Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supporting Information: Equilibration of ion distribution at polymer/ceramic interface

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Flow Chart

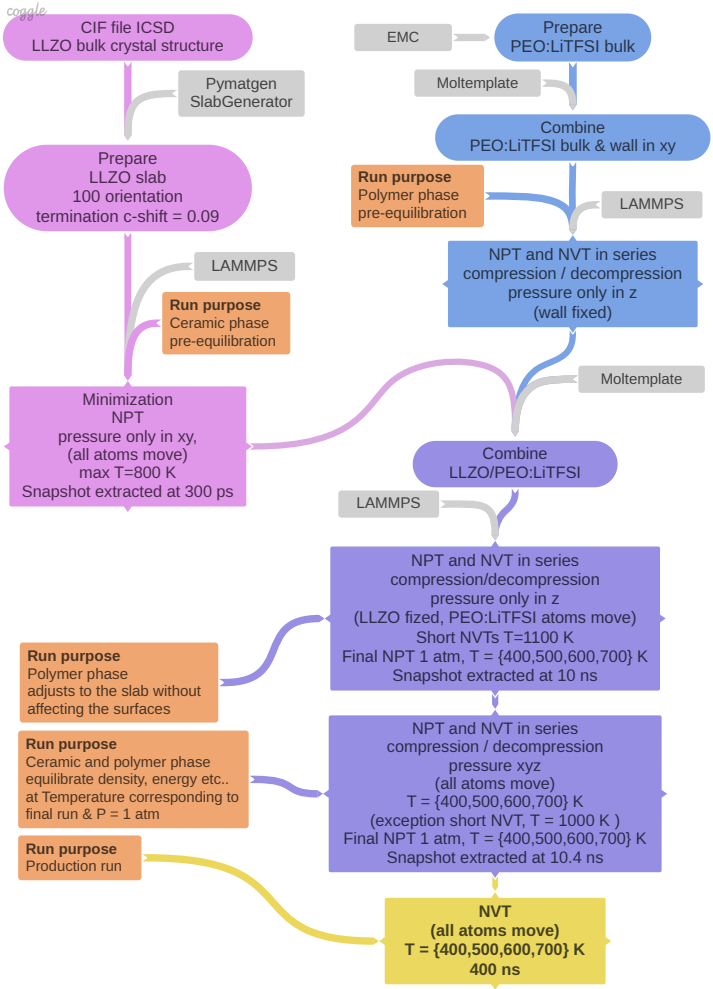

Figure S1: Flow chart describing the equilibration procedure from bulk ceramic and polymer phases to production runs of LLZO/PEO:LiTFSI interface.

