Supporting Information

Li-Diffusion at the Interface between Li-Metal and [Pyr$_{14}$][TFSI]-Ionic Liquid: Ab Initio Molecular Dynamics Simulations

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Table S1. Ion diffusivity, D×10^{11}, m^2/s, in the SEI compact layer of the smaller 83Li/2[TFSI] and larger 164Li/4[TFSI] systems at 400 K.

System	C	F	O	N	S	Li
83Li/2[TFSI]	0.421	0.758	0.356	0.623	0.213	3.192
164Li/4[TFSI]	0.948	2.213	0.244	0.204	0.268	3.528

The higher D value for the F atoms in the larger system is due to a jump of ~7 Å of two of the 24 F atoms at ~45 and 70 ps, respectively. The other F atoms have D values similar to those in the smaller system. If these two F atoms are excluded from the D calculation for the F atoms, the value will be much closer to that in the smaller system, 1.166×10^{-11} m^2/s *vs.* 0.758×10^{-11} m^2/s. Possibly diffusivity of the F atoms in the larger system would be close to that in the smaller system for a longer simulation (similar to the time of the simulation on the smaller system, ~700 ps).

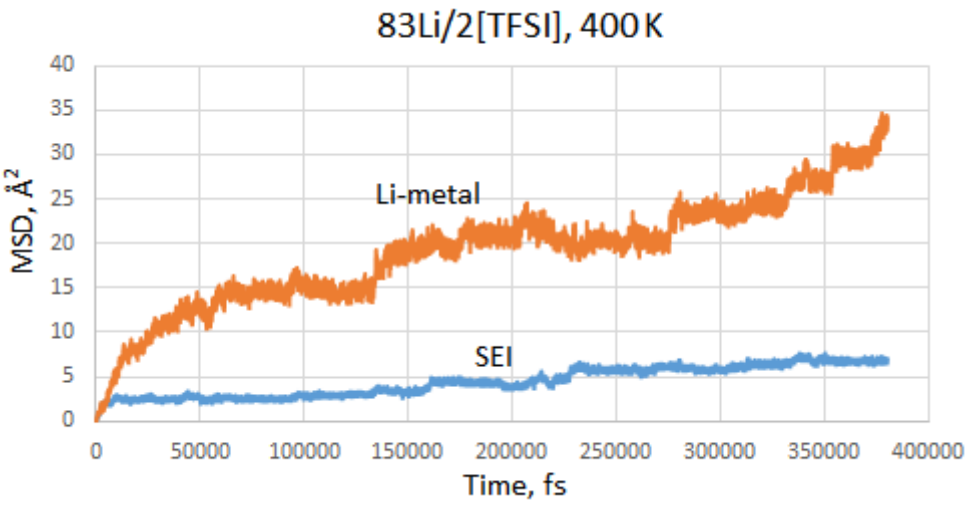

Figure S1. Mean square displacements (MSD) of Li atoms in the Li-metal region and SEI compact layer (SEI CL) in the equilibrated region of the trajectory for the smaller 83Li/2[TFSI] system at 400 K.

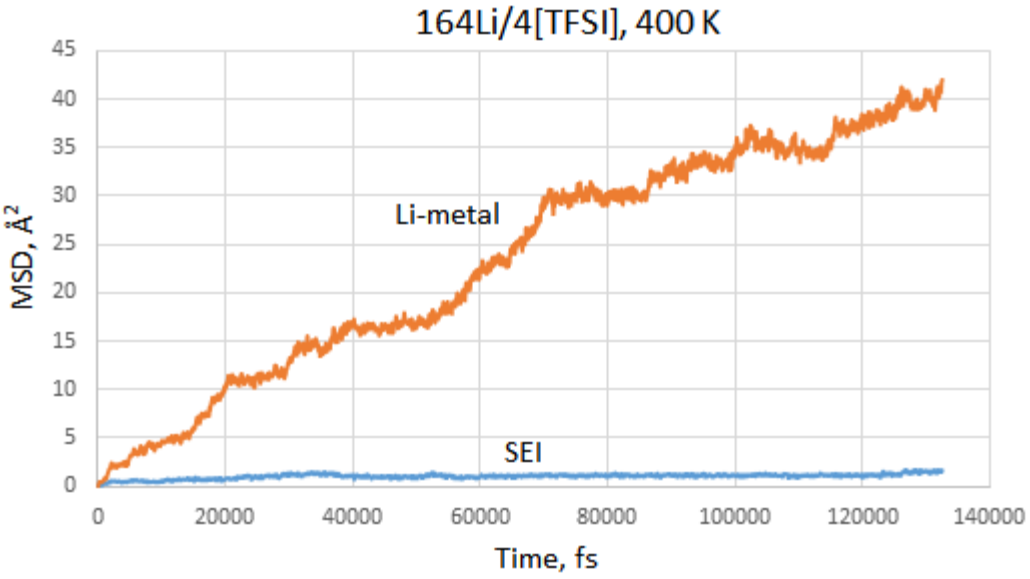

Figure S2. Mean square displacements (MSD) of Li atoms in the Li-metal region and SEI compact layer (SEI CL) in the equilibrated region of the trajectory for the larger 164Li/4[TFS] system at 400 K.

