

Supporting Information

Lessons Learned from Semi-Empirical Methods for the Li-Ion Battery Solid Electrolyte Interphase

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Table S1: List of reaction energies for all the methods used.

Reactions	PBE-dDsC	GFN1-xtb	GFN2-xtb	PM6-D3	PM7-D3
1	-201	-395	-486	-431	-406
2	-137	-222	-286	-233	-233
3	-227	-197	-401	-185	-212
4	-76	-75	-158	-75	-76
5	59	30	-88	80	86
6	61	21	-91	98	119
7	98	101	87	163	134
8	165	236	254	100	149
9	286	227	314	265	298
10	39	71	175	83	48
11	4	2	-6	11	22
12	-63	-117	-183	-224	-212
13	-48	-113	-174	-238	-230
14	-95	-30	-31	-12	-33
15	-49	27	26	48	32
16	61	213	161	214	203
17	81	193	158	163	159
18	-124	-145	-146	-148	-144
19	-183	-190	-190	-205	-204
20	-56	22	-24	12	-20
21	13	77	100	27	-2
22	-174	-173	-140	-182	-187
23	-99	-19	-9	-11	-45
24	-437	-664	-696	-564	-568
25	-383	-496	-504	-260	-263
26	-519	-620	-622	-384	-401
27	-322	-561	-717	-353	-365
28	-373	-618	-565	-394	-405
29	-45	-100	-109	-68	-11
30	52	50	60	75	100
31	-296	-241	-378	-289	-307
32	-217	-292	-305	-219	-209

Table S2: Absolute % deviation (A%D) and absolute deviation (AD) of all reactions relative to PBE-dDsC

Reactions	GFN-xtb		GFN2-xtb		PM6-D3		PM7-D3	
	A%D	AD	A%D	AD	A%D	AD	A%D	AD
1	97	194	142	285	115	230	102	205
2	61	84	108	149	70	96	70	96
3	13	29	77	175	19	42	6	15
4	2	2	106	81	2	2	1	1
5	49	29	249	147	36	21	46	27
6	65	39	250	152	62	37	97	58
7	3	3	11	11	67	66	37	36
8	43	72	54	89	39	65	9	16
9	20	58	10	28	7	21	4	13
10	82	32	351	136	114	44	23	9
11	66	3	238	11	151	7	403	18
12	85	54	191	120	255	161	236	149
13	135	65	263	126	397	190	379	182
14	69	65	67	64	88	83	66	62
15	155	76	153	75	198	97	165	80
16	246	151	161	99	248	152	231	142
17	140	113	96	77	102	82	97	78
18	17	21	18	22	19	24	16	20
19	4	7	4	7	12	22	11	21
20	139	78	58	32	122	68	63	35
21	478	63	657	87	104	14	116	15
22	0	1	19	34	5	9	7	13
23	81	80	91	90	89	88	54	54
24	52	228	59	259	29	127	30	131
25	30	113	32	121	32	123	31	120
26	19	101	20	103	26	135	23	118
27	75	240	123	395	10	31	13	43
28	66	245	51	191	6	21	8	32
29	120	55	139	63	48	22	76	34
30	3	2	15	8	44	23	91	47
31	19	55	28	82	2	7	4	11
32	35	75	41	89	1	3	3	7