Additional table

Table S1: Bins msd $z \in \{..\}$ Å

Li^+	-55	-40	-32	-23	-15	-5	5	15	23	32	40	55
$TFSI^-$	-55	-40	-32	-26	-19	-	-	19	26	32	40	55

Additional figures

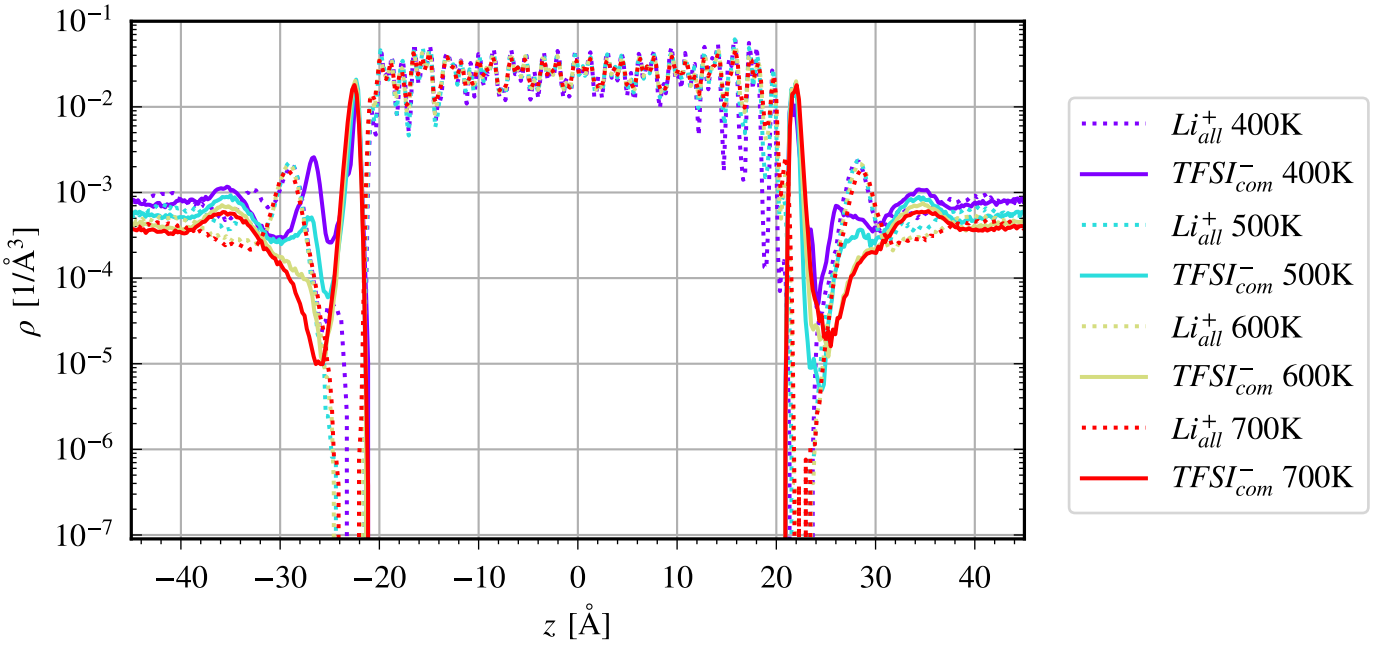

Figure S2: Mean atom density profile of Li^+ and $TFSI^-$ at different temperatures (400K, 500K, 600K and 700K).

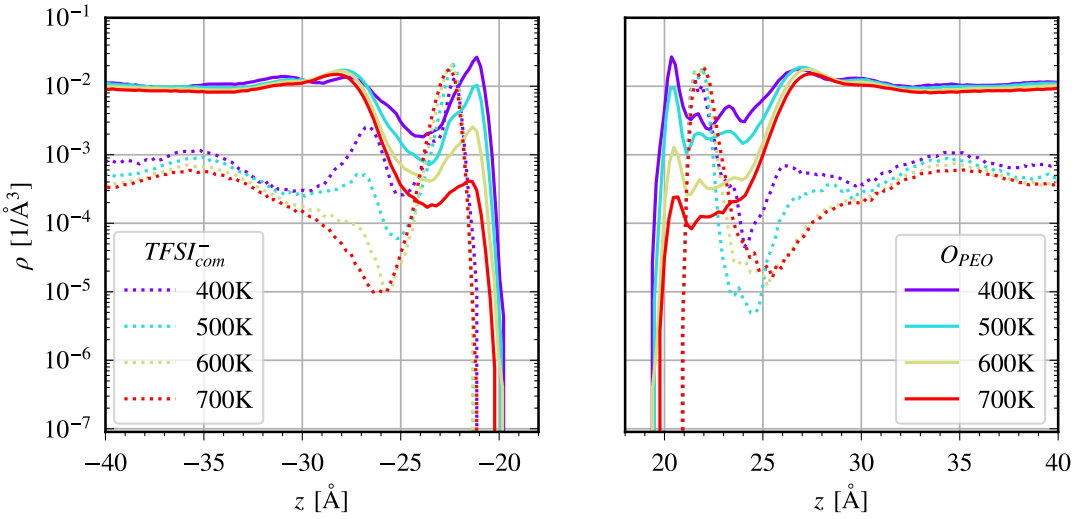

Figure S3: Mean atom density profile of $TFSI^-$ and O_{PEO} at the LEFT and RIGHT interface of the LLZO slab at at different temperatures (400K, 500K, 600K and 700K).

