

Supporting information for: Implications of Occupational Disorder on Ion Mobility in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Battery Materials

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Validation of the interatomic potential

Employed interatomic potential

All potential based calculations are performed using the code package LAMMPS¹ developed at Sandia National Labs. The long-range Coulomb and short-range van der Waals interactions are modelled by the Buckingham potential:

$$U_{ij} = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} + A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} \quad (1)$$

where ϵ_0 corresponds to the dielectric constant in vacuum, r_{ij} to the ion distance, q_i are parametrized partial ion charges, and A_{ij} , ρ_{ij} , C_{ij} are parameters for the short-range interactions. Polarization is included via the core/shell or shell model where the polarizable ion is composed of a core particle as the inner part of the ion and a satellite particle corresponding to an outer electron hull.² Both

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pseudoparticles possess charges which sum up to the effective partial ion charge and are bound by a harmonic spring:

$$U_{c-s} = k \cdot r_{c-s}^2 \quad (2)$$

where r_{c-s} represents the core/shell distance and k is parametrized together with the shell charge q_s to reproduce the ion polarizability α .

$$\alpha = \frac{q_s^2}{k} \quad (3)$$

Parameters for the interatomic potential of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ have been developed by Kerisit *et al.* starting from a TiO_2 force field by Matsui and Akaogi.³ The interaction parameters were derived via lattice parameters, lattice constants and bulk modulus of Li_2O ^{4,5} and the shell model constants from the ion free polarizability (see Eq. (3)) obtained by electronic structure calculations.⁶ In the case of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ only the O^{2-} ions are treated as polarizable ions. In accordance with the primary literature/potential by Kerisit *et al.* a cutoff of 9 Å is chosen for the short-range interactions and periodic boundary conditions are applied where the Coulombic long-range forces are treated by a particle-particle particle-mesh solver.⁷

Details to DFT reference calculations

All DFT reference calculations are conducted with the FHI-aims code⁸ using a PBE functional. The electronic states are described with an all-electron basis set as implemented in the FHI-aims code. Depending on the structure dimensions consistent k-point grids and scf-convergence criteria are employed as indicated.

Validation of configuration space representation

To determine the performance of the interatomic potential, the configuration dependent energy and forces are validated via electronic structure calculations. As a reference the configuration space in the smallest possible stoichiometric unit cell in $R\bar{3}m$ space group with the chemical formula $\text{Li}_8\text{Ti}_{10}\text{O}_{24}$ is compared. The mixed occupancy of the $R\bar{3}m$ representation results in the distribu-

tion of 2 Li and 10 Ti ions on the octahedral sites giving $12!/(10! \times 2!) = 66$ possible configurations which reduce to 6 inequivalent configurations due to symmetry (see Figure 1).⁹ For the DFT reference calculations a $4 \times 4 \times 2$ k-point grid as well as the tight settings for the basis set and the scf convergence criteria are employed. Figure 1 shows the relative energies of configurations 1-6

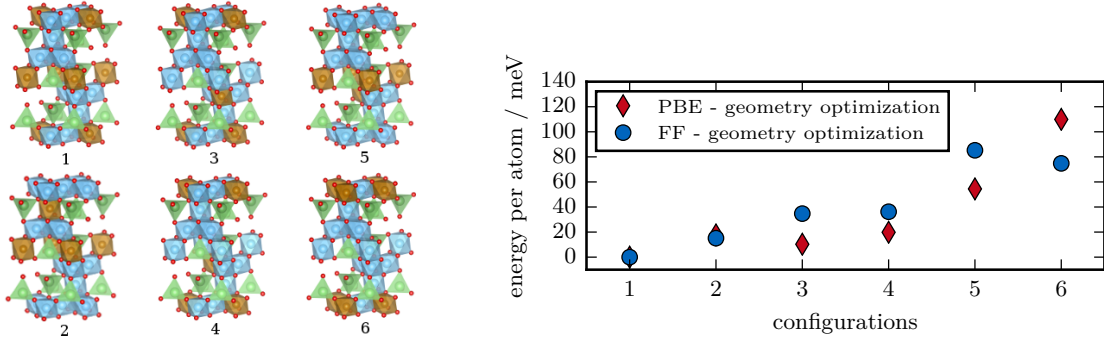


Figure 1: (left) Symmetry inequivalent configurations of $\text{Li}_8\text{Ti}_{10}\text{O}_{24}$ in the $R\bar{3}m$ space group. Oxygen is shown in red, Ti in octahedral sites in blue, Li in octahedral sites in gold and Li in tetrahedral sites in green. (right) Relative energies of the geometry optimized symmetry inequivalent configurations of $\text{Li}_8\text{Ti}_{10}\text{O}_{24}$ via the applied potential and DFT-PBE. The energies are referenced to the minimum energy configuration 1 (denoted as “ $R\bar{3}m$ ” in the main text).

