Support Information

The mechanism of Li-ion transport in carbonate-based electrolyte

We conducted molecular dynamics (MD) simulations of bulk electrolytes using an all-atom, all-flexible model with non-polarizable force field in the following form,

$$V = \sum_{\text{bonds}} k_b(r_{ij} - r_0)^2 + \sum_{\text{angles}} k_\theta(\theta_{jik} - \theta_0)^2 \#$$
$$+ \sum_{\text{dihedrals}} \frac{1}{2}\{V_1[1 + \cos(\varphi)] + V_2[1 - \cos(2\varphi)] + V_3[1 + \cos(3\varphi)]\}$$
$$+ \sum_i \sum_{j>i} \left\{ 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{1}{4\pi\varepsilon_0}\frac{q_i q_j}{r_{ij}} \right\} \#(S1)$$

in which the first three terms represent the bond, angle and dihedral interactions, and the last term represents the long-range interactions, including van der Waals and Coulombic interactions. The solvent molecules Ethylene carbonate (EC), dimethyl carbonate (DMC), anion PF_6^- and cation Li^+, along with their restrained electrostatic potential (RESP)[1] atomic charges, are depicted in Figure. S1. All the force filed parameters, including bond, angle, dihedral and Lennard-Jones terms are listed in Tables S1 – S4.

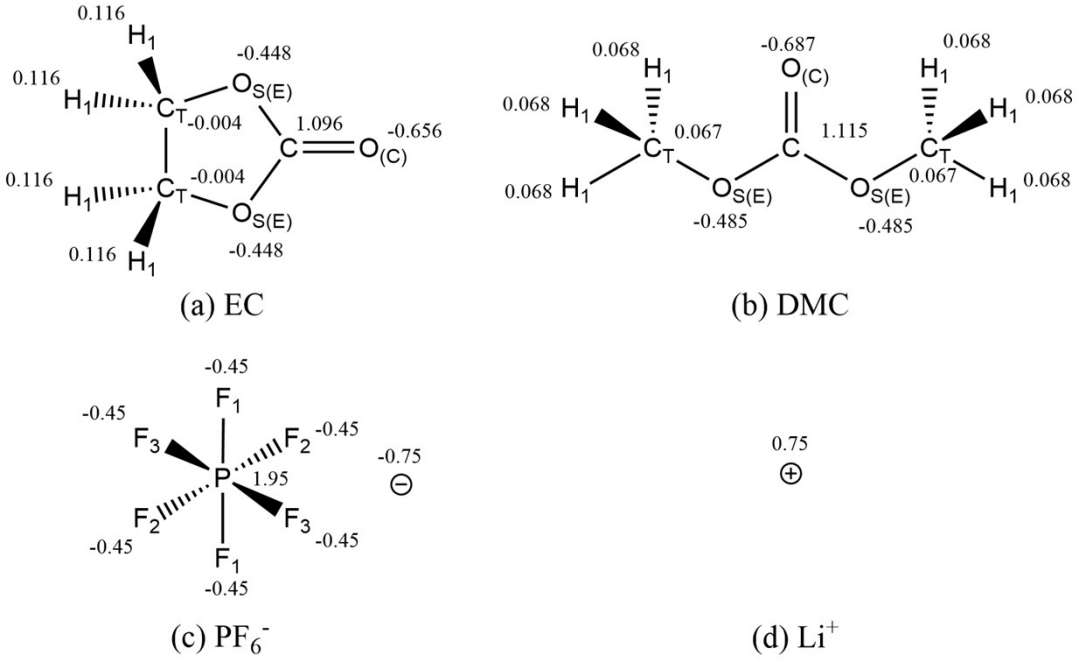

Figure S1. All-atom representation of (a) EC, (b) DMC, (c) PF_6^-, and (d) Li^+.