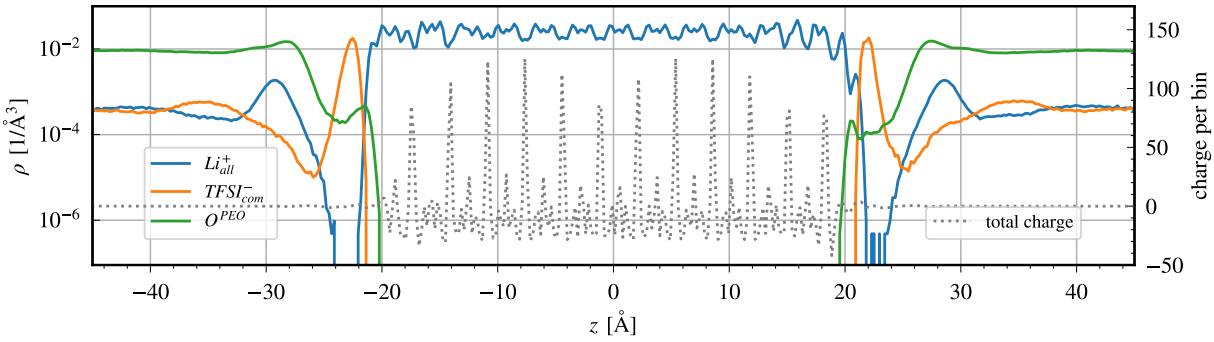

Figure S4: Mean atom density profile of Li^+ , $TFSI^-$ and O_{PEO} at 700K and distribution of total charge.

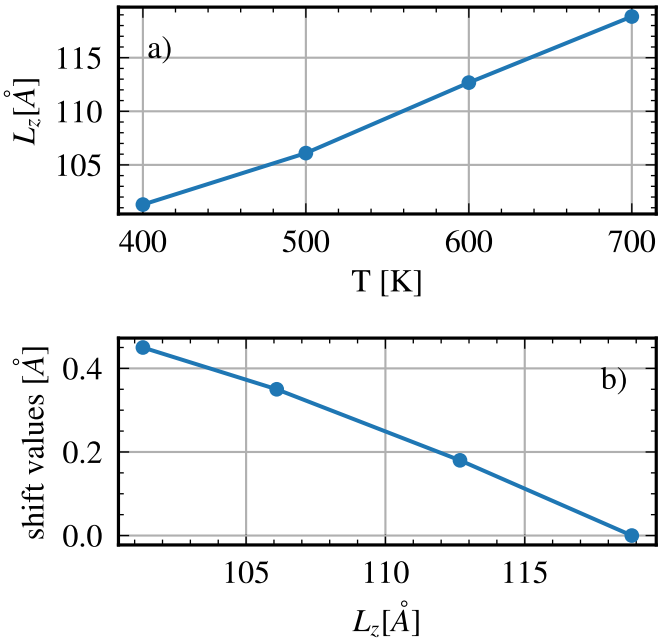

Figure S5: a) Simulation box length, perpendicular to the LLZO surface L_z, in the final NVT run as a function of simulation temperature. b) Shift values as a function of L_z (see also figure S6).