optimized via DFT and the employed potential. In both cases, the optimization of atomic positions are started from structures based on the experimental lattice parameters.¹⁰ It can be seen that the potential reproduces the general trend of the energetic order, however deviations are seen in the energetically close lying structures yielding a reversed order for the configurations 2-3 and 5-6. Due to the qualitative agreement with the DFT results and a successful application in thermodynamic and kinetic studies,^{4-6,11,12} we trust the potential to yield sufficiently accurate energetics and forces in order to sample the configuration space of a larger ensemble.

Validation of Ti^{16c} defect predictability

To validate the description of Ti^{16c} defects via the force field, the defects are systematically investigated within a spinel-LTO structure small enough for a rigorous sampling. Hereby all possible Ti^{16c} defects are introduced in the $1 \times 1 \times 1$ and $2 \times 2 \times 1$ supercell of the lowest energy configuration in the $R\bar{3}m$ space group representation (see above). A prior optimization of the atomic

positions on basis of the force field allows to distinguish stable defects. From this, randomly chosen low energy candidates are re-optimized via DFT, hereby using a $4 \times 4 \times 2$ k-point grid for the $1 \times 1 \times 1$ and a $3 \times 3 \times 2$ k-point grid for the $2 \times 2 \times 1$ supercell, as well as the tight default settings for the basis set and the scf convergence criteria. All geometry optimizations showed the defects to remain stable and therefore represent local minima in the DFT energy landscape emphasizing a reliable force prediction of the potential. Comparing the resulting relative energies referenced to the defect-free configuration (see Figure 2) however shows deviation of the force field in the $1 \times 1 \times 1$ supercell where defects appear at lower energies overestimating thermodynamic stability. Since this deviation disappears in the $2 \times 2 \times 1$ supercell, its origin can be linked to strong electronic defect-defect interaction in the small periodic supercell. In the larger supercell the relative energies either coincide remarkably well or are even overestimated by the potential. Qualitatively indicated by a Mulliken charge analysis, the latter derives from a charge transfer which the force field fails to describe by design.

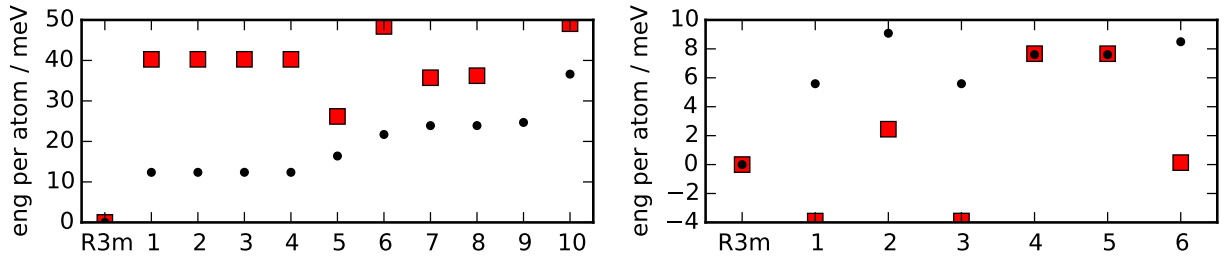


Figure 2: Comparative calculations by means of the interatomic potential and DFT calculations for randomly chosen, stable Ti^{16c} defect candidate structures (1-x) referenced to their defect free structure ($R\bar{3}m$) for a $1 \times 1 \times 1$ (left) and $2 \times 2 \times 1$ supercell (right). Black dots represent geometry optimizations on force field level, the red squares on DFT level.

Based on our findings we assess the predictability of the employed force field as adequate since defects correctly appear as local minima with well coinciding relative energies. Identified shortcomings have no effect on the conclusions put forward in the main text: Firstly the underestimation of thermodynamic stability due to charge transfer in the comparably small reference structure leads to a possible underestimation of the defect formation probability which is considered. Secondly the underlying deviation in the defect-defect interactions appears only at very high concentrations

(1 in 10 Ti-ions), which are found to be improbable and therefore negligible based on relative energies already at the underestimating force field level.

