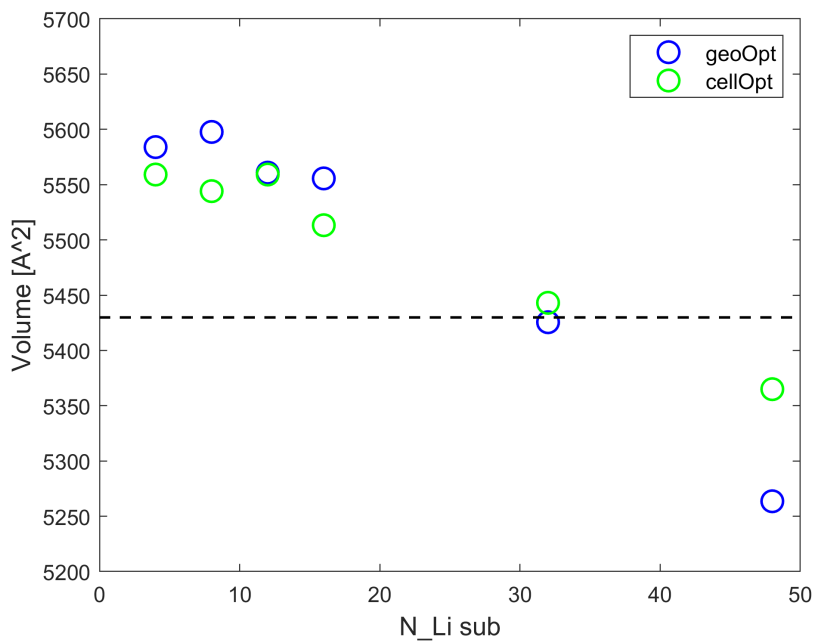


Figure S10: Change in the cell volume of the geometry optimized and cell optimized systems. The dashed line shows the cell volume of the LTP cell obtained from Materials project.

Finally, we show a comparison of the diffusion constants for the initial, geometry-optimized and cell-optimized structures with a flexible (Figure S11) and fixed(Figure S12) framework. When the framework atoms are not fixed, the two optimization strategies do not result in significantly different diffusion constants. When fixing the framework atoms during the MD simulations, the local rearrangements from the full geometry optimization significantly reduce the diffusion constants. Li^+ ions diffuse enough to extract a diffusion coefficient only in the system with the lowest substitution concentration ($x = 0.67$).

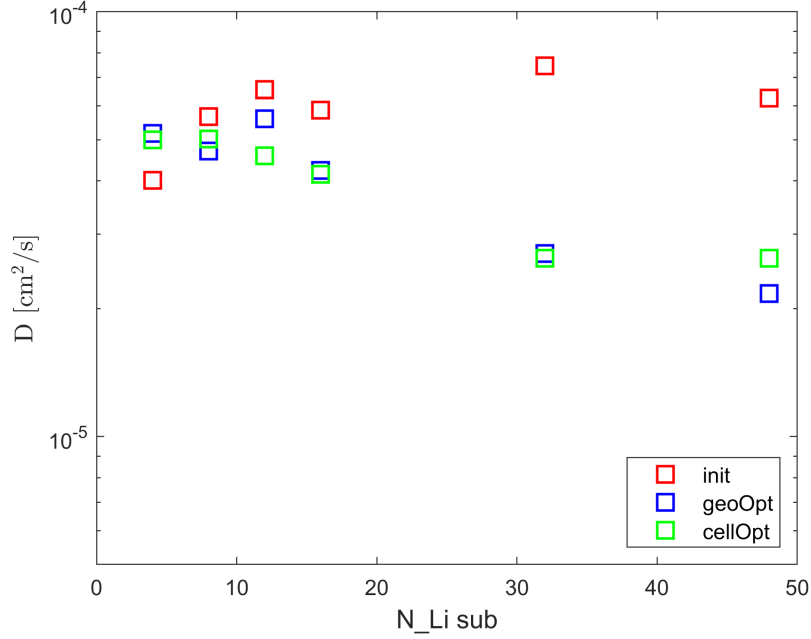


Figure S11: Comparing diffusion constants for three different unit cell geometries, when not fixing the framework atoms: The initial LTP unit cell, the geometry optimized simulation cells where both cell volume and the position of the framework atoms were allowed to relax and the cell optimized simulation cell where only the cell volume and the position of the Li atoms were allowed to relax.

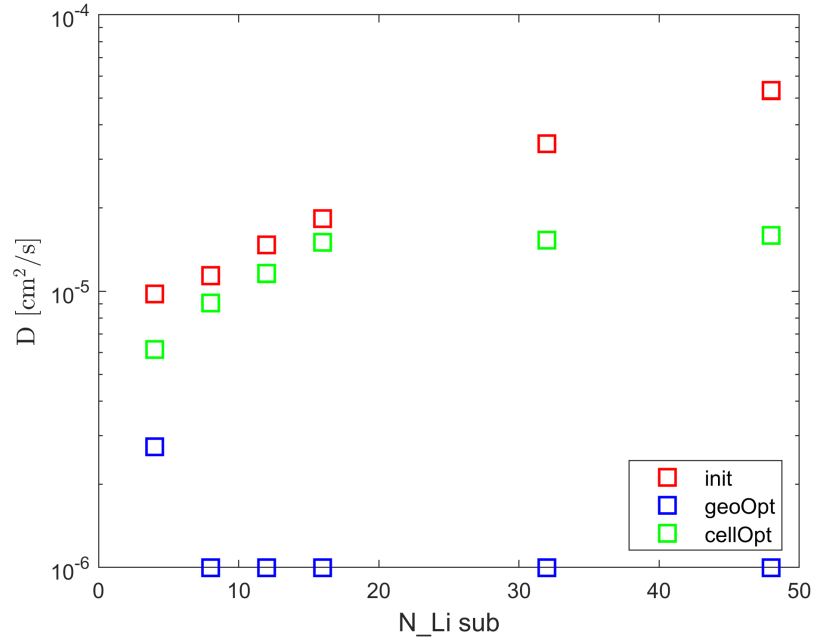


Figure S12: Comparing diffusion constants for three different unit cell geometries when fixing the framework atoms: The initial LTP unit cell, the geometry optimized simulation cells where both cell volume and the position of the framework atoms were allowed to relax and the cell optimized simulation cell where only the cell volume and the position of the Li atoms were allowed to relax. Values of 10^{-6} mean that the Li^+ ions did not diffuse sufficiently to extract diffusion coefficients from the MD simulations.