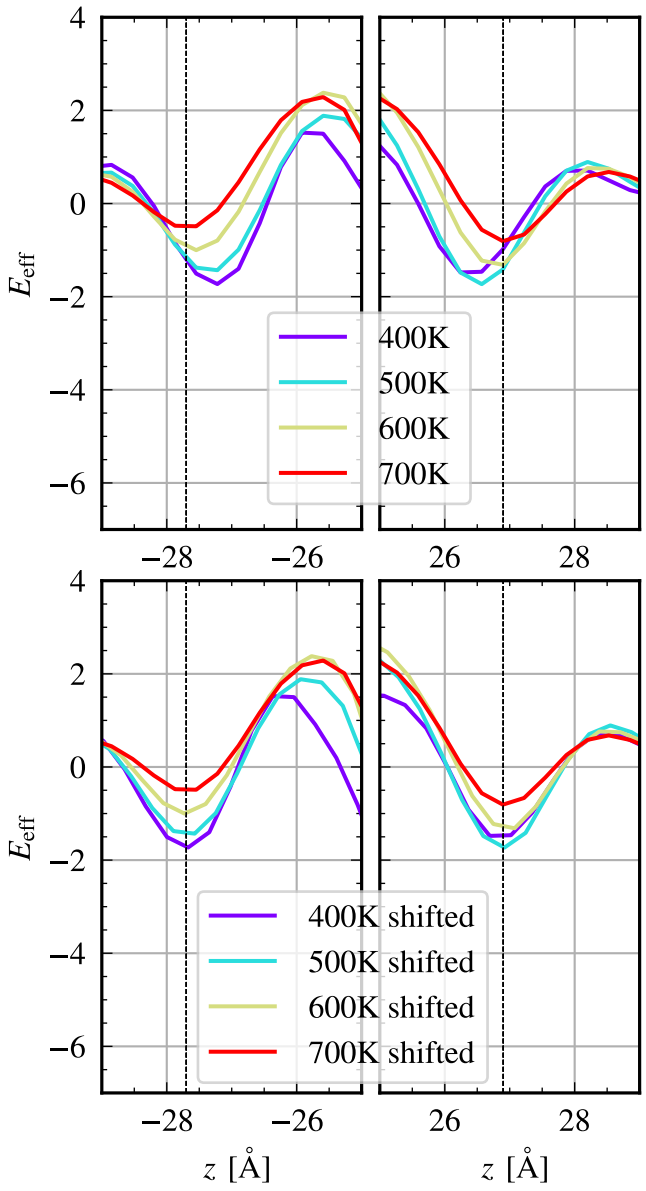

Figure S6: Integrated total charge around the LEFT and RIGHT LLZO-SPE interface for simulations at 400 K, 500 K, 600 K and 700 K. The second row is shifted (shift values in order of legend: [0.45, 0.35, 0.18, 0], - for LEFT, + for RIGHT side)

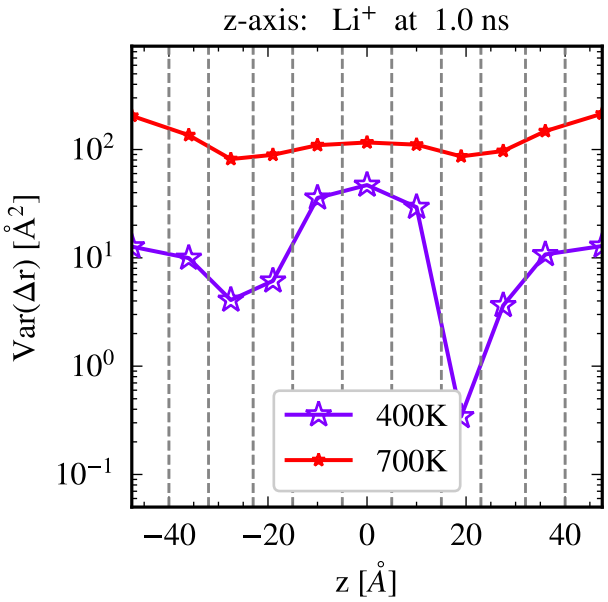

Figure S7: Displacement variance of Li^+ at 1 ns in z-axis (perpendicular to LLZO surface) as a function of ions position perpendicular to the LLZO surface. The vertical gray dashed lines indicate the bins used for the calculation of specially resolved $Var(\Delta r)$. Last 300 ns of NVT trajectories at 400 and 700 K were taken for the analysis.

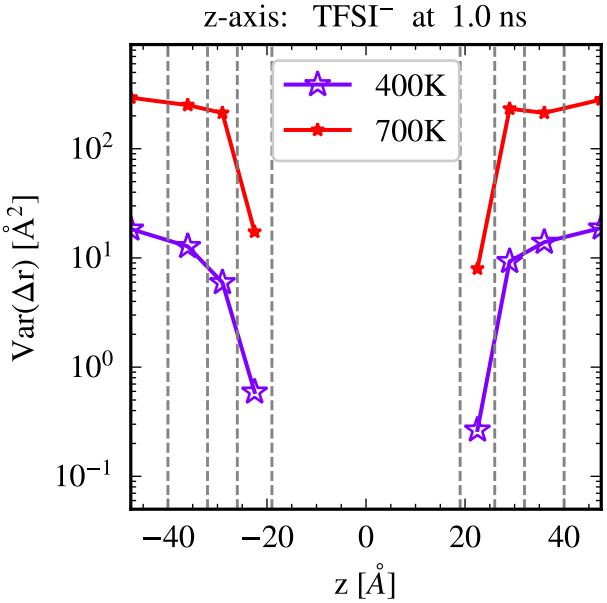

Figure S8: Displacement variance of $TFSI^-$ at 1 ns in z-axis (perpendicular to LLZO surface) as a function of ions position perpendicular to the LLZO surface. The vertical gray dashed lines indicate the bins used for the calculation of specially resolved $Var(\Delta r)$. Last 300 ns of NVT trajectories at 400 and 700 K were taken for the analysis.

