Supporting Information: The sensitive aspects of modelling polymer-ceramic composite solid-state electrolytes by molecular dynamics simulations

Melania Kozdra[1], Daniel Brandell[1], C. Moyses Araujo[2, 3], and Amber Mace[1]

[1]Department of Chemistry - Ångström Laboratory, Uppsala University, Box 538, 75121 Uppsala, Sweden, E-mail: amber.mace@kemi.uu.se
[2]Department of Engineering and Physics, Karlstad University, Karlstad, Sweden.
[3]Materials Theory Division, Department of Physics and Astronomy, Uppsala University, Box 516, 75120 Uppsala, Sweden.

A Determination of partial charges

Table S0: Partial charges

Atom type	REPEAT	OX	DDEC
C_{PEO}	0.2823	0.2823	-0.0086
H_{PEO}	-0.0036	-0.0036	0.0644
O_{PEO}	-0.5502	-0.5502	-0.2404
La_{LLZO}	2.0530	2.1000	1.8744
Li_{PEO}, Li_{LLZO}	0.8370	0.7000	0.8160
O_{LLZO}	-1.3530	-1.4000	-1.3050
Zr_{LLZO}	2.1090	2.8000	2.1624
C_{TFSI}	0.2930	0.2930	0.2856
S_{TFSI}	0.8545	0.8545	0.8323
O_{TFSI}	-0.4440	-0.4440	-0.4324
N_{TFSI}	-0.5520	-0.5520	-0.5386
F_{TFSI}	-0.1340	-0.1340	-0.1306

All density functional theory (DFT) calculations were performed with the generalized-gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) [1] functional together with Grimme's D3 dispersion correction [2] as implemented in CP2K package [3]. In order to account for the nuclear cores Godecker-Tetter-Hutter [4] norm-conserving pseudo potentials were used. Double- ζ shorter-range (DZVP-MOLOPT-SR-GTH) basis sets [5] were used to expand the Kohn-Sham orbitals. Periodic boundary conditions were used in all 3 dimensions for all calculations.

In order to determine partial charges on PEO atoms a single repeating unit of the polymer was placed in the simulation box to create an infinite chain in y-axis with 10 Å vacuum in x and

z axes. Moreover, a planewave cutoff and real cutoff were equal 600 Ry and 60 Ry respectively while Gaussians were mapped onto 5 grid levels. The accuracy of an SCF cycle was kept at the level of $1 \cdot 10^{-6}$. Cell optimisation calculations were performed in order to determine a converged number of repeating units in the box. The convergence criterion was that the cell length per PEO unit was changing by less than 1 %. The converged polymer length was fount to reach 8 repeating units with final ABC cell vectors equal to 10.000 Å, 56.682 Å and 10.000 Å respectively.

For the purpose of obtaining partial charges for LLZO atoms an *ab initio* Molecular dynamics was performed in the NVT ensemble with a time step of 0.5 fs to obtain 100 ps of trajectory. The temperature was kept constant at 400 K by means of a Nose-Hoover thermostat with a time constant of 20 fs and a chain length of 3. Here, a planewave cutoff and real cutoff were equal 400 Ry and 50 Ry respectively while Gaussians were mapped onto 5 grid levels. The accuracy of an SCF cycle was kept at the level of $5 \cdot 10^{-7}$. Cubic box had a length equal to 12.943 Å. 236 configurations were extracted from the MD runs in order to obtain meaningfully averaged partial charges.

Next, single point calculations were performed for both the PEO structure and LLZO snapshots to obtain REPEAT [6] charges as implemented in CP2K [3] as well as electron density with (1,1,1) stride. Finally, the obtained electron densities were used as input for CHARGEMOL package to fit partial charges with DDEC6 [7], [8] method. An average was taken to determine partial charges of each species. The final results are listed in Table S0.

B Trajectories

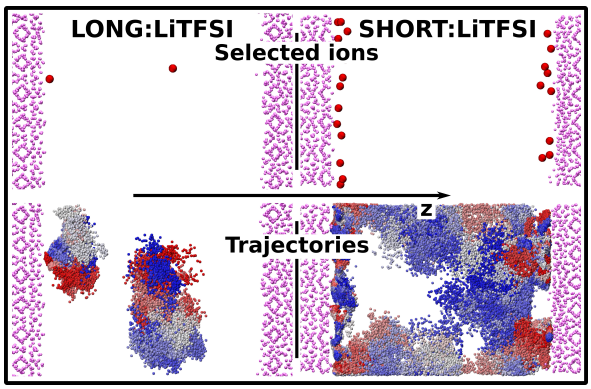

Fig. S1: Last 100 ns of $C_{PEO}^{terminal}$ trajectories in LONG:LiTFSI and SHORT:LiTFSI systems. In the SHORT:LiTFSI simulations, only $C_{PEO}^{terminal}$ that are found within 3 Å from a surface are selected. Red, white and blue spheres indicate the beginning, middle and the end of the trajectory. Purple spheres indicate the LLZO phase.

