Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Interfacial Structure and Electrochemical Stability of Electrolytes: Methylene Methanedisulfonate as Additive

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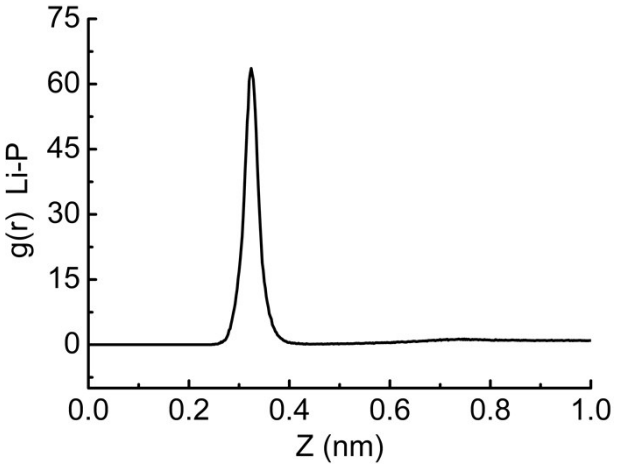

Figure S1. Radial distribution function for Li^+ with PF_6^- (Li-P) in MMDS-containing electrolytes.

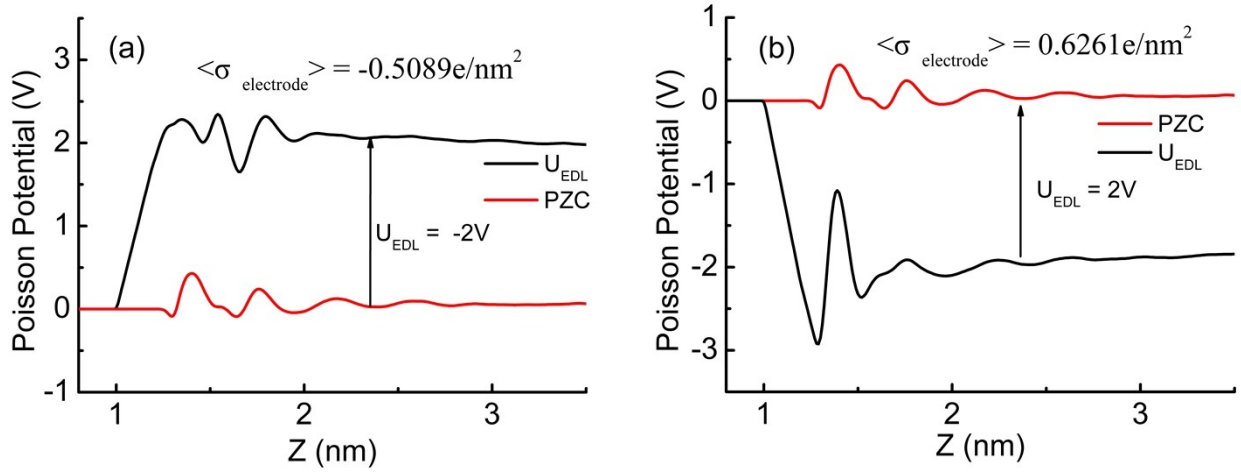

Figure S2. The representative examples of Poisson potential for the MMDS-containing electrolytes. Here, PZC is -0.08V, a negative value indicates that the positively charged Li^+ ion in the electrolyte has a lower propensity for the electrode surface than the negatively charged species.