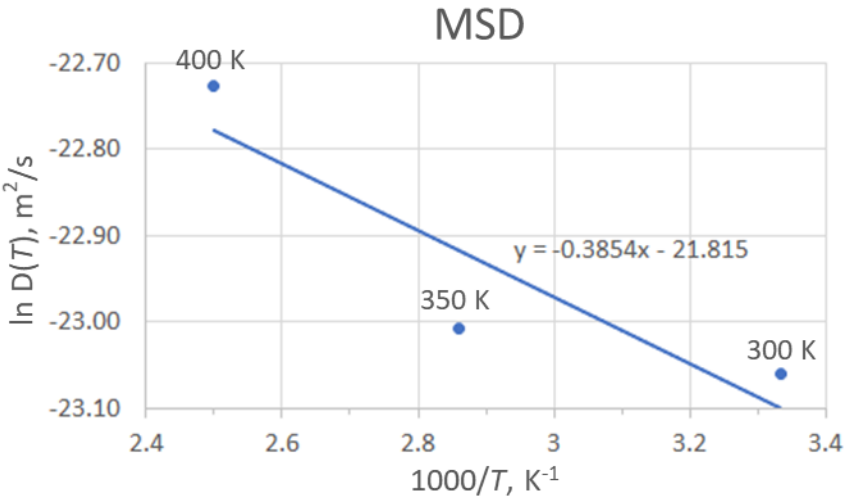

Figure S3. Arrhenius plot of the Li-diffusivity calculated from MSD in the Li-metal region ($D_{Li\text{-}metal}$) of the smaller 83Li/2[TFSI] system. The corresponding activation energy E_a = 0.03 eV.

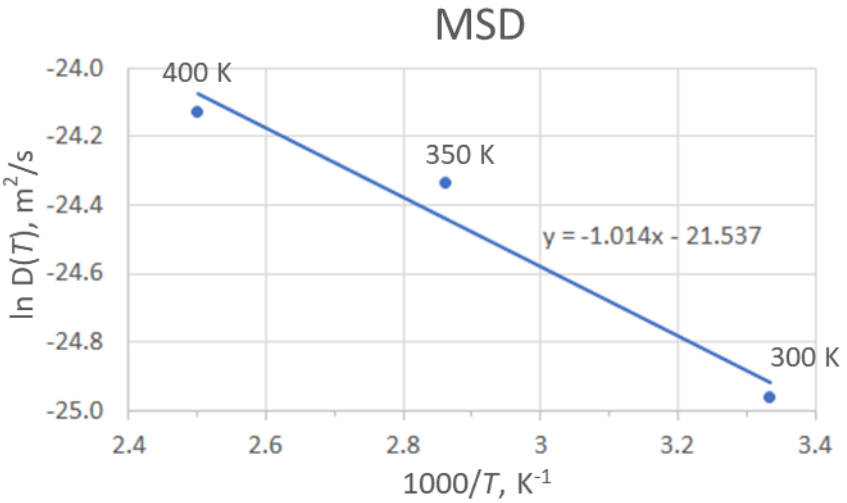

Figure S4. Arrhenius plot of the Li-diffusivity calculated from MSD in the SEI compact layer (D_{SEI}) of the smaller 83Li/2[TFSI] system. The corresponding activation energy E_a = 0.09 eV.

