Ion Solvation and Dynamics at Solid Electrolyte Interphases: A Long Way from Bulk?

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Supporting Information

Table S1. Number of molecules used in each simulation cell.

SEI Composition	EC	$LiPF_6$	Li_2EDC	LiF	Li_2CO_3
Li_2EDC	1213	115	404	-	-
10% LiF	1213	115	404	277	-
25% LiF	1213	115	404	867	-
50% LiF	1213	115	404	2503	-
10% Li_2CO_3	1213	115	374	-	89
25% Li_2CO_3	1213	115	322	-	235
50% Li_2CO_3	1213	115	232	-	505
LiF	1380	126	-	1080	-
Li_2CO_3	1426	130	-	-	1008

Bulk-Ion Solvation Structure:

The solvation structure for lithium ions and PF_6^- anions at the center of the simulation cells used in this work are shown in Figures S1 and S2 in order to verify their correspondence to the expected bulk environments. Figure S1 also demonstrates that the environment of the lithium ions in the amorphous Li_2EDC agrees with previous bulk SEI studies by reproducing the appropriate RDFs. The first peak in each RDF was used to calculate coordination numbers used in generating Figures 4, 5, and S3.

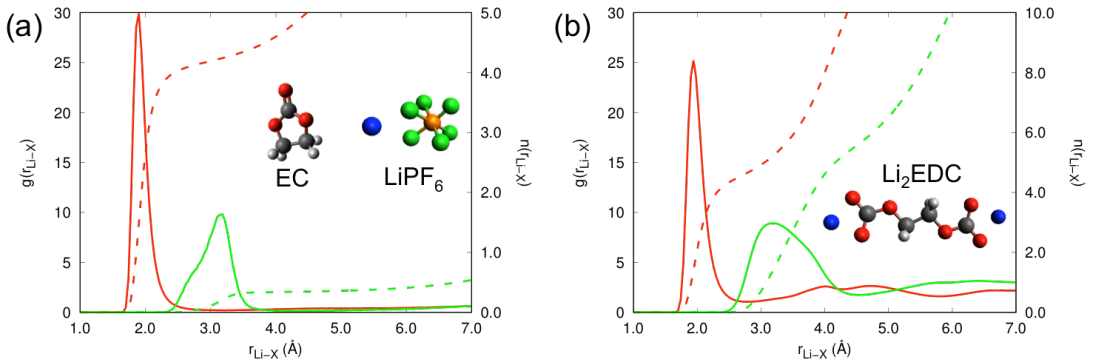

Figure S1. Radial distribution functions (RDFs) between Li^+ and (a) atoms in the electrolyte and (b) atoms in the SEI layer. In the left-hand panel, the RDF for the carbonyl oxygen of EC (red solid, scaled by a factor of 2 for graphing purposes) and the phosphorous atom in PF_6^- (green solid) in bulk electrolyte are shown. In the right-hand panel, the RDF for the carbonate oxygens of EDC^{2-}(red solid, scaled by a factor of 1.5 for scaling purposes) and other Li^+ cations (green solid) are shown. The corresponding coordination numbers are plotted (dashed lines, follow the right-hand y-axes) along with insets showing the atomic structure of each molecule with carbon atoms in black, oxygen in red, hydrogen in gray, lithium in blue, phosphorous in orange, and fluorine in green.

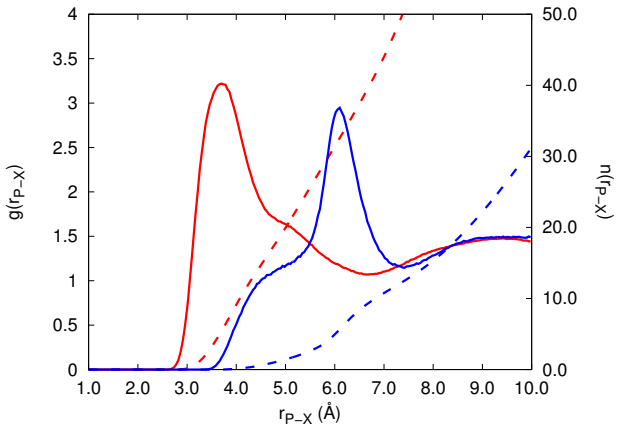

Figure S2. Radial distribution function (RDF) between the phosphorus atom of PF_6^- and species "X" corresponding to either the hydrogens of EC (red solid line) or the carbonyl carbon of EC (blue solid line). The accompanying coordination numbers are shown as dashed lines and follow the right hand y-axis.

