

Supporting Information for:

Structures of FEC-containing Electrolytes and Stabilization

Mechanism at High Voltage and Elevated Temperature

Yamin Wang,[†] Debing Li,[†] Xiaoying Yu,[†] Chao Shang,[‡] Yingchun Liu,[†] and Qi Wang^{*,†}

[†] Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China

[‡] King's Academy, Madaba, 16188, Jordan

* Q. Wang. Fax: +86 571 87951895. E-mail: qiwang@zju.edu.cn

Table S1. Comparison of calculated density with the literature reported at 300 K.

Entry (300K)	This work ^a			Reported (from SciFinder)		
	FEC	EC	EMC	FEC	EC	EMC
Density (g/cm ³)	1.46	1.34	1.05	1.45	1.32	1.00

a: The densities in this work are obtained by simulating pure solvent system, each system contains 1000 molecules, simulation details are uniform with the mixed system. The densities of pure solvent are consistent with those in literature reported. And mixed densities for G2, E1, E2 are 1.23g/cm³, 1.25g/cm³, 1.22g/cm³, respectively, which are within a reasonable range of values. The force field parameters for Li⁺ and PF₆⁻ are obtained from the studies of Tenney et al.¹

Table S2. Comparison of calculated self-diffusion coefficients with the literature reported at 300 K

Species	Self-diffusion coefficients D (m ² /s)	
	This work ^a (system G2)	Reported ^b (from Fig.2 in Ref. ¹)
Li ⁺	2.46×10 ⁻¹¹	6.6×10 ⁻¹¹
PF ₆ ⁻	2.47×10 ⁻¹¹	6.6×10 ⁻¹¹
EC	1.05×10 ⁻¹⁰	2.1×10 ⁻¹⁰
EMC or DMC	1.08×10 ⁻¹⁰	2.4×10 ⁻¹⁰

a: 1.2M LiPF₆ in EC / EMC. b: 1.0 M LiPF₆ in EC / DMC. Values for D are averages taken over the last 8 ns of 20 ns trajectories. Although the system G2 differs from the literature reported,¹ the corresponding Ds are in the same order of magnitude. When compared with experimental data (see Table 4 in ref.2, 1.0 M LiPF₆ in EC/DEC at 303K), corresponding solvent Ds are in the same order magnitude, and ion Ds is lower than experimental data. However, based on classical Stokes–Einstein

Equation formula, D_s become smaller as the temperature decreases (300K in this work vs. 303K in experiment). And previous researches have reported that ion D_s decrease with the increasing ion concentration.^{3, 4} (1.2M in this work vs. 1.0M in experiment). Considering the differences of temperature and concentration. The D values of ion in this work should be smaller than experiment data in ref.2. In other words, Our simulation results of self-diffusion coefficients are in good agreement with the previous simulation and experimental data.

RDFs. The primary peak positions of RDF are consistent with previous results calculated by molecular dynamics (MD),^{1, 5, 6} *ab initio* molecular dynamics (AIMD)⁵ and experimental data measured by Time-of-flight neutron diffraction.⁷ Good agreements are found compared with those in the literature for Li–O,^{1, 5, 8} Li–P,^{1, 6, 7} and Li–Li¹ respectively, showing that conventional MD are accurate enough to describe correctly the short-range microscopic structure of the system, it is consistent with the reported conclusion that microscopic structure can be modeled well by conventional MD.^{1, 9-12}

Table S3. Coordination number N of each solvent within the first coordination shell of Li^+ ions for systems G2, E1 and E2 at different temperatures.

Field strength	G2		E1			E2	
	Li–EC	Li–EMC	Li–FEC	Li–EC	Li–EMC	Li–FEC	Li–EMC
250 K	1.31	2.33	0.41	0.57	2.25	0.71	2.41
300 K	0.87	2.05	0.15	0.34	2.11	0.26	2.13
330 K	0.79	1.78	0.10	0.26	1.89	0.19	2.00