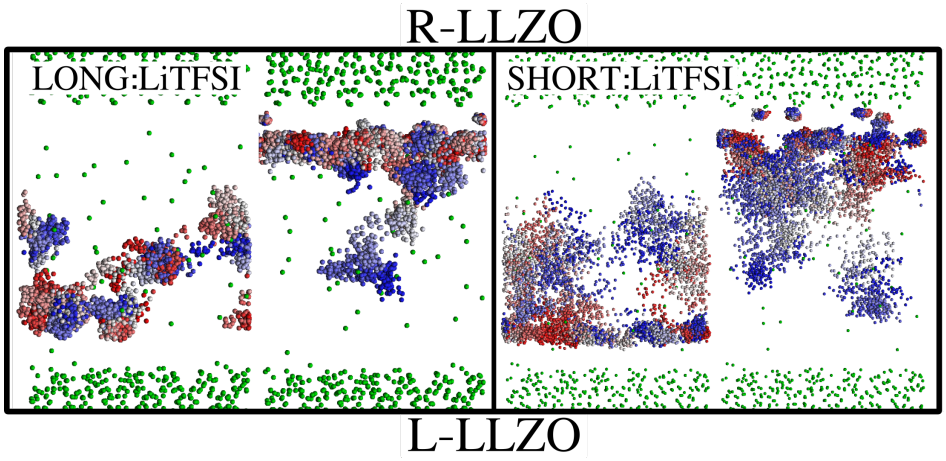

Fig. S2: Last 100 ns of $TFSI^-$ trajectories in LONG:LiTFSI and SHORT:LiTFSI systems at several layers in the simulation box, here anion is identified by the positions of N_{TFSI^-} atom. Red, white and blue spheres indicate the begging, middle and the end of the trajectory. Green spheres are all Li^+ in the system.

C Number of Li in LLZO phase and its surface

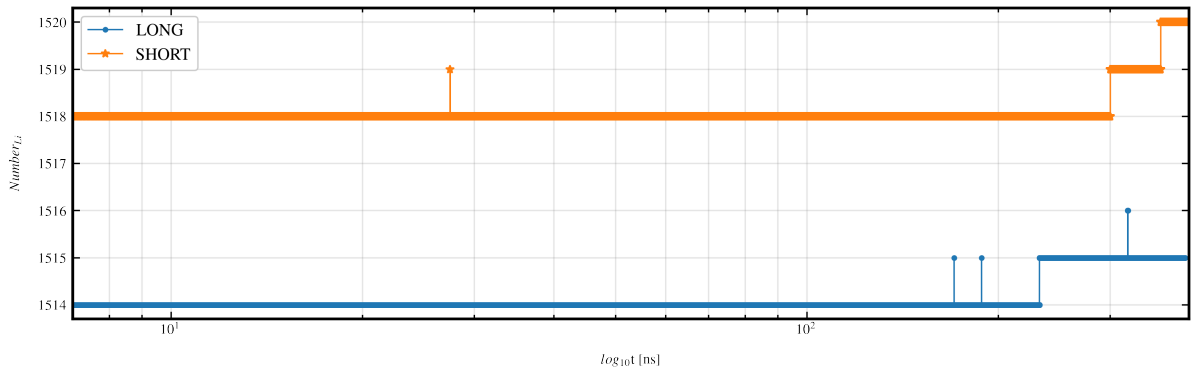

Fig. S3: Number of Li^+ found in the LLZO crystal structure and its surface as a function of the simulation time.