Table S1. Bond parameters (k_b in kcal·mol^{-1}·Å^{-2} and r_0 in Å).[a]

EC and DMC						PF_6^-		
Bonds	k_b	r_0	Bonds	k_b	r_0	Bonds	k_b	r_0
C_T-H_1	340.0	1.090	C_T-O_S	320.0	1.410	P-F_1	370.5	1.606
C-O_S	214.0	1.327	C-O	570.0	1.229	P-F_2	370.5	1.606
C_T-C_T	268.0	1.529				P-F_3	370.5	1.606

[a]Parameters without explicit citation were taken from OPLS force field and generated by LigParGen.[3-6]

Table S2. Angle parameters (k_θ in kcal·mol^{-1}·radian^{-2} and θ_0 in degree).[a]

EC and DMC			PF_6^-		
angle	k_θ	θ_0	angle	k_θ	θ_0
H_1-C_T-H_1	33.0	107.8	F_1-P1-F_1	34.78	180.0
H_1-C_T-C_T	37.5	110.7	F_2-P1-F_2	34.78	180.0
H_1-C_T-O_S	35.0	109.5	F_3-P1-F_3	34.78	180.0
C_T-C_T-O_S	50.0	109.5	F_1-P1-F_2	139.22	90.0
C_T-O_S-C	83.0	116.9	F_1-P1-F_3	139.22	90.0
O_S-C-O	83.0	123.4	F_2-P1-F_3	139.22	90.0
O_S-C-O_S	69.9	118.18			

[a]Parameters without explicit citation were taken from OPLS force field and generated by LigParGen.[3-6]

Table S3. Dihedral and Improper dihedral parameters (V_i in kcal·mol^{-1}).[a]

EC and DMC							
Dihedral	V_1	V_2	V_3	Dihedral	V_1	V_2	V_3
H_1-C_T-C_T-H_1	0.000	0.000	0.300	C_T-C_T-O_S-C	-1.220	-0.126	0.422
H_1-C_T-O_S-C	0.000	0.000	0.198	C_T-O_S-C-O_S	4.669	5.124	0.000
C_T-O_S-C-O	0.000	5.124	0.000	Improper	$V_n/2$	γ^b	n[c]
O_S-C_T-C_T-O_S	-0.550	0.000	0.000	C-X-X-X	10.5	180	2
H_1-C_T-C_T-O_S	0.000	0.000	0.468				

[a]Parameters without explicit citation were taken from OPLS force field and generated by LigParGen.[3-6]

[b]Phase offset in deg.

[c]The periodicity of the torsion.

Table S4. Lennard-Jones parameters (σ_i in Å and ϵ_i in kcal·mol^{-1}).[a]

EC and DMC			Li^{+7} and PF_6^-		
Types	σ_i	ϵ_i	Types	σ_i	ϵ_i
CT	3.500	0.066	Li	2.026	0.0183
OS	2.900	0.140	P1	3.740	0.200
C	3.550	0.007	F1	3.120	0.061
H1	2.500	0.030	F2	3.120	0.061
O	2.960	0.210	F3	3.120	0.061

[a]The Lennard-Jones parameters between different atomic types *i* and *j*, ϵ_{ij} and σ_{ij} are handled by Lorentz-Berthelot mixing rule,[8] i.e., $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$ and $\sigma_{ij} = (\sigma_i + \sigma_j)/2$. Parameters without explicit citation were taken from OPLS force field and generated by LigParGen.[3-6]

Table S5. The fitted residence time ($\tau_{Li^+ - X}$ in ns) for the EC and DMC at different temperature (*T* in K).