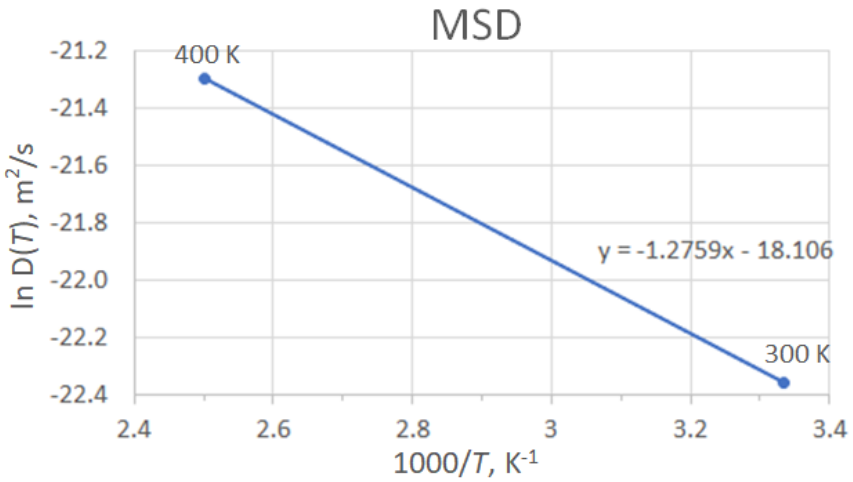

Figure S5. Arrhenius plot of the Li-diffusivity calculated from MSD in the Li-metal region ($D_{Li\text{-}metal}$) of the larger 164Li/4[TFSI] system. The corresponding activation energy E_a = 0.11 eV.

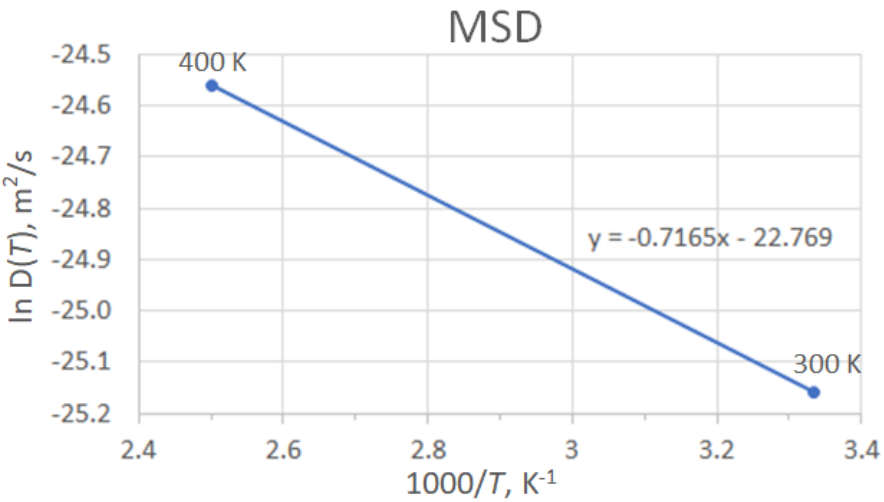

Figure S6. Arrhenius plot of the Li-diffusivity calculated from MSD in the SEI compact layer (D_{SEI}) of the larger 164Li/4[TFSI] system. The corresponding activation energy E_a = 0.06 eV.

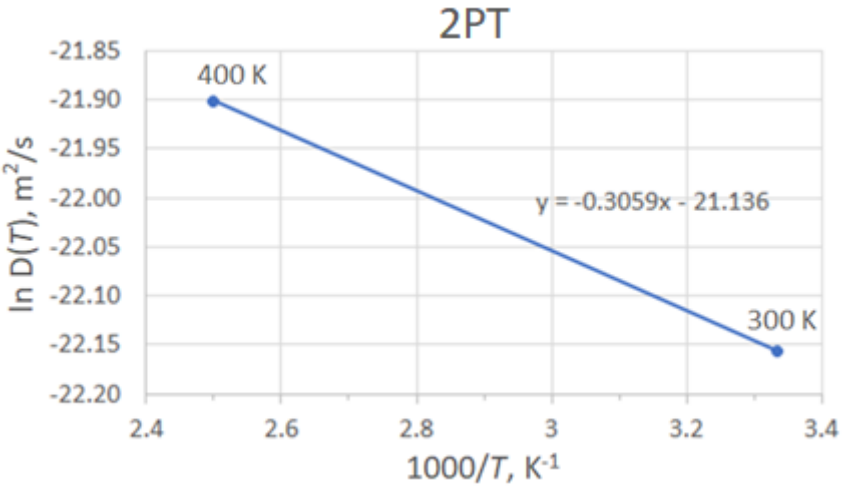

Figure S7. Arrhenius plot of the Li-diffusivity in the Li-metal region ($D_{Li\text{-}metal}$) of the smaller 83Li/2[TFSI] system, calculated using the 2PT method. The corresponding activation energy E_a = 0.03 eV.