Monte-Carlo sampling details

Geometry optimizations, structure validation, configuration recognition

The geometry optimizations conducted during the Monte-Carlo samplings follow a two step protocol. In the first step only the atom positions are optimized without allowing the core/shell degree of freedom (DOF) to relax. In the second step atom positions, core/shell DOFs and the cell constants are allowed to relax. The described two step procedure was chosen to avoid any artifacts arising from optimization channels opening up due to the core/shell relaxation.

Occasionally resulting glass-like structures at very high energies are considered as artifacts of the employed force field and discarded. A structure evaluation based on deviation of the cell volume and the radial distribution function of O-O distances is hereby employed. Structures are rejected if the cell volume deviates more than 3 % from the experimental volume and if the first and second averaged coordination sphere deviates about 1.75 and 2.75 atoms respectively from the ideal fcc coordination sphere.

It is necessary to extract the occupation of Li and Ti ions in octrahedral sites of a structure after each geometry optimization since it serves as the starting point for the next Monte-Carlo step. Hereby the geometries are discretized by projecting the structure on the distorted (geometry-adjusted) fcc crystal lattice. The distortion of said lattice is based on the oxygen displacement during the geometry optimization. All tetrahedral and octahedral positions are moved in accordance to the displacement of the coordinating oxygen ions. The resulting configuration is then determined by sorting the ions by distance to the closest crystal positions.

Metropolis Monte-Carlo pre-sampling

To pre-sample the configuration space and assess a rough energy distribution of available configurations, we employ the Metropolis acceptance criterion to obtain a preliminary multicanonical ensemble at a given temperature T . In this sampling a new configuration is accepted based on the previous configuration via:

$$p_A = \min \left(1, \exp \left(-\frac{E_{n+1} - E_n}{kT} \right) \right) \quad (4)$$

where E_{n+1} and E_n are the total energies of the newly generated and previous structure, respectively, and k_B the Boltzmann constant.

In order to globally sample the corrugated potential energy landscape, we sample at the ultra-high temperatures 700 K, 1800 K and 4200 K starting from a high energy structure for the first case and the ordered “R $\bar{3}$ m” structure for the other cases. We thereby pre-access the possible disorder of the configuration space on grounds of 4121, 4759, and 4547 accepted of 791277, 74255, 25313 trial structures for the three temperatures respectively (see Figure 3).

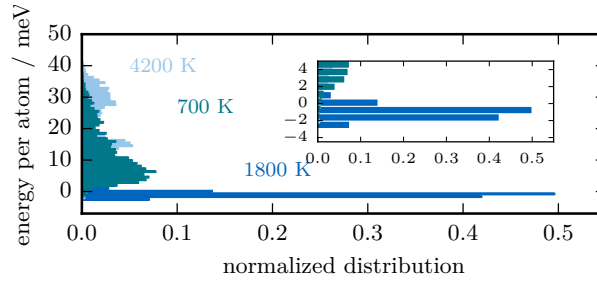


Figure 3: Normalized energetic distribution of the structures belonging to the created ensembles at 700, 1800 and 4200 K. The energy of the idealized “R $\bar{3}$ m” structure is taken as zero reference.

Parallelized Wang-Landau sampling details

In the energy range of the pre-sampled non-converged multicanonical ensemble we run a Wang-Landau sampling - tailored to the high computational cost - to estimate the density of states $g(E)$ and therefore the probability distribution of ordered and disordered configurations.

The relevant energy range is split into intervals of 0.18 eV leading to 331 bins. This conveniently chosen number of bins fits roughly to the number of probed 432 $16d$ sites in our model, a rule of thumb found in the Ising model for an efficient sampling.¹³ The sampling is trivially parallelized using 33 random walkers each covering 14 bins thus leading to an overlap of 4 bins to the adjacent walkers.¹⁴ Starting configurations for each walker in its respective energy range are drawn from the pre-sampling. To capture boundary effects, steps outside of a walkers energy span are counted to the originating bins¹⁵ and a localized sampling is avoided by drawing new random structures after 100 consecutive non-accepted steps.¹³ The flatness criterion for the bias refinement (initial bias $f = e$) is chosen as low as 50% due to the rough energy landscape and is checked every 100 MC time (MC time = trial MC steps / bins).^{13,16}