T	$\tau_{Li^+ - EC}$	$\tau_{Li^+ - DMC}$
298.15	0.102	0.221
273.15	0.176	0.381
253.15	0.314	0.677
233.15	0.549	1.186
213.15	1.451	3.387

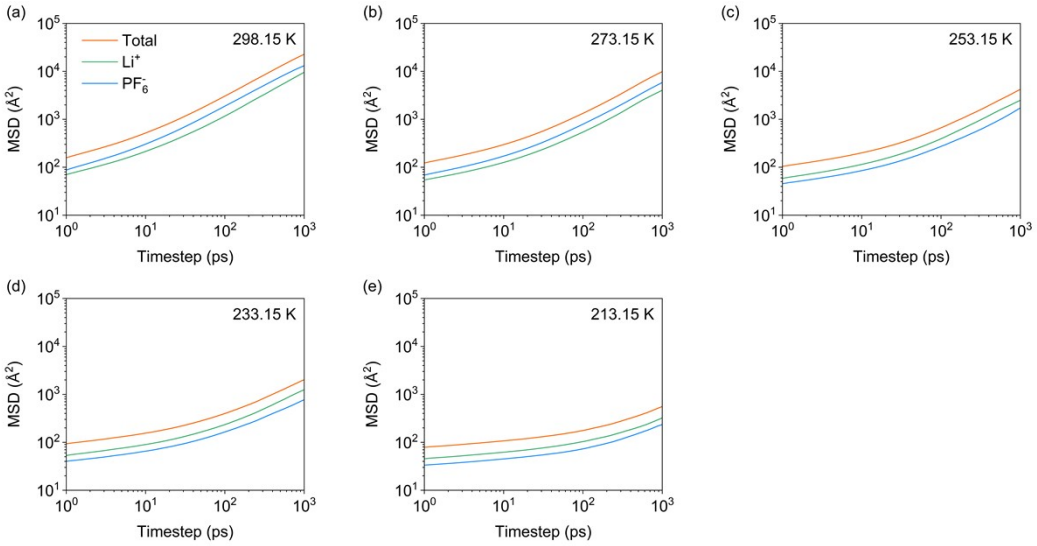

Figure S2. Charge mean square displacement (CMSD) $M_x(t)$ at temperatures of (a) 298.15 K, (b) 273.15 K, (c) 253.15 K, (d) 233.15 K, and (e) 213.15 K, respectively. Specifically, $M(t) = e^2\left\langle \sum_{i=1}^{N_i}\sum_{j=1}^{N_j} z_i z_j \Delta r_i(t) \cdot \Delta r_j(t) \right\rangle$ denotes total CMSD, $M_{\mathrm{Li}^+}(t) = e^2\left\langle \sum_{i=1}^{N_{\mathrm{Li}^+}}\sum_{j=1}^{N_j} z_i z_j \Delta r_i(t) \cdot \Delta r_j(t) \right\rangle$ denotes the partial CMSD of Li^+, and $M_{PF_6^-}(t) = e^2\left\langle \sum_{i=1}^{N_{PF_6^-}}\sum_{j=1}^{N_j} z_i z_j \Delta r_i(t) \cdot \Delta r_j(t) \right\rangle$ denotes the partial CMSD of PF_6^-, in which the symbols are the same as Eq. (1) in the main text. The total ionic conductivity σ, as well as the partial ionic conductivities σ_{Li^+} and $\sigma_{PF_6^-}$ are calculated by taking the slope of the corresponding $M(t)$, $M_{\mathrm{Li}^+}(t)$, and $M_{PF_6^-}(t)$ as t approaching 1 ns at different temperatures and dividing by $6Vk_BT$, according to Eq. (1) in the main text.