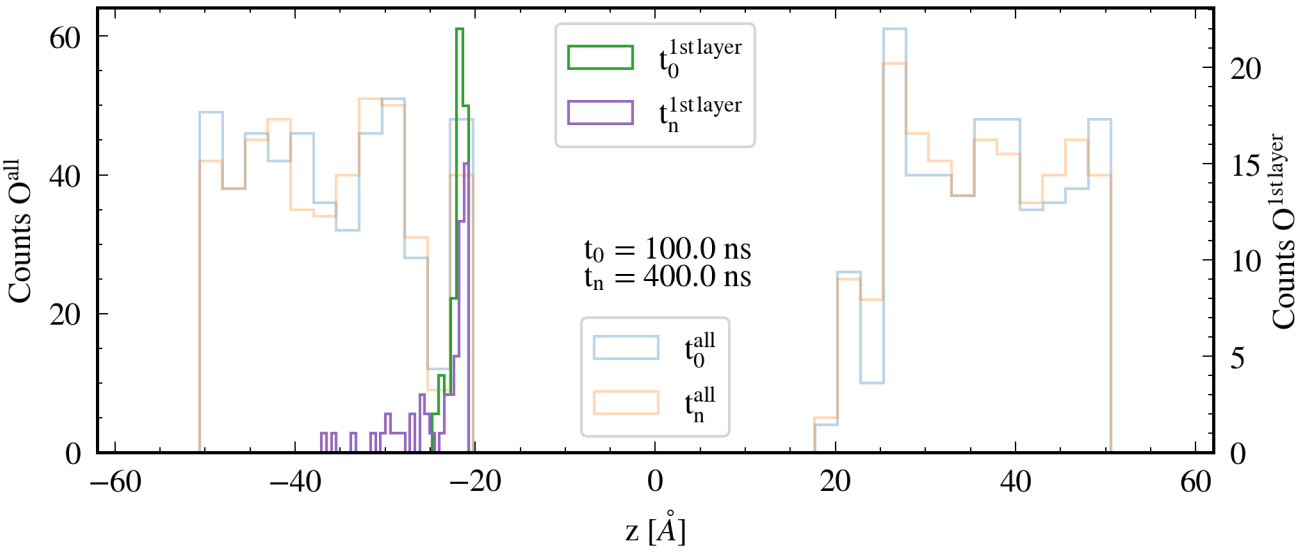

Figure S9: Histograms at 400 K at two different times (100 ns and 400 ns). First, the distribution of all O^{PEO} are shown at both times. Second, at 100 ns the LEFT $O^{1st\ layer}$ are displayed (green histogram) as well as their positions at 400 ns (violet histogram).