The DOS $g(E)$ independently sampled by each walker is joined at the best coinciding inverse microcanonical temperature within the overlap region $1/T = d(S(E))/dE = d(\ln(g(E)))/dE$.¹⁴ To avoid propagating errors based on the approximated microcanonical temperature via finite differences as is regularly suggested in literature, $\ln(g(E))$ is treated via a noisy data approach. B-spline functions are used to obtain a smoother gradient (see Figure 4) for each $\ln(g(E))$. A high robustness of this procedure is obtained by fitting the spline functions with a weighting of the reciprocal distance of each data point to a linear fit. This way outliers are discarded and a minimal smoothing factor of 20 can be used. The individual $\ln(g(E))$ are then scaled at their best coinciding gradients and a second global spline (with a somewhat larger smoothing factor) is fitted to the conjoined data.

The individual walkers are sampled until convergence of $f_{final} = \exp(10^{-3})$ reaching close to the $1/t$ domain, which is substantially higher than values of $\exp(10^{-6})$ - $\exp(10^{-8})$ normally applied for the Ising model. As shown in Figure 4, $\ln(g(E))$ is changing only slightly in the final refinement cycles, and is even less pronounced in the relevant canonical distributions at 700 and 1300 K. This latter effect justifies an early convergence criterion as a trade-off to computational cost and it can be attributed to the here newly applied noisy data approach.

During sampling no configuration at energies below the low bound of the pre-determined en-

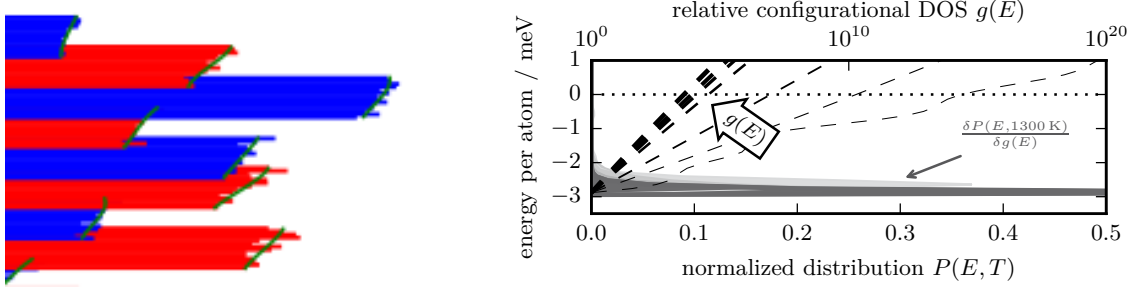


Figure 4: (left) Example of splines approximating a smooth gradient of $\ln(g(E))$ for each walker (blue and red alternating). (right) DOS convergence according to the biasing factors: 1.064, 1.0317, 1.0157, 1.0078, 1.0039, 1.001 of the 5th-10th refinement (from right to left) and of the according canonical distributions at $T=1300$ K.

ergy range is found confirming the reliability of the sampled thermal ensemble. Additionally only the lowest tenth of the sampled energy range reveals to be relevant for the thermal ensemble $P(E, T) = g(E)e^{-E/k_B T}$ owed to the high weight of the Boltzmann factor.

Computational details MD

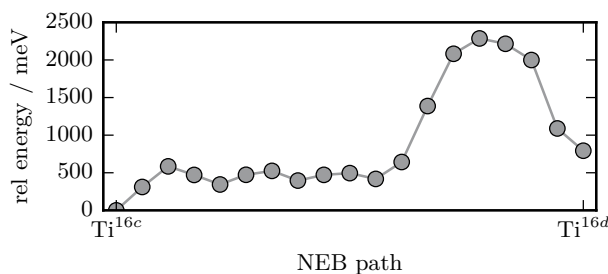
Per configuration and temperature 7 trajectories are run at a 0.2 fs time step in the NVE ensemble with a sampling time of 1.7 ns (total 11.9 ns). Priorly an equilibration is performed for 50 ps based on a Nose-Hoover chain thermostat and a Hoover chain barostat^{17,18} followed by 250 ps without thermostating in an NVE ensemble. During the MD simulation core/shell particles are treated by the adiabatic core/shell model¹⁹ which was implemented into the employed LAMMPS code¹ for this work.

Details of Ti^{16c} defects

The newly discovered Ti^{16c} defects consist of a displacement of one Ti ion from a 16d site to a neighboring 16c site and a displacement of a Li ion in an adjacent 8a site to the original 16d site (as illustrated in the main text).