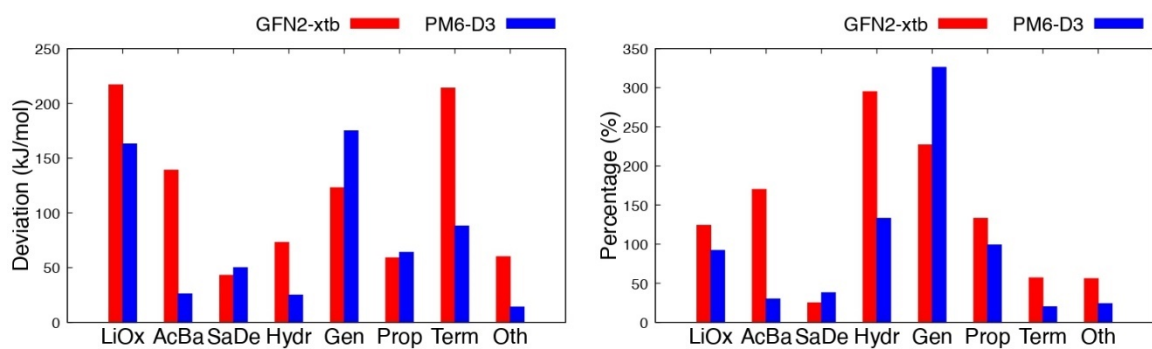


Figure S1: Left: The mean absolute deviation (MAD) and right the mean absolute percentage deviation for GFN2-xtb and PM6-D3 against PBE-dDsC, reported in terms of the eight groups of reaction types defined in Figure 1.

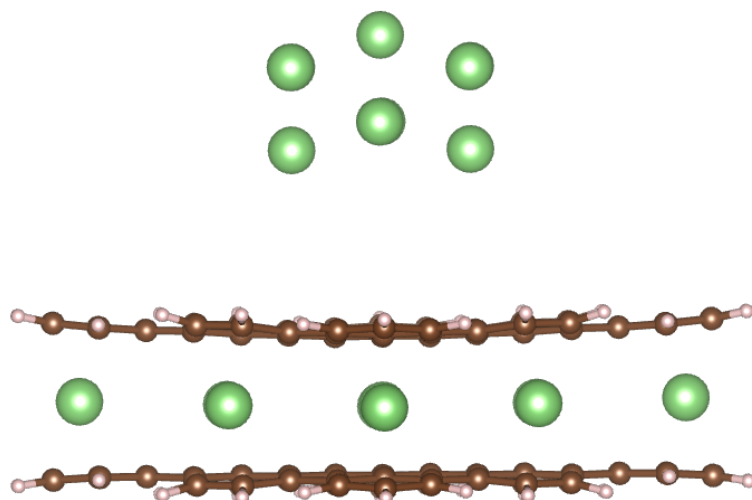
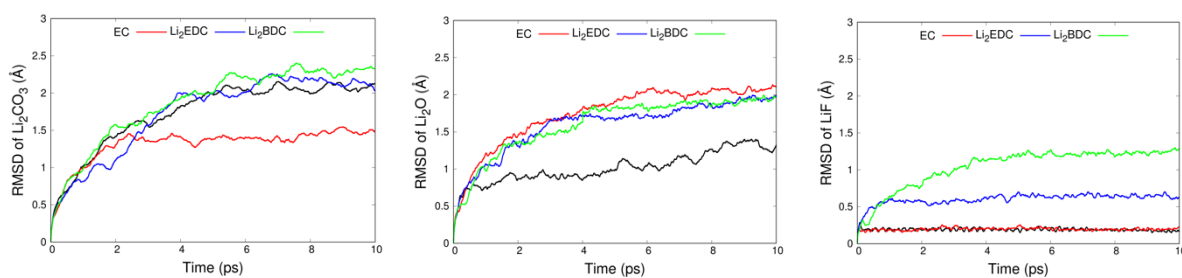