D Density plots

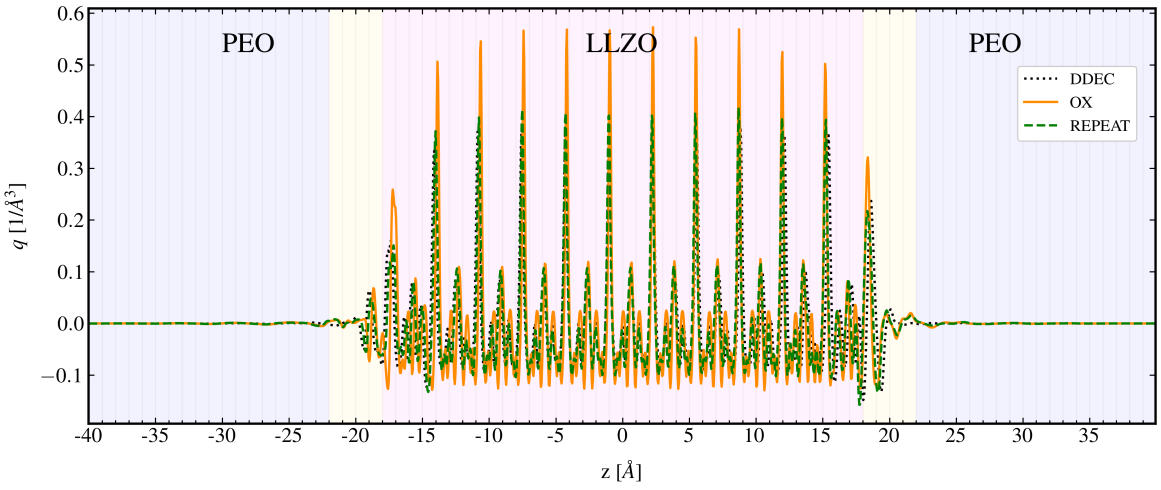

Fig. S4: Charge density profiles $q(z)$ centered around the LLZO phase. The yellow background indicates the 4 Å (arbitrary thickness) interface region.

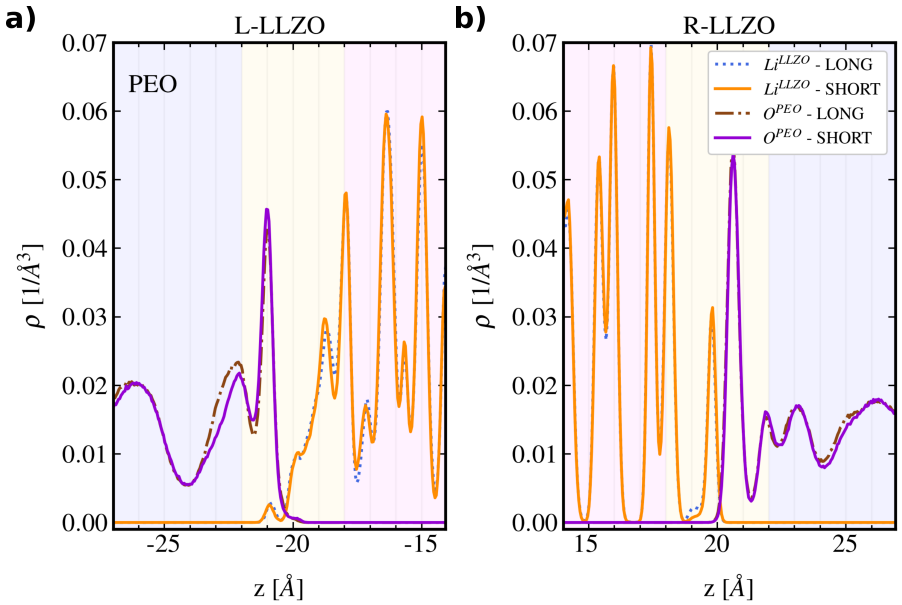

Fig. S5: Atom number density profiles $\rho(z)$ centered around the LLZO phase. Comparison of results of the simulations with different polymer chain lengths without the LiTFSI in the polymer phase, zoom: a) at the L-LLZO surface and b) at the R-LLZO surface. The yellow background indicates the 4 Å (arbitrary thickness) interface region. Blue and purple background are the PEO and LLZO phase respectively.