Thermal stability of defects

Considering the lifetime of a Ti^{16c} defect at room or operational temperatures, a possible thermal deactivation needs to be investigated. Hereby all possible deactivation pathways of a Ti ion from a 16c to a neighboring 16d site are investigated by nudged-elastic-band (NEB) calculations on grounds of the employed potential in one candidate structure taken from the ensemble. For this 19 images are created for each pathway and a harmonic NEB interaction force between images of $0.5 \text{ eV/\AA}$ is applied where a convergence criterion at $0.02 \text{ eV/\AA}$ between image interaction is set. In order to avoid any artificial long range interaction on the NEB path, only ions in the vicinity of the event are considered for the NEB image interaction.



reflecting again a high accuracy of the employed potential. Deviation from the original pathway in the large simulation cell (see Figure 5) originate from the stronger mirror image interaction due to the truncation of the periodic box.

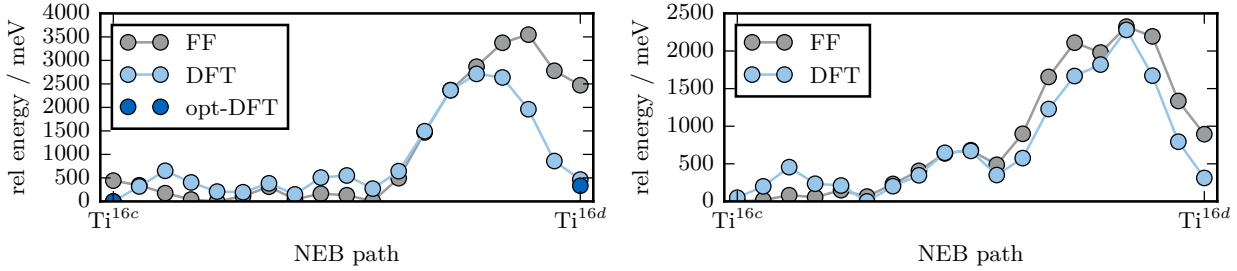


Figure 6: Relative single point energies at DFT-PBE and force field level of the NEB-images of the Ti^{16c} defect deactivation pathway isolated in a truncated structure. The two local minima defined by the Ti ions in either the 16c or 16d site are marked on the x-axis. The deactivation pathway is isolated in a $\text{Li}_{64}\text{Ti}_{80}\text{O}_{192}$ structure (left) and a $\text{Li}_{36}\text{Ti}_{45}\text{O}_{108}$ structure (right).

Defect formation probability

The distribution of relative defect formation energies $p(\Delta E^{\text{Ti}^{16c}})$ is investigated by a series of geometry optimizations of single Ti^{16c} defects introduced into randomly chosen configurations. The resulting energies are referenced to the defect free structures. For configurations situated in the relevant thermal ensemble, the sampled relative defect formation energies follow a gaussian distribution (see Figure 7). Hereby $p(\Delta E^{\text{Ti}^{16c}})$ of configurations originating from the same energy level E_i found in the DOS $g(E_i)$ vary only slightly with a maximum deviation of 3 % and 8 % for the mean and standard deviation. Thus we approximate a single distribution for all configurations belonging to the same energy E_i . Even higher similarities are found for the mean distributions $\langle p(\Delta E^{\text{Ti}^{16c}}) \rangle$ for different energy levels with a deviation of 0.5 % and 3 % for the mean and the standard deviation (see Figure 7). This allows to approximate the same defect formation energy distribution for the total thermal ensemble. It needs to be noted that this behavior changes substantially at higher energies above the thermal ensemble for which even negative formation energies are found.

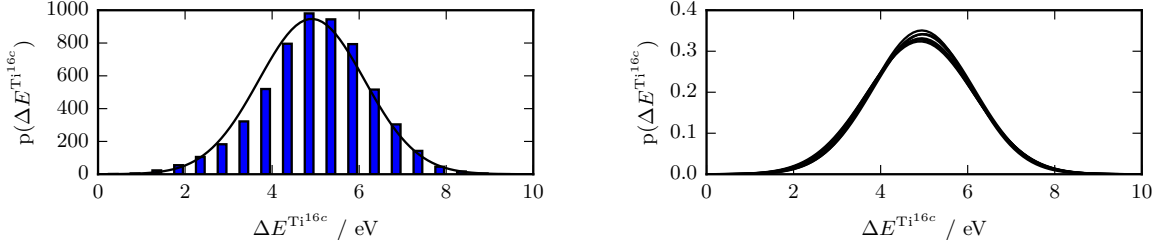


Figure 7: (left) Typical defect formation energy distribution $p(\Delta E^{\text{Ti}^{16c}})$ as found in a single configuration. (right) Comparison of the normalized defect formation energy distributions belonging to the energy levels E_i relevant for the thermal distributions $P(E_i, T)$.