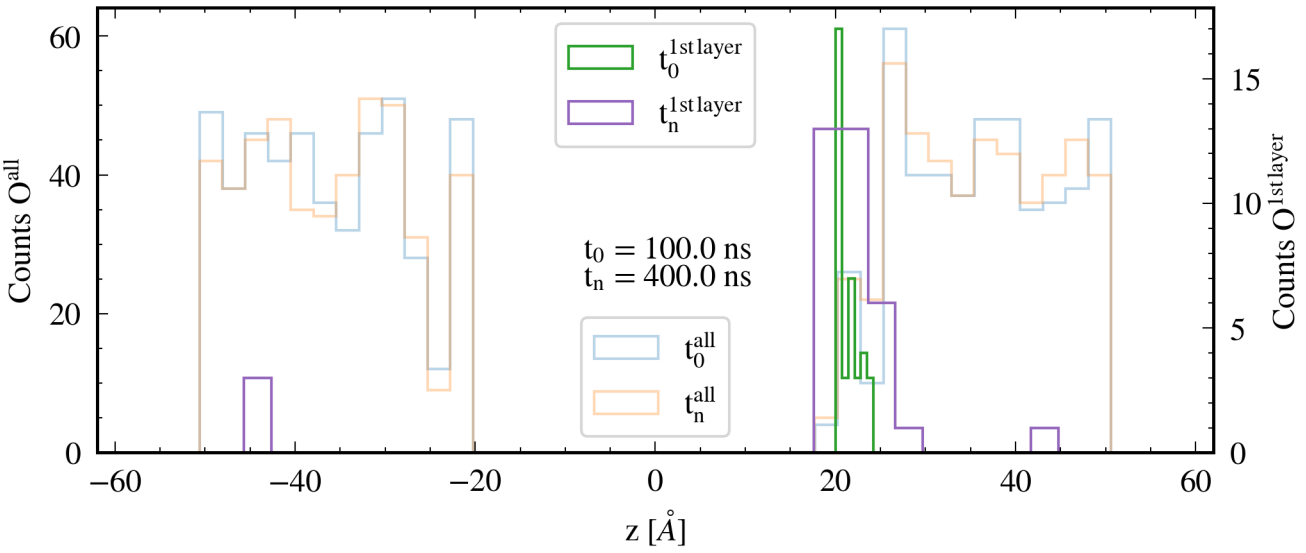

Figure S10: Histograms at 400 K at two different times (100 ns and 400 ns). First, the distribution of all O^{PEO} are shown at both times. Second, at 100 ns the RIGHT $O^{1st\ layer}$ are displayed (green histogram) as well as their positions at 400 ns (violet histogram).

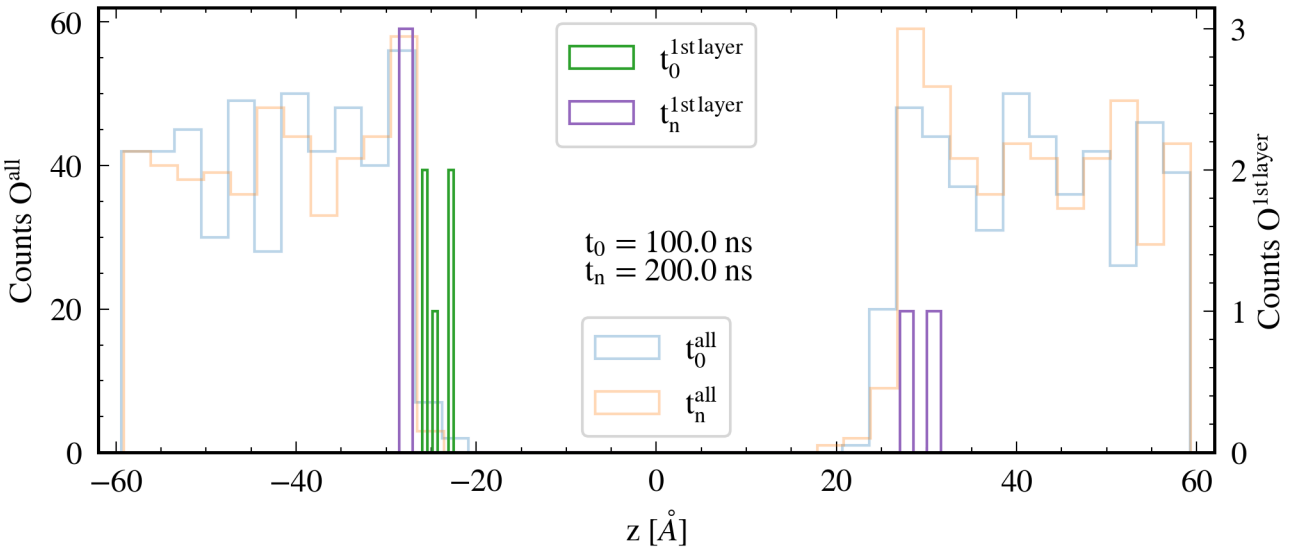

Figure S11: Histograms at 700 K at two different times (100 ns and 200 ns). First, the distribution of all O^{PEO} are shown at both times. Second, at 100 ns the LEFT $O^{1st\ layer}$ are displayed (green histogram) as well as their positions at 200 ns (violet histogram).