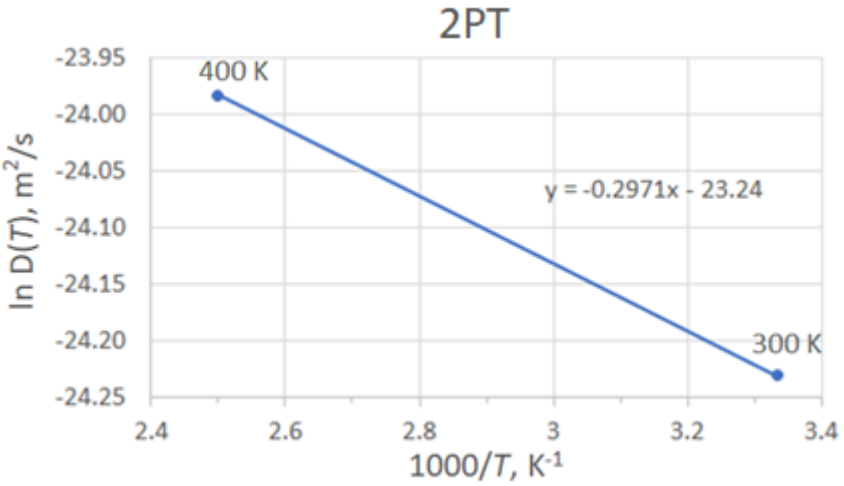

Figure S8. Arrhenius plot of the Li-diffusivity in the SEI compact layer (D_{SEI}) of the smaller 83Li/2[TFSI] system, calculated using the 2PT method. The corresponding activation energy E_a = 0.03 eV.

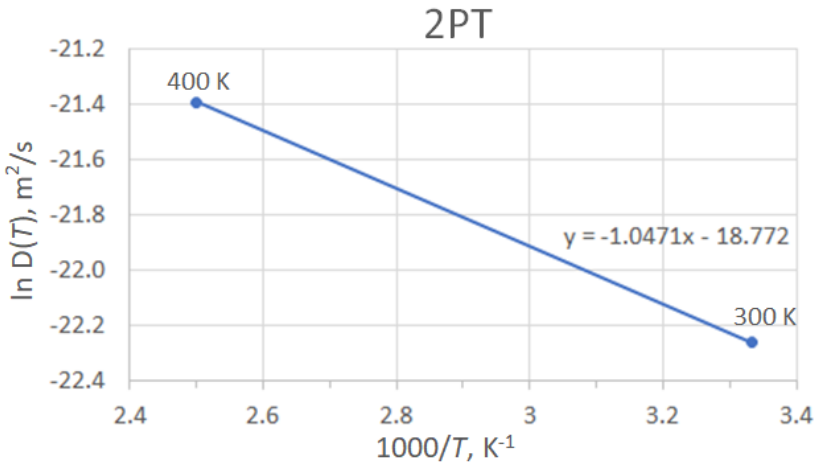

Figure S9. Arrhenius plot of the Li-diffusivity in the SEI compact layer ($D_{Li\text{-}metal}$) of the larger 164Li/4[TFSI] system, calculated using the 2PT method. The corresponding activation energy E_a = 0.09 eV.

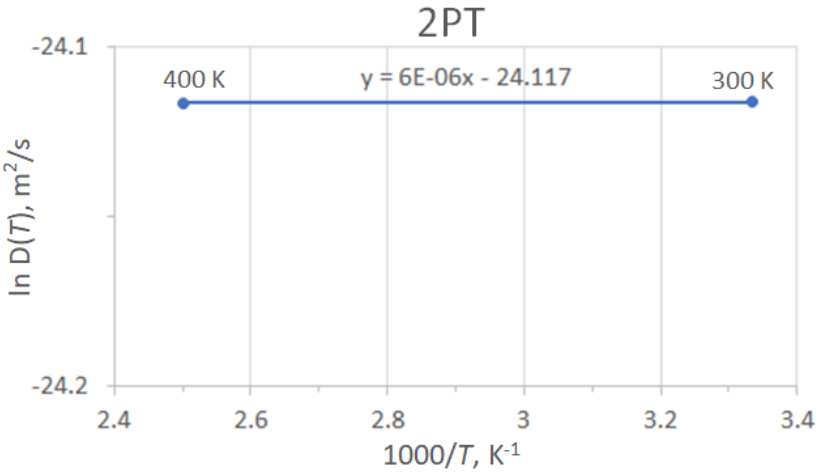

Figure S10. Arrhenius plot of the Li-diffusivity in the SEI compact layer (D_{SEI}) of the larger 164Li/4[TFSI] system, calculated using the 2PT method. The corresponding activation energy E_a = 0.00 eV.