Figure S2: The final geometry of LiC₆ using GFN-xtb

PM7-D3



GFN-xtb

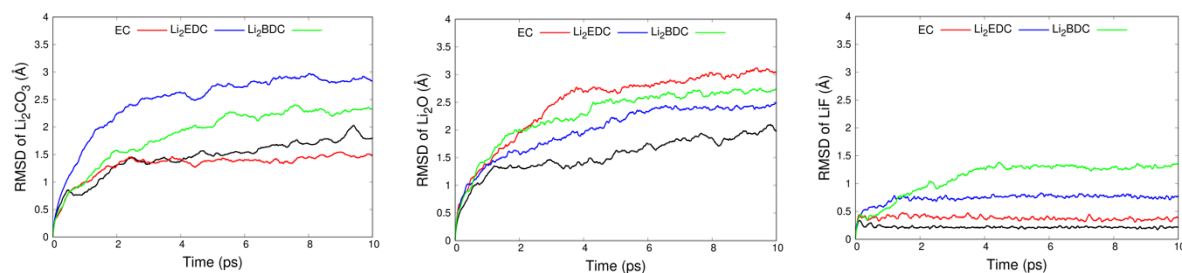


Figure S3: RMSD values over time for the nanoparticles (from left to right: Li_2CO_3 , Li_2O and LiF) through the 10 ps molecular dynamics' simulation using PM7-D3 (top) and GFN-xtb (bottom). The black line represents the RMSD values for the free nanoparticles (not surrounded by any organics).

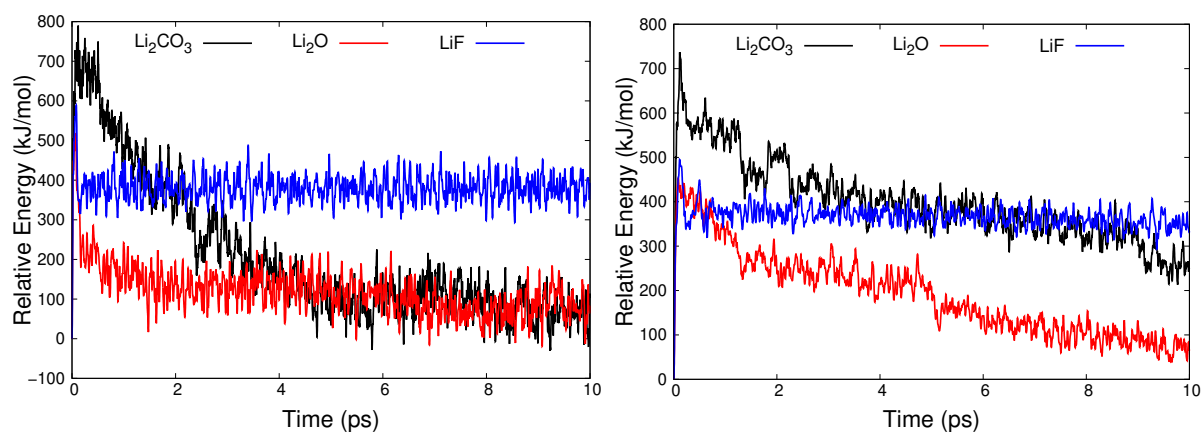


Figure S4: Total potential energies relative to the initial (optimized) geometry as a function of time for the bare nanoparticles. On the left: PM7-D3, on the right GFN-xtb.