From the normalized relative formation energy distribution $\langle p(\Delta E^{\text{Ti}^{16c}}) \rangle = 1$ a defect formation probability $p^{\text{Ti}^{16c}}$ can be computed by integration with the Boltzmann factor:

$$\int_{-\infty}^{\infty} \langle p(\Delta E^{\text{Ti}^{16c}}) \rangle \exp(-\Delta E / k_B T) d\Delta E \quad (5)$$

Approximating $\langle p(\Delta E^{\text{Ti}^{16c}}) \rangle$ to be independent from the configurational DOS within the energy range $E_{\min}$ - $E_{\max}$ relevant to the thermal ensembles, allows to determine a total defect probability by multiplication with the respective canonical distribution giving:

$$\int_{E_{\min}}^{E_{\max}} \int_{-\infty}^{\infty} \langle p(\Delta E^{\text{Ti}^{16c}}) \rangle \exp(-\Delta E / k_B T) P(E_i, T) d\Delta E dE \quad (6)$$

which can be simplified due to a discrete configurational DOS:

$$\sum_{i_{\min}}^{i_{\max}} p^{\text{Ti}^{16c}} P(E_i, T) \quad (7)$$

Since the thermal ensembles within the relevant energy range include virtually all occurring configurations we can approximate $\sum_{i_{\min}}^{i_{\max}} P(E_i, T) = 1$, leaving us with the probability $p^{\text{Ti}^{16c}}$ per defect realization.

The resulting probabilities for creating a Ti^{16c} defect are small enough to assume no effective interaction, thus justifying the investigation of single defects. Since for every Ti ion four surrounding 16c sites allow an exchange with two Li^{8a} ions each, a per Ti ion defect probability of

$p_{\text{Ti}}^{\text{Ti}^{16\text{c}}} = 8 p^{\text{Ti}^{16\text{c}}}$ can be defined ($\approx 4.79 \cdot 10^{-5}$ for $T_S = 700$ K and $\approx 1.12 \cdot 10^{-4}$ for $T_S = 1300$ K). From this a defect density can be determined, based on the simulation cell volume ($\approx 16234 \text{ \AA}^3$) including 360 Ti ions leading to $\approx 1.07 \cdot 10^{-6} \text{ \AA}^{-3}$ for $T_S = 700$ K and $\approx 2.49 \cdot 10^{-6} \text{ \AA}^{-3}$ for $T_S = 1300$ K.

Localized diffusion

Investigated configurations

The MD simulations for this study are performed in the regular LTO-configurations 1, 2, 3, 4, and “R $\bar{3}$ m” as well as the $\text{Ti}^{16\text{c}}$ defect structures a, b, c, d and e which spread over the an energy range relevant for the thermal ensembles (see Figure 8).

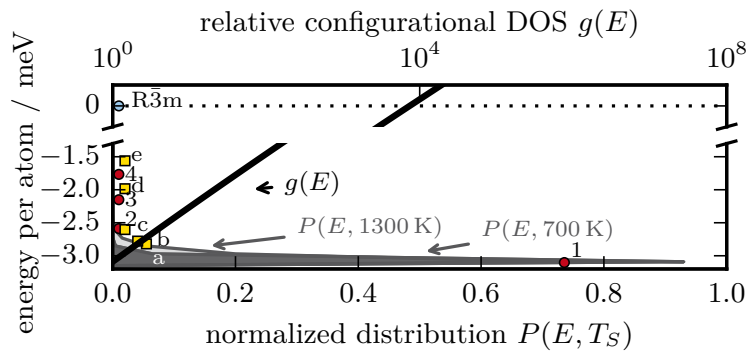


Figure 8: (left) Configurational density of states $g(E)$ (black), as well as canonical distributions at 700 K (dark gray) and 1300 K (light gray). The energy of the idealized “R $\bar{3}$ m” structure is taken as zero reference. The energetic position of “R $\bar{3}$ m” (blue), the regular configurations 1, 2, 3, 4 (red) as well as the $\text{Ti}^{16\text{c}}$ defect structures a, b, c, d, e (yellow) are marked (see text).