As an extension, electric fields are considered during the analysis of structures of electrolytes. Similar to the temperature, Figure S1 and Table S4 show the changes in radial distribution function $g(r)$ and coordination number (N) with the increase of external electric field. Figure S1 shows the short-range order and strong solvation effects of ions in the structures of electrolytes. It also shows that the position of the primary peaks and first valley of the RDF do not change with the electric field, even in strong electric field ($E = 1000 \text{ V}/\mu\text{m}$). And the primary Li–O peaks at approximately 0.21 nm is the highest and $N_{\text{Li-O}} = 3.40$, and the others (Li–P, Li–Li, and P–O) display significantly lower

for strong electric fields. It suggests that a strong electric field leads to the enhancement of Li^+ solvation (Li-O coordination number) but depression for Li-P, Li-Li, and P-O. A slight lower total N indicates that the effects of strong electric field on decreasing of Li-P, Li-Li and P-O are greater than increasing of Li-O. But for weak electric fields ($0 < E < 1.0 \text{ V}/\mu\text{m}$), no significant changes in $g(r)$ and N were observed in external electric fields. In summary, the external electric field does not exhibit noticeable effects on ion solvations and electrolyte structures except for an extremely strong electric field.

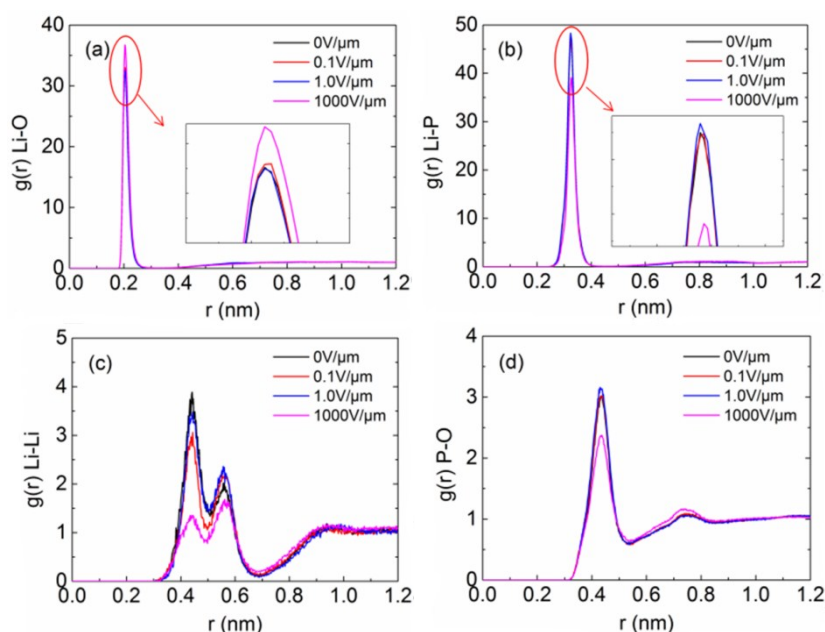


Figure S1. Radial distribution function $g(r)$ for Li^+ with solvent carbonyl oxygen atom (a. Li-O, solvent including EC and EMC), PF_6^- (b. Li-P), other Li^+ (c. Li-Li), and PF_6^- with solvent carbonyl oxygen (d. P-O) for system G2 at different external electric fields.

Table S4. Coordination number N of species within the first coordination shell of ions for system G2 at different external electric fields and $T = 300 \text{ K}$.

Field strength	Li-O ^a	Li-P	Li-Li	P-O	total
0 $\text{V}/\mu\text{m}$	2.98	1.61	0.49	4.35	9.43
0.1 $\text{V}/\mu\text{m}$	2.99	1.58	0.38	4.51	9.46
1.0 $\text{V}/\mu\text{m}$	2.80	1.63	0.44	4.62	9.49
1000 $\text{V}/\mu\text{m}$	3.40	1.31	0.22	3.86	8.79

a: See Table S6 (for system G2) for N of each solvent within the first coordination shell of Li^+ ions.

Table S5. Coordination number N of species within the first coordination shell of ions for systems E1 and E2 at different external electric fields and $T = 300$ K

Field strength	E1				E2			
	Li-O ^a	Li-P	Li-Li	P-O	Li-O	Li-P	Li-Li	P-O
0 V/ μm	2.60	1.85	0.69	4.73	2.39	1.97	0.85	4.86
0.1 V/ μm	2.72	1.75	0.56	4.63	2.51	1.90	0.68	4.97
1.0 V/ μm	2.54	1.88	0.64	4.84	2.46	1.94	0.77	4.89
1000 V/ μm	3.19	1.45	0.30	4.12	3.08	1.50	0.33	4.40

a: See Table S6 (for systems E1 and E2) for N of each solvent within the first coordination shell of Li^+ ions.