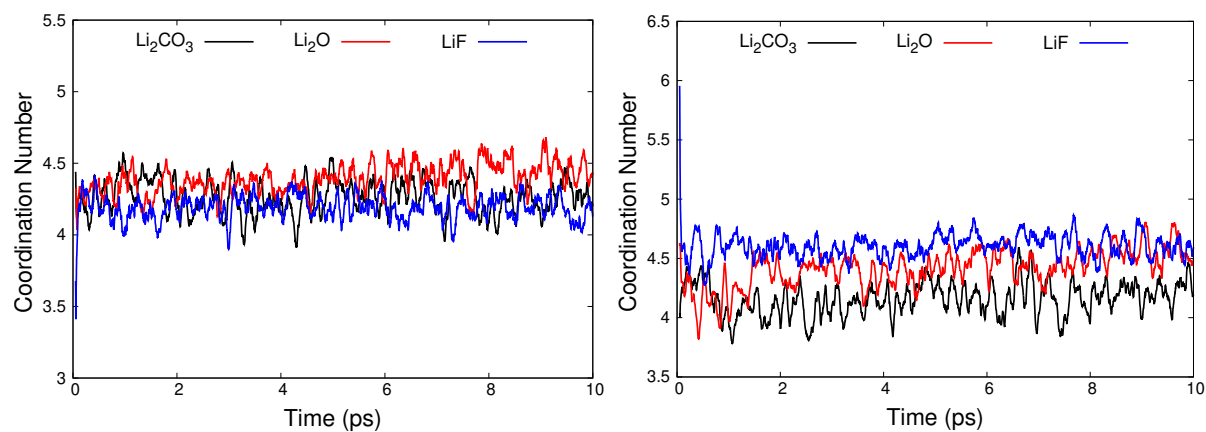


Figure S5: Moving averages (over 100 points, i.e., 100 fs) of the average coordination number of Li during dynamics of bare nanoparticles. The coordination numbers are computed using the parameter free anisotropically corrected solid-angle nearest neighbours (ASANN) algorithm. On the left: PM7-D3, on the right GFN-xtb.

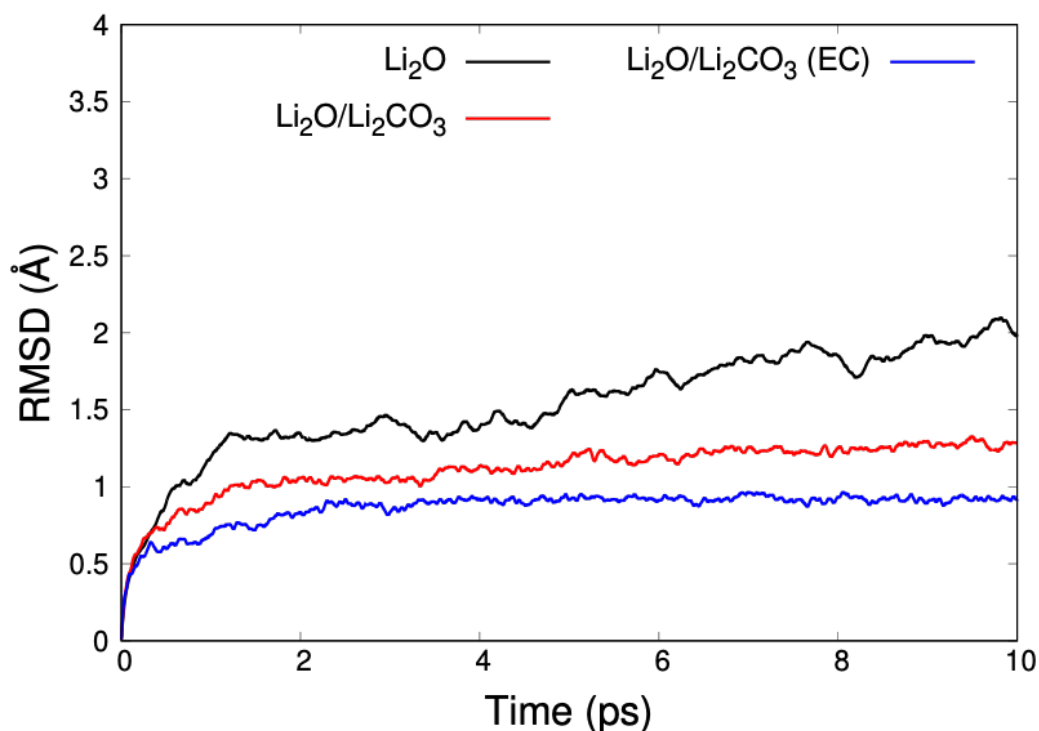


Figure S6: RMSD values over time for Li_2O : the bare Li_2O nanoparticle in black, the Li_2O core protected by a Li_2CO_3 shell in presence of EC (blue) and the bare Li_2O core, Li_2CO_3 shell structure in red. The starting structures for blue and red are identical (except for the presence/absence of EC). All these MD simulations are performed at 300 K with GFN-xtb.