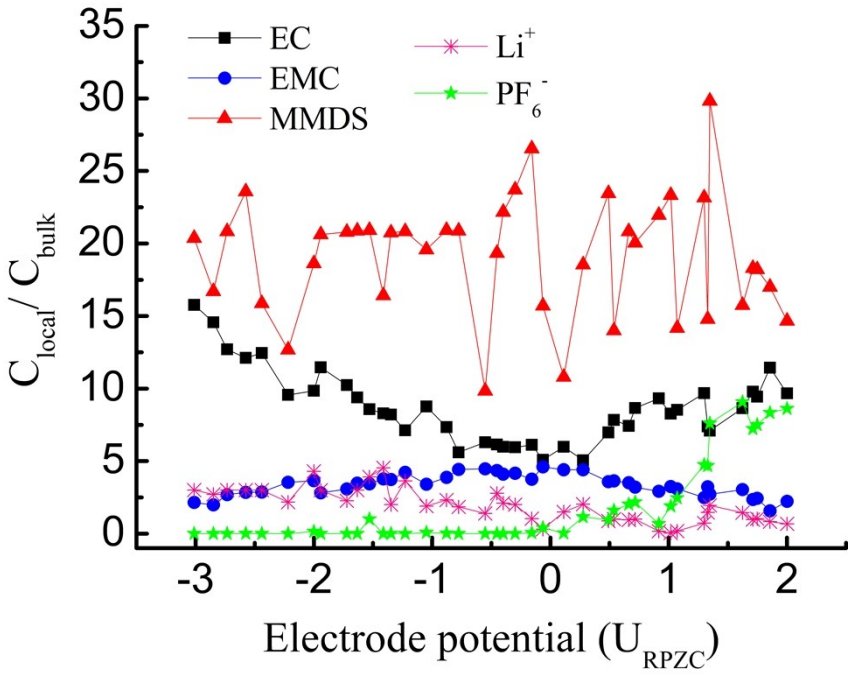

Figure S3. Relative concentrations (C_{local}/C_{bulk}) of components as a function of electrode potential in MMDS-containing electrolytes, where C_{local} is defined as the interfacial concentration within 0.6 nm. PF_6^- population follows expected charge-repulsion behavior, the density of Li^+ in the surface layer in contrast does not decrease on the positive plate with increasing positive potential. However, this trend is still in accord with the reported work (see Figure 6 in the work[1] by Oleg Borodin and Janel Vatmanu).

Table S1. The Orbit Energy of solvent molecules and their affinity to electrode surface (C_{local}/C_{bulk}) in the interfacial width of 0.45 nm.

	Orbit Energy		C_{local} / C_{bulk}		
Molecules	HOMO (ev)	LUMO (ev)	-1 V	0 V	1 V
FEC	-8.975	-0.386	5.00	4.17	7.02
EC	-8.778	-0.072	5.79	5.43	5.59
EMC	-8.855	-0.068	3.48	3.84	3.00

In FEC-containing electrolytes, there is no significant difference in orbit energy and the affinity between FEC additive and solvents (EC or EMC). These behaviors are dissimilar to those in MMDS-containing electrolytes, where the LUMO energy of MMDS is 1.4eV lower than that of solvents (see Table 3), and the relative concentration (C_{local}/C_{bulk}) of additive MMDS is much higher than any of solvents no matter what the electrode potential is (see Figure 3 or Figure S3).

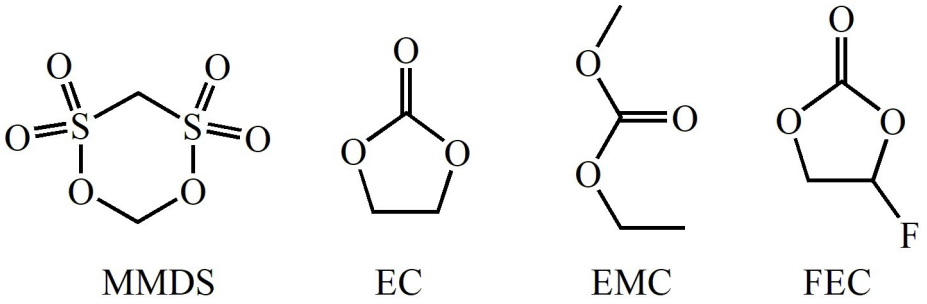

Figure S4. Structure of electrolyte molecules

Key Force Field parameters

Table S2. Nonbonded Lennard-Jones parameters

Atom	σ (Å)	ε (kcal mol^{-1})
C (sp3)	3.400	0.458
C (sp2)	3.400	0.360
H (in MMDS)	2.293	0.066
H (-CH-O)	2.650	0.066
H	2.471	0.066
O=	2.960	0.879
O-	3.000	0.711