Table S6. Coordination number N of each solvent within the first coordination shell of Li^+ ions for systems G2, E1 and E2 at different external electric fields and $T = 300$ K.

Field strength	G2		E1			E2	
	Li-EC	Li-EMC	Li-FEC	Li-EC	Li-EMC	Li-FEC	Li-EMC
0 V/ μm	0.92	2.06	0.15	0.34	2.11	0.26	2.13
0.1 V/ μm	0.87	2.12	0.14	0.39	2.19	0.26	2.25
1 V/ μm	0.78	2.02	0.12	0.32	2.10	0.24	2.22
1000 V/ μm	1.31	2.09	0.43	0.54	2.22	0.73	2.35

Key Force Field parameters

Some key Force field parameters originally built via Antechamber using GAFF (Generalized Amber Force Field) by linuxuser. The force field parameters for Li^+ and PF_6^- are taken from the studies of Tenney et al.¹

Table S7. Nonbonded Lennard-Jones

Atom	σ (Å)	ϵ (kcal mol ⁻¹)
C (sp3)	3.400	0.458
C (sp2)	3.400	0.360
H	2.471	0.066
H (H-CHF)	2.293	0.066

H (CH ₃ -O)	2.650	0.066
O=	2.960	0.879
O-	3.000	0.711
F	3.118	0.255

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
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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 FEC

index	name	type	charge	x	y	z	! 10
1	C1	c	0.81284	-1.130822	-0.128270	-0.016797	
2	O1	os	-0.33427	-0.673759	1.123608	-0.266342	
3	O2	os	-0.35567	-0.111290	-0.900845	0.509053	
4	O3	o	-0.50754	-2.240637	-0.517396	-0.200401	
5	C2	c3	0.00724	0.687684	1.242117	0.178195	
6	H1	h1	0.09917	1.285442	1.705088	-0.612946	
7	H2	h1	0.09917	0.714140	1.849302	1.092247	
8	C3	c3	0.33833	1.102554	-0.206326	0.435328	
9	H3	h2	0.07599	1.688753	-0.393809	1.340610	
10	F1	f	-0.23526	1.840074	-0.694294	-0.637638	

Example of Gromacs simulation Script

Title = OPLS Lysozyme MD simulation

; Run parameters

integrator = md ;
nsteps = 25000000 ;
dt = 0.001 ;

; Output control

nstxout = 5000 ;
nstvout = 5000 ;
nstenergy = 5000 ;
nstlog = 5000 ;
nstxtcout = 5000 ;

; Bond parameters

continuation = yes ;
;constraint_algorithm = lincs ;
;constraints = all-bonds ;

constrained

;lincs_iter = 1 ;
;lincs_order = 4 ;

; Neighborsearching

;cutoff-scheme = Verlet
ns_type = grid ;
nstlist = 10 ;
rcoulomb = 1.0 ;
rvdw = 1.0 ;

; Electrostatics

coulombtype = PME ;
pme_order = 4 ;
fourierspacing = 0.16 ;

; Temperature coupling is on

tcoupl = Nose-Hoover ;
tc-grps = EMC ECX LIX PF6 ;
tau_t = 0.1 0.1 0.1 0.1 ;
ref_t = 300 300 300 300 ;

; Pressure coupling is on

pcoupl = Parrinello-Rahman ;
pcoupltype = isotropic ;

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tau_p          = 2.0          ;
ref_p          = 1.0          ;
compressibility = 4.5e-5      ;

; Periodic boundary conditions
pbc           = xyz          ;

; Dispersion correction
DispCorr      = EnerPres    ;

; Velocity generation
gen_vel       = no          ;

; Electric fields
; Format is number of terms (int) and for all terms an amplitude (real)
; and a phase angle (real)
E-x           =
E-xt          =
E-y           =
E-yt          =
E-z           =
E-zt          =

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