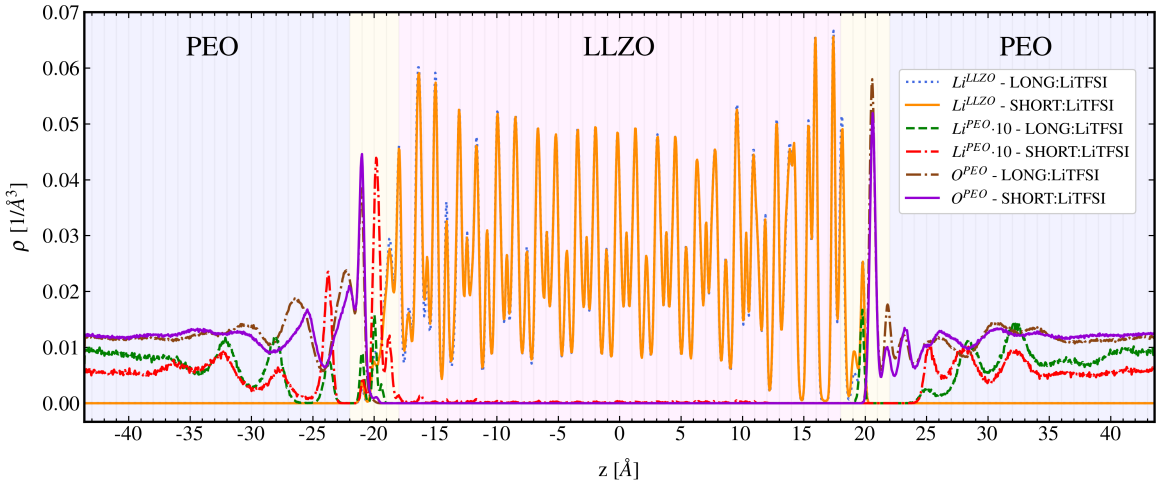

Fig. S6: Atom number density profiles $\rho(z)$ centered around the LLZO phase. Comparison of results of the simulations with different polymer chain lengths, zoom: a) at the L-LLZO surface and b) at the R-LLZO surface. The yellow background indicates the 4 Å (arbitrary thickness) interface region. Blue and purple background are the PEO and LLZO phase respectively.

References

[1] John P. Perdew, Matthias Ernzerhof, and Kieron Burke. Rationale for mixing exact exchange with density functional approximations. *Journal of Chemical Physics*, 105(22):9982–9985, 1996.

[2] Stefan Grimme, Jens Antony, Stephan Ehrlich, and Helge Krieg. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *Journal of Chemical Physics*, 132(15):1–19, 2010.

[3] Thomas D. Kühne, Marcella Iannuzzi, Mauro Del Ben, Vladimir V. Rybkin, Patrick Seewald, Frederick Stein, Teodoro Laino, Rustam Z. Khaliullin, Ole Schütt, Florian Schiffmann, Dorothea Golze, Jan Wilhelm, Sergey Chulkov, Mohammad Hossein Bani-Hashemian, Valéry Weber, Urban Borštnik, Mathieu Taillefumier, Alice Shoshana Jakobovits, Alfio Lazzaro, Hans Pabst, Tiziano Müller, Robert Schade, Manuel Guidon, Samuel Andermatt, Nico Holmberg, Gregory K. Schenter, Anna Hehn, Augustin Bussy, Fabian Belleflamme, Gloria Tabacchi, Andreas Glöß, Michael Lass, Iain Bethune, Christopher J. Mundy, Christian Plessl, Matt Watkins, Joost VandeVondele, Matthias Krack, and Jürg Hutter. CP2K: An electronic structure and molecular dynamics software package - Quickstep: Efficient and accurate electronic structure calculations. *Journal of Chemical Physics*, 152(19):194103, 2020.

[4] S. Goedecker and M. Teter. Separable dual-space Gaussian pseudopotentials. *Physical Review B - Condensed Matter and Materials Physics*, 54(3):1703–1710, 1996.

[5] Joost VandeVondele and Jürg Hutter. Gaussian basis sets for accurate calculations on molecular systems in gas and condensed phases. *Journal of Chemical Physics*, 127(11), 2007.

[6] Carlos Campañá, Bastien Mussard, and Tom K. Woo. Electrostatic potential derived atomic charges for periodic systems using a modified error functional. *Journal of Chemical Theory and Computation*, 5(10):2866–2878, 2009.

[7] Thomas A. Manz and Nidia Gabaldon Limas. Introducing DDEC6 atomic population analysis: Part 1. Charge partitioning theory and methodology. *RSC Advances*, 6(53):47771–47801, 2016.

[8] Nidia Gabaldon Limas and Thomas A. Manz. Introducing DDEC6 atomic population analysis: Part 2. Computed results for a wide range of periodic and nonperiodic materials. *RSC Advances*, 6(51):45727–45747, 2016.