Supplementary Information for

Effects of Self-Assembled Monolayers on Thermal and Lithium-ion Transport at SEI/PEO-based Polymer Electrolyte Interface: A Molecular Dynamics Study

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Potential parameters

The 6-12 Lennard -Jones potential parameters[1] and atomic charges for Li and F of lithium fluoride bulk are shown in table 1. The PEO-LiTFSI electrolyte and three SAMs involved are all described by the nonpolarizable OPLS-AA force field, where the total energy consists of nonbonded interactions, harmonic bond stretching, angle bending, and torsional energy:

$$E_{nonbond} = \sum_i \sum_{j>i} \left\{ \frac{q_i q_j e^2}{r_{ij}} + 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] \right\} \quad (1)$$

$$E_{bonds} = \sum_i k_{r,i} \left(r_i - r_{0,i} \right)^2 \quad (2)$$

$$E_{angles} = \sum_i k_{\theta,i} \left(\theta_i - \theta_{0,i} \right)^2 \quad (3)$$

$$E_{torsion} = \sum_i \left[\frac{1}{2} V_{1,i} (1 + \cos \varphi) + \frac{1}{2} V_{2,i} (1 - \cos 2\varphi) + \frac{1}{2} V_{3,i} (1 + \cos 3\varphi) + \frac{1}{2} V_{4,i} (1 + \cos 4\varphi) \right] \quad (4)$$

$$E_{total} = E_{nonbond} + E_{bonds} + E_{angles} + E_{torsion} \quad (5)$$

Overall, the OPLS-AA force field parameters associated with PEO and three SAMs originate from reference[2], while those associated with LiTFSI are from reference[3]. Besides, the charge distribution of PEO and charge scaling factors for PEO and LiTFSI need to be emphasized to ensure the reproducibility of this work. The atomic partial charges of PEO chains were determined by reparametrized OPLS^R model[4]. The charge scaling factors of 0.55 and 0.8 were respectively adopted to LiTFSI and PEO to compensate for the incapability of nonpolarizable OPLS-AA force field in describing charge transfer between ions and polymer[4]. All key parameters involved are demonstrated in table 1.

Table S1. 12-6 Leenard Jones potential parameters for LiF and OPLS-AA force field parameters for PEO-LiTFSI solid polymer electrolyte.

LiF	atom type	ε(kcal/mol)	σ(Å)	Q(e)
	Li	0.05766	1.715	1
	F	0.006465	3.954	-1
LiTFSI	atom type	ε(kcal/mol)	σ(Å)	Q(e)
	Li	0.0005	2.87	1
	F	0.053	2.95	-0.16
	C	0.066	3.5	0.35
	S	0.25	3.55	1.02
	O	0.21	2.96	-0.53
	N	0.17	3.25	-0.66
	bonds	k_r(kcal/mol/Å^2)		r_0(Å)
	N-S	374.88		1.57
	S-O	637.07		1.437
	S-O	233.03		1.818
	C-F	441.92		1.323
	angles	k_θ((kcal/mol/°^2		θ_0(°)
	N-S-O	94.29		113.6
	N-S-C	91.3		103.5
	S-C-F	82.93		111.7
	S-N-S	80.19		125.6
	C-S-O	103.97		102.6
	O-S-O	115.8		118.5
	F-C-F	93.33		107.1
	torsion	V_1	V_2	V_3	V_4
	N-S-C-F	0	0	0.316	0
	S-N-S-O	0	0	-0.004	0
	S-N-S-C	7.833	-2.49	-0.764	0
	O-S-C-F	0	0	0.347	0
PEO	atom type	ε(kcal/mol)	σ(Å)	Q(e)
	O, ROR	0.14	2.9	*
	C1, CH3OR	0.066	3.5	*
	C2, RCH2OR	0.066	3.5	*
	H, CHnOR	0.03	2.5	*
	bonds	k_r(kcal/mol/Å^2)		r_0(Å)
	O-C	320		1.41
	C-H	340		1.09
	C-C	268		1.529
	angles	k_θ((kcal/mol/°^2		θ_0(°)
	C-C-O	50		109.5

	C-C-H		37.5		110.7
	O-C-H		35		109.5
	H-C-H		33		107.8
	C-O-C		60		109.5
	torsion	V_1	V_2	V_3	V_4
	O-C-C-H	0	0	0.468	0
	O-C-C-O	-0.55	0	0	0
	H-C-C-H	0	0	0.3	0
	C-C-O-C	0.65	-0.25	0.67	0
	H-C-O-C	0	0	0.76	0