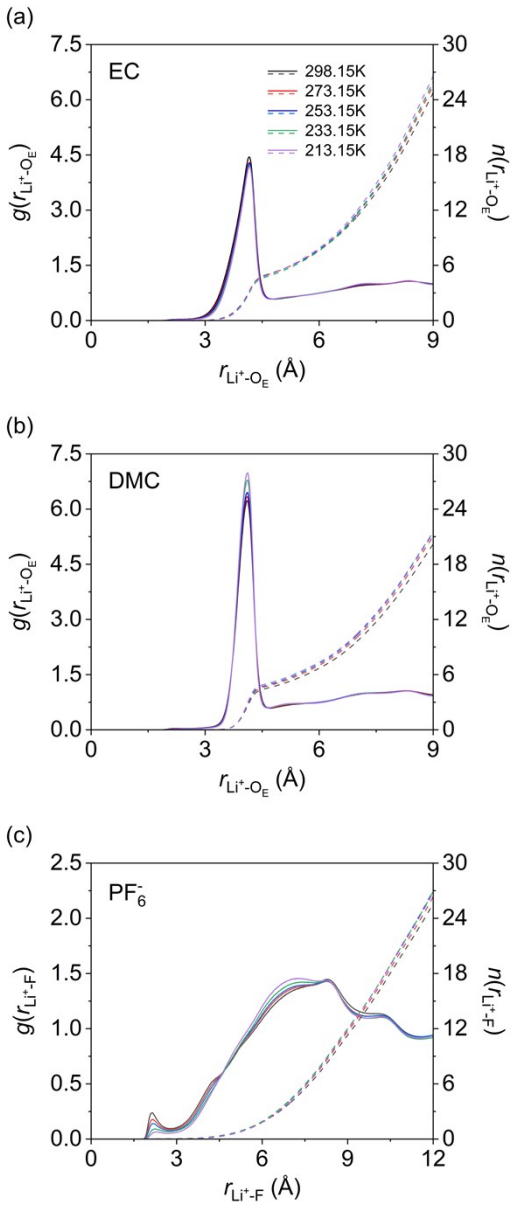

Figure S3. RDFs (solid lines) and corresponding CNs (dashed lines) for Li^+ with different atoms from 298.15 to 213.15 K. (a) Li^+-O_E(EC); (b) Li^+-O_E(DMC); (c) Li^+-F(PF_6^-).

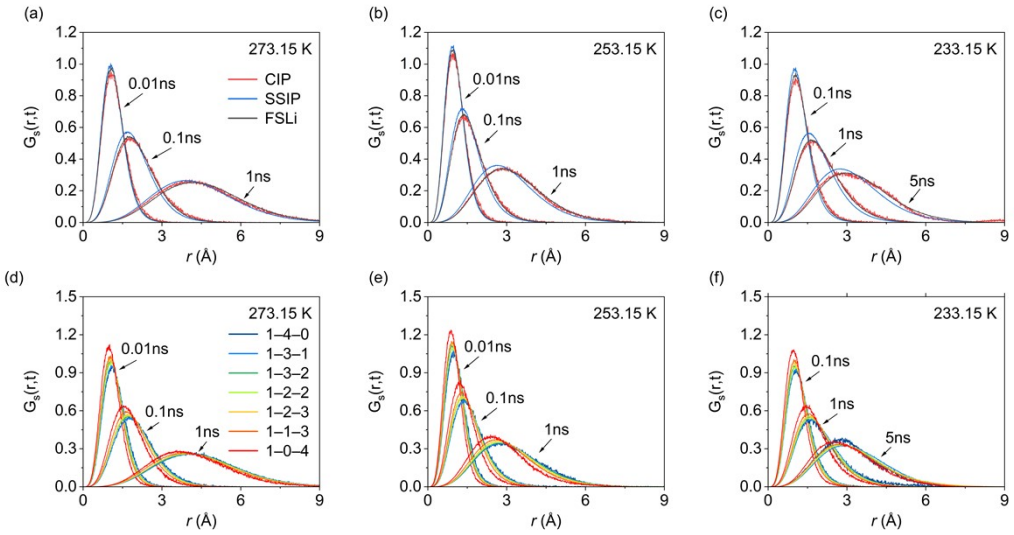

Figure S4. Distributions of the conditional self-part of the van Hove function $G_s(r, t)$ for Li^+ in various solvation clusters at different temperatures and time delays *t* (in ns): (a) 273.15 K and (b) 253.15 K (c) 233.15 K for Li^+ located in CIP, SSIP, and FSLI clusters. (d) 273.15 K and (e) 253.15 K (f) 233.15 K for Li^+ located in Li^+–EC_X–DMC_Y type clusters.

Reference:

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