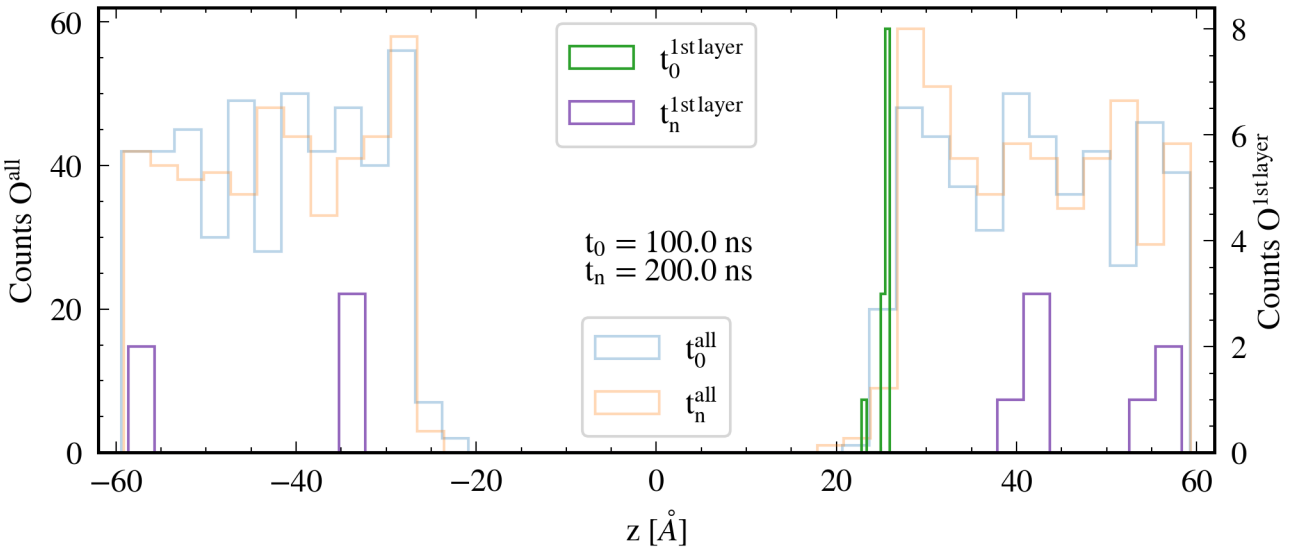

Figure S12: Histograms at 700 K at two different times (100 ns and 200 ns). First, the distribution of all O^{PEO} are shown at both times. Second, at 100 ns the RIGHT $O^{1st\ layer}$ are displayed (green histogram) as well as their positions at 200 ns (violet histogram).

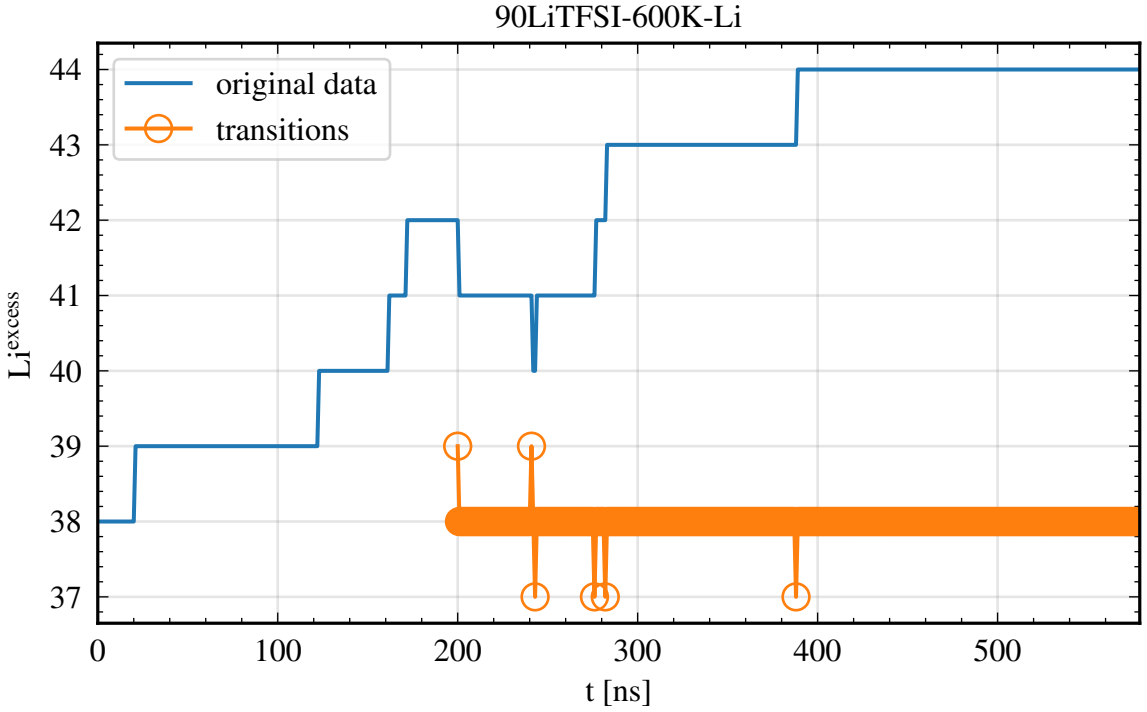

Figure S13: Li^+ in and out LLZO region transitions at 600 K.