Surface-Ion Solvation Structure for 10% LiF and 50% Li2CO3:

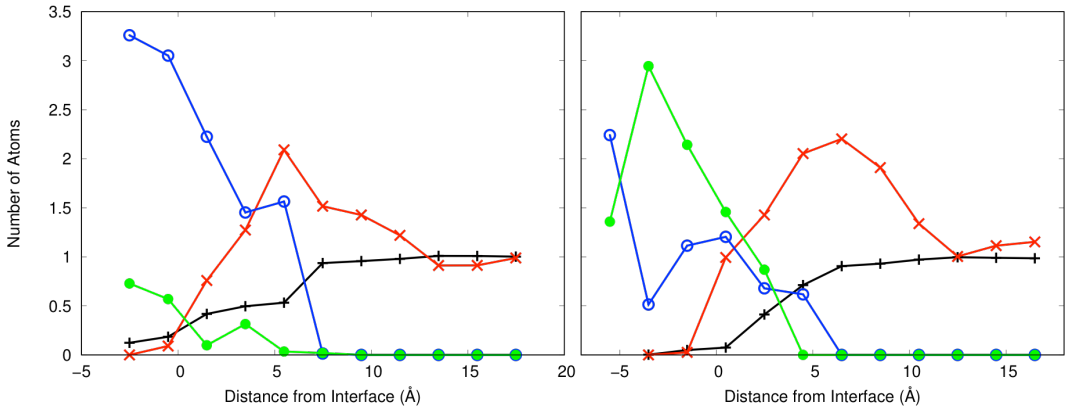

Figure S3. The change in average coordination is shown for lithium cations as a function of distance from the amorphous SEI containing 10% LiF by mass (left panel) as well as the SEI containing 50% Li_2CO_3 by mass (right panel). As in Figure 4, coordination of lithium by phosphorus (red x's), EC carbonyl oxygens (black crosses), and EDC^{2-} oxygens (blue circles) are shown along with fluoride (left panel – green circles) and CO_3^{2-} oxygens (right panel – green circles). Coordination by EC and phosphorous were scaled with respect to bulk electrolyte values while the SEI coordination numbers in the left panel have not been scaled. For graphing purposes, the SEI values in the right panel have been scaled by 1.5.

Ion Solvation Dynamics:

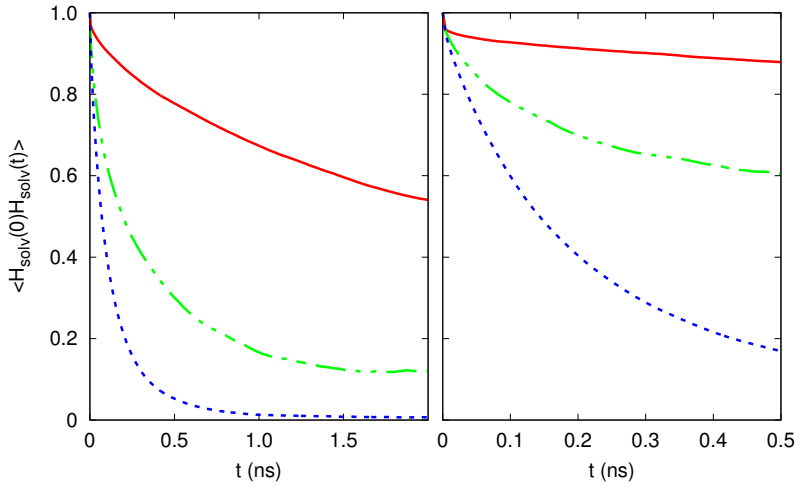

Figure S4. The solvation residence time correlation function is shown for EC (left panel) and PF_6^- (right panel) coordinated to lithium in the electrolyte near the interface of a pure amorphous Li_2EDC film. For both graphs the correlation function is shown at z = -4.66Å (red solid), 7.34Å (green dot-dashed), and 26.34Å (blue dashed) with respect to the SEI interface.