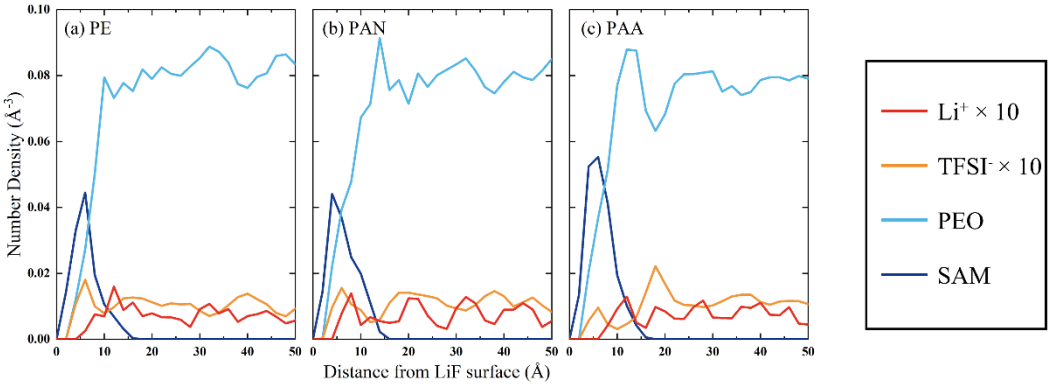

Figure S1. The atomic number density profiles of Li^+, $TFSI^-$, PEO and SAMs along the interface normal direction, for (a) PE, (b) PAN, (c) PAA binder systems. z = 0 A˚ denotes the outmost layer of LiF.

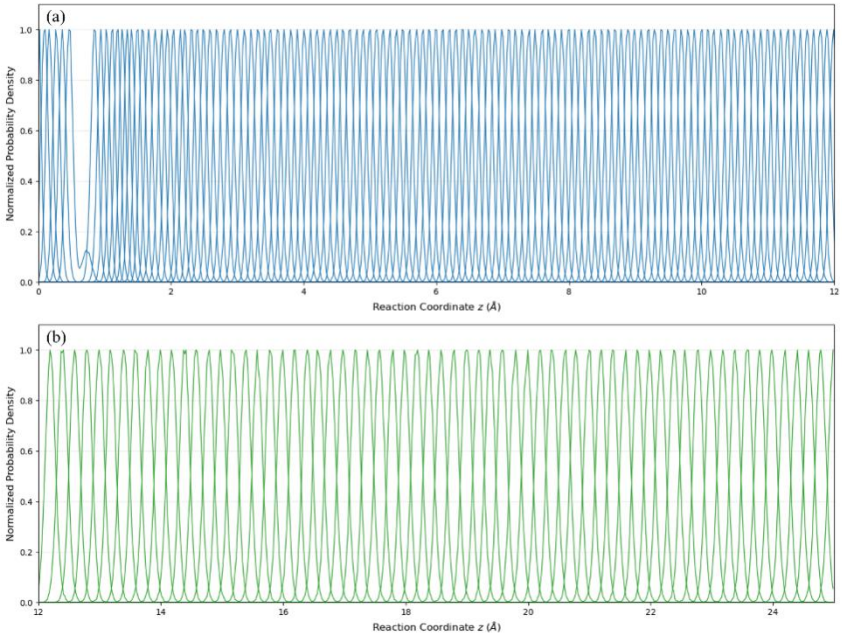

Figure S2. The global histogram of umbrella sampling simulations on pristine interface system.

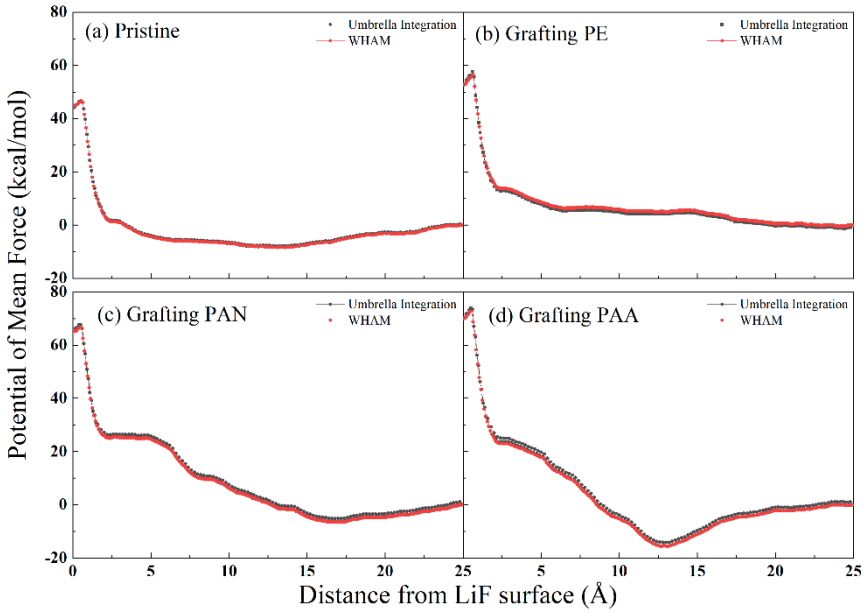

Figure S3. Comparison of the PMF obtained by umbrella integration and WHAM methods.

References

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4. C. E. Fang, Y. C. Tsai, C. Scheurer and C. C. Chiu, *Polymers (Basel)*, 2021, **13**, 1131.