Energy-minimized *ab initio* structure and atom charge

! ATOM:

!! index (int): atom index

!! name (str): atom name (required)

!! type (str): atomtype name

!! charge (float, e): partial atomic charge

!! x (float, angstrom): atom coordinate

!! y (float, angstrom): atom coordinate

!! z (float, angstrom): atom coordinate

MOLECULE EC

index	name	type	charge	x	y	z	! 10
1	C1	c	0.84495	0.852909	-0.000012	-0.000195	
2	O1	os	-0.37347	0.073901	1.114400	-0.099196	
3	O2	os	-0.37347	0.073873	-1.114396	0.099123	
4	O3	o	-0.54569	2.047751	-0.000011	0.000122	
5	C2	c3	0.08932	-1.305804	0.758294	0.110486	
6	H1	h1	0.06726	-1.586511	1.039717	1.134701	
7	H2	h1	0.06726	-1.919381	1.310006	-0.609218	
8	C3	c3	0.08932	-1.305820	-0.758281	-0.110403	
9	H3	h1	0.06726	-1.586677	-1.039710	-1.134579	
10	H4	h1	0.06726	-1.919342	-1.309963	0.609376	

MOLECULE EMC

index	name	type	charge	x	y	z	! 15
1	C1	c	1.00191	-0.544561	0.164360	0.000006	
2	O1	o	-0.61727	-0.734971	1.362517	-0.000056	
3	O2	os	-0.55116	0.647234	-0.447869	0.000098	
4	O3	os	-0.39105	-1.497690	-0.781881	0.000025	

5	C2	c3	0.50520	1.799892	0.434646	0.000105
6	H1	h1	-0.05682	1.747278	1.076836	-0.888573
7	H2	h1	-0.05682	1.747440	1.076592	0.888973
8	C3	c3	-0.00991	-2.848210	-0.281121	-0.000041
9	H3	h1	0.07455	-3.031369	0.325729	-0.894888
10	H4	h1	0.07455	-3.482875	-1.171546	-0.000290
11	H5	h1	0.07455	-3.031580	0.325361	0.895016
12	C4	c3	-0.25170	3.037307	-0.439960	-0.000115
13	H6	hc	0.06799	3.932394	0.197185	-0.000081
14	H7	hc	0.06799	3.067841	-1.080054	0.891295
15	H8	hc	0.06799	3.067716	-1.079786	-0.891721

MOLECULE MMDS

index	name	type	charge	x	y	z	! 14
1	S1	s6	0.879830	0.869930	1.072471	-0.268633	
2	O1	o	-0.395762	2.032635	1.660197	-0.948647	
3	O2	o	-0.395762	0.000000	2.155627	0.210655	
4	C1	c3	-0.509412	0.000000	0.000000	-1.360913	
5	H1	h2	0.258076	0.624365	-0.605392	-1.984266	
6	H2	h2	0.258076	-0.624365	0.605392	-1.984266	
7	S2	s6	0.879830	-0.869930	-1.072471	-0.268633	
8	O3	o	-0.395762	-2.032635	-1.660197	-0.948647	
9	O4	o	-0.395762	0.000000	-2.155627	0.210655	
10	O5	os	-0.361909	-1.237805	-0.147095	1.035658	

11	O6	os	-0.361909	1.237805	0.147095	1.035658
12	C2	c3	0.357021	0.000000	0.000000	1.842685
13	H3	h2	0.091723	-0.124603	0.868060	2.455748
14	H4	h2	0.091723	0.124603	-0.868060	2.455748

References:

1 J. Vatamanu, O. Borodin and G. D. Smith, *J. Phys. Chem. C*, 2012, **116**, 1114-1121.