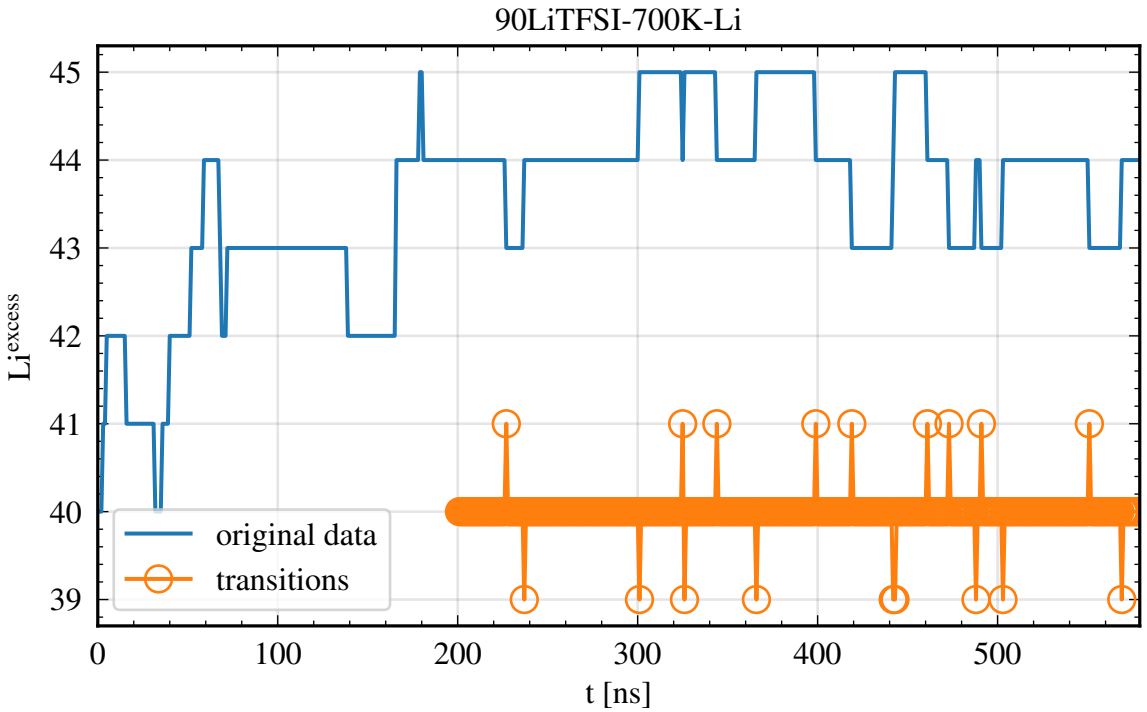

Figure S14: Li^+ in and out LLZO region transitions at 700 K.

Rationalization of the specific form of EC

To rationalize this approach we consider the situation of a symmetric two-state system (the states being denoted A and B) and consider a non-equilibrium (neq) population (3N particles in A, N particles in B) as well as an equilibrium (eq) population (N particles in A, N particles in B) with N much larger than one. From studying the binomial distribution for large N one can calculate the probabilities p_{neq} and p_{eq}, respectively, that after 2k transitions one has exactly k transitions from A to B and k from B to A. One expects that this probability is smaller for the non-equilibrium case (denoted p_{neq}) than for the equilibrium case (denoted p_{eq}). A short calculation yields $p_{neq}/p_{eq} = (3/4)^k$. This implies that for larger values of k it becomes more and more

unlikely that a non-equilibrium initial condition gives rise to an equal number of transitions from A to B and vice versa. In an ad hoc manner, we choose $p_{neq}/p_{eq} \approx e^{-1}$ as the limit where we use the observation of an equal number of transitions from A to B and from B to A, respectively, as an indicator of an equilibrium situation. Thus, the chosen functional form of EC should fulfill the condition that for an equal number of transitions it starts to be small for $k \leq 4$ (no clear statement about initial equilibrium) and becomes larger for $k > 4$ (stronger indication of initial equilibrium). Applying the functional form, suggested in this work, to the present example one obtains $EC = 2k/(2k+\lambda)$. Thus, the requirements are fulfilled if one chooses $\lambda/2$ to be, e.g., 5, implying $\lambda = 10$. Naturally, in case of a different initial ratio this value would change (e.g. the transition value is 8 in case of a 2N:N distribution).