As depicted in Table 1 the regular configurations 1, 2, 3, 4 and “R $\bar{3}$ m” do not show any interstitial diffusion within the time limit of the MD simulations. In contrast to this one can see that all $\text{Ti}^{16\text{c}}$ defect structures a, b, c, d and e show interstitial diffusion for a small share of Li ions located around the defect site. Hereby it shall be noted that the amount of participating Li ions varies uncorrelated to the energy of the defect structure.

Table 1: Ratio (%) of mobile Li ions with a migrated distance of $d_{\text{Td-Oh}} \leq d < 2d_{\text{Td-Oh}}$ (m_{short}) and $d \geq 2d_{\text{Td-Oh}}$ (m_{long}) (see main text) for the configurations “R $\bar{3}m$ ” 1, 2, 3, 4 and a, b, c, d, e at 300 K.

	“R $\bar{3}m$ ”	1	2	3	4
m_{short}	0.0	0.0	0.0	0.0	0.0
m_{long}	0.0	0.0	0.0	0.0	0.0
	a	b	c	d	e
m_{short}	0.5	1.0	0.3	0.6	1.6
m_{long}	0.05	0.1	0.02	0.2	2.6

Reoccurring localized diffusion

To visualize the diffusion, the superimposed positions of Li ions which moved in between interstitial sites according to the displacements $d_{\text{Td-Oh}} \leq d < 2d_{\text{Td-Oh}}$ and $d \geq 2d_{\text{Td-Oh}}$ (see main text) are depicted in Figure 9 for each trajectory of configurations b and c. It can be seen that mobile Li ions reoccur around the same positions in vicinity of the Ti^{16c} defect in most trajectories showing a localized diffusion. Depending on the initial velocity seed of our simulations different ions interact, leading to changing percolation channels/events during the trajectories. It can be expected that each trajectory would reach the maximum extent of the observed percolation volume for a long enough simulation time.

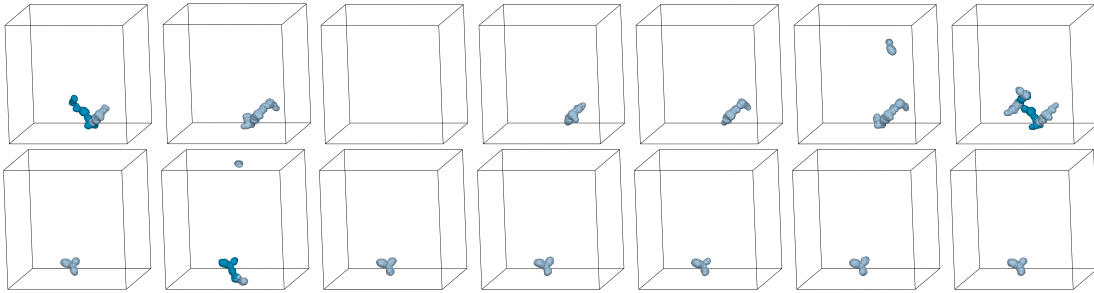


Figure 9: Superimposed positions of all mobile Li ions belonging to regime 2 ($d_{\text{Td-Oh}} \leq d < 2d_{\text{Td-Oh}}$) in lightblue and regime 3 ($d \geq 2d_{\text{Td-Oh}}$) in dark blue during the seven trajectories (from left to right) at 300 K for the Ti^{16c} defect structures b (top) and c (bottom)

The regions in which the localized correlated diffusion occurs around a Ti^{16c} defect vary for the investigated configurations. The spacial extend is bound to the chemical environment (i.e. the local occupation) around the defect on the one hand and to the time limit of the simulation on the

other (thereby always representing a minimum). In order to estimate the volume of said regions we measure the maximum distance of all positions which the mobile Li ions were found in during the course of the simulation and assume it to be the diameter of a spherical volume. This way we overestimate linear but underestimate more complex branched percolation channels (compare Figure 9). For the investigated defect structures b and c we find maximal distances of 12 and 8 Å which translate to a volume of ≈ 268 and ≈ 905 Å³, or 2-6 % of the simulation cell volume.