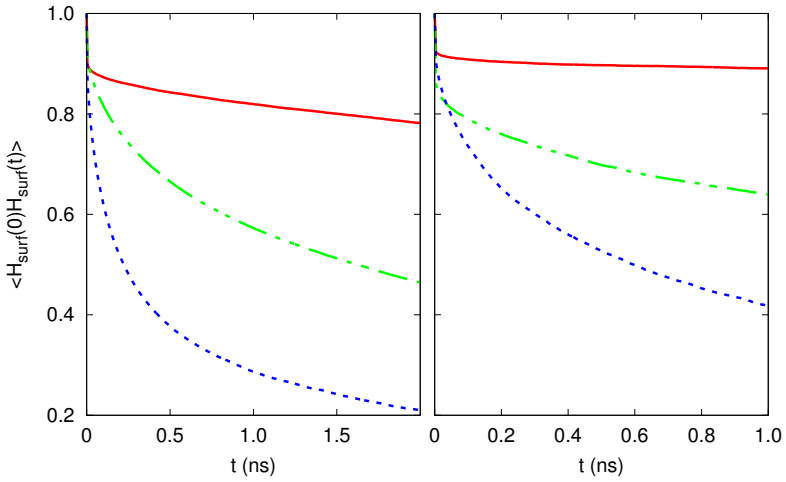

Figure S5. The surface residence time correlation function is shown for EC (left panel) and Li^+ (right panel) near the SEI interface of a pure amorphous Li_2EDC film. For both graphs the correlation function is shown at z = -1.66Å (red solid), 4.34Å (green solid), and 10.34Å (blue solid) with respect to the SEI interface.

Table S2. Integrated densities of electrolyte components for each interface region defined in Figure 4-5, S3.

SEI Film	EC			PF_6^-			Li^+		
	n_{abs}	n_{ads}	n_{diff}	n_{abs}	n_{ads}	n_{diff}	n_{abs}	n_{ads}	n_{diff}
Li_2EDC	3.45	37.79	76.84	0.07	4.55	12.84	5.22	9.82	4.61
+ 10 % LiF	17.92	43.95	105.71	0.00	0.81	17.78	6.42	10.23	6.20
+ 25 % LiF	27.89	28.52	108.30	2.66	5.68	8.95	17.21	2.29	7.83
+ 50 % LiF	5.28	18.33	60.65	0.00	5.0E-5	10.99	6.59	4.43	3.68
+ 10 % Li_2CO_3	22.77	46.91	100.79	0.00	2.23	13.86	7.5	6.00	8.02
+ 25 % Li_2CO_3	26.35	48.71	77.26	0.00	3.7E-4	15.29	8.42	4.27	5.94
+ 50 % Li_2CO_3	28.12	25.83	72.97	0.00	5.68	7.31	13.95	1.21	4.25
LiF Cyrstal	–	17.71	68.44	–	7.05	7.30	–	12.00	2.28
Li_2CO_3 Crystal	–	60.85	87.14	–	4.79	18.71	–	13.42	9.43

Table S3. Surface residence times in nanoseconds for EC, PF_6^-, and Li^+ initially located in each interface region defined in Figure 4-5,S3. In contrast to solvation residence times, these time constants, τ_{abs} , τ_{ads} , and τ_{diff}, refer to residence times for species in the regions defined in Figures 4-5, S3, regardless of their association with lithium cations. In the case of the LiF crystal, the diff region has been split up in two layers for this table with the layer closer to the crystal used for τ_{ads}.

SEI Film	EC				PF_6^-				Li^+			
	τ_{abs}	τ_{ads}	τ_{dif}	τ_{bulk}	τ_{abs}	τ_{ads}	τ_{dif}	τ_{bulk}	τ_{abs}	τ_{ads}	τ_{dif}	τ_{bulk}
Li_2EDC	6.34E4	3.95	0.551	0.191	3.58E15	1.83E2	0.901	0.283	6.50E12	23.9	1.36	0.337
+ 10 % LiF	1.05E4	2.46	0.464	0.192	1.83E5	26.3	0.915	0.305	1.61E5	29.1	1.19	0.317
+ 25 % LiF	14.7	0.844	0.375	0.202	1.12E5	3.99	0.477	0.297	2.30E5	2.22	0.672	0.338
+ 50 % LiF	6.70E2	2.76	0.444	0.177	1.06E7	29.6	0.729	0.238	1.66E12	7.75	1.04	0.306
+ 10 % Li_2CO_3	3.36E3	4.31	0.555	0.190	2.12E4	1.23E2	0.891	0.256	2.50E21	2.20E2	1.65	0.295
+ 25 % Li_2CO_3	3.08E3	2.92	0.508	0.206	6.54E10	53.8	0.610	0.317	1.43E14	22.5	0.994	0.402
+ 50 % Li_2CO_3	9.94E2	2.82	0.501	0.208	1.10E31	41.0	0.725	0.300	8.27E19	4.64	0.875	0.366
LiF crystal	5.14E4	1.95	0.955	0.845	5.64E9	2.95	1.57	0.829		5.48E12	9.71	1.28
Li_2CO_3 crystal	7.74E7	32.7	2.95	1.16	3.68E8	1.61E2	6.91	2.06	1.72E8	5.14E3	15.8	1.44