Correlated motion

To obtain clear evidence for correlated motion, the dynamical rare-events are isolated using NEB calculations on force field level. For this the first and last snapshot of a recorded ionic hop over multiple sites is taken. Additionally consecutive steps, resembling the isolated motion are implemented randomly into defect free moieties to compare the energetic barriers. Depending on the length of the estimated diffusion path, 7-11 images are created for each pathway and a harmonic NEB interaction force between images of 0.5 eV/Å is applied whereby a convergence criterion at 0.02 eV/Å between image interaction is set. In order to avoid any artificial long range interaction on the NEB path, only ions in the vicinity of the event are considered for the NEB image interaction. Two example NEB-calculations are shown in Figure 10 emphasizing the lowered energy barrier around the Ti^{16c} defect.

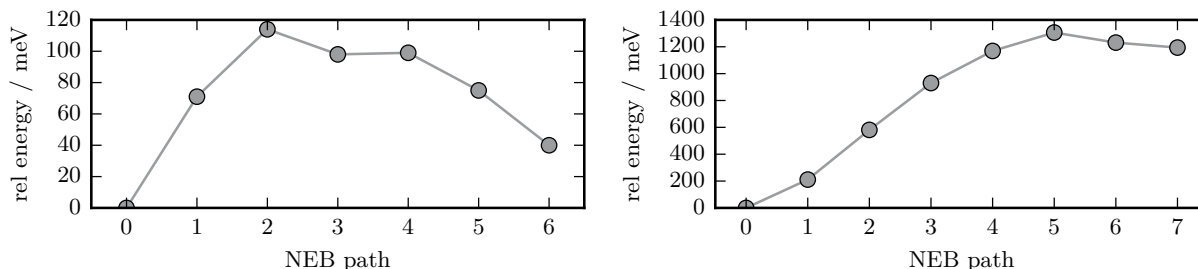


Figure 10: Relative energies of the NEB pathway of the isolated correlated Li ion motion in proximity of a Ti^{16c} defect (left) and imposed correlated Li ion motion afar any Ti^{16c} defect (right) on force field level.

Discretization procedure for MD simulations

In order to track the detailed ion dynamics, a discretization procedure is utilized where all ion positions during the complete trajectory are projected on the fcc crystal lattice and its interstitial sites. In contrast to the discretization of single geometries during the Monte-Carlo sampling (see Figure 10) the lattice is adjusted to the thermal equilibrium positions of the oxygen ions as found in each trajectory. Additionally, core sets^{20,21} are used during the distance-ranked mapping of ions to sites which represent minimal distances of 0.55 Å on which a transition of one ion to a new site is accepted. This way recrossing events are filtered out. Based on the crystal lattice and the occupation of the interstitial sites, all crystallographic sites based on the $Fd\bar{3}m$ space group can be assigned.

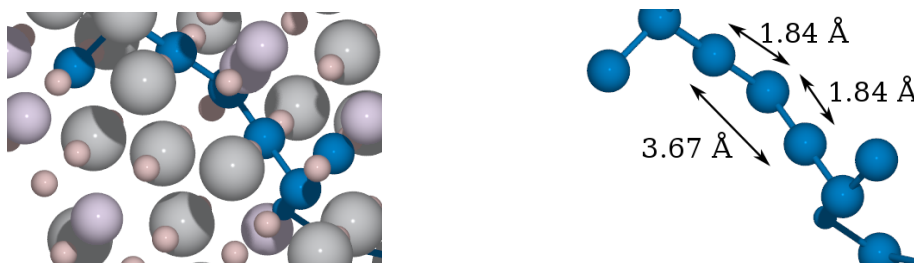


Figure 11: Excerpt of a discretized trajectory shown in a graph-representation with the surrounding ions (left) and without (right). It can be seen that only distances over 3.6 Å represent a true diffusive motion via an intermediate site i.e. ($8a \rightarrow 16c \rightarrow 8a$).

Tracking all ion positions for every snapshot allows the detailed determination of the diffusion paths. An excerpt in the graph representation for all ions during one trajectory is shown in Figure 11 where balls represent crystallographic sites and the sticks show how these are connected during dynamics. In the localized diffusion the ions exchange many times between sites in a diffuse manner masking the correlated mechanisms found in rare multiple site exchanges. Based on the known pathways the maximum traveled distance during a trajectory can be associated with the number of site exchanges. This way we can distinguish mobile Li ions from immobile ones as described in the main text.

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