Electronic Supplementary Material (ESI) for Chemical Science.
This journal is © The Royal Society of Chemistry 2021

Supporting Information

The Underlying Mechanism for Reduction Stability of Organic Electrolytes in Lithium Secondary Batteries

Xiaohui Shen[a]†, Peng Li[a]†, Xingwei Liu[a], Shengli Chen[a], Xinping Ai[a], Hanxi Yang[a], Yuliang Cao[a]*

[a] College of Chemistry and Molecular Sciences, Hubei Key Laboratory of Electrochemical Power Sources. Wuhan University, Wuhan 430072, China.

*Corresponding author. E-mail address: ylcao@whu.edu.cn

Experimental Procedures

DFT calculation details: Density functional theory calculation were conducted using Gaussian 16 software package.[1] All structures were optimized at the B3LYP/6-311++G(d, p) level,[2] followed by normal frequency analyses. All structures were minimized, and no imaginary frequencies were found. The visual LUMOs are processed by Multiwfn 3.8 program.[3] At B3LYP/6-311++G(3df,3pd) level, the single point energy of all structures were calculated to obtain more accurate results. $\Delta G = \Delta\varepsilon 0 + \Delta G$corr, $\Delta H = \Delta\varepsilon 0 + \Delta H$corr. $\varepsilon 0$ represents the SCF energy change at B3LYP/6-311++G(3df,3dp) level. ΔGcorr and ΔHcorr represent the thermal correction to Gibbs free energy and thermal correction to enthalpy of reaction obtained at B3LYP/6-311++G(d,p) level.

AIMD calculation details: Ab initio molecular dynamics simulation (AIMD) calculations were carried out using Vienna ab-initio simulation package (VASP).[4] Electron-ion interactions were described by the projector-augmented wave (PAW)[5] pseudopotentials with the cutoff energy of 400eV. The Perdew-Burke-Ernzerhof (PBE) type generalized gradient approximation (GGA)[6] was used to describe the exchange-correlation potential. The DFT-D3 method[7] was applied to include the van der Waals (vdW) correlation. A canonical (NVT) ensemble was use for the whole simulation process and a Nosé thermostat[8] was adopted to control the temperature at 300K. A time step of 1fs was applied, and the simulation lasted for 20000 steps (20ps). The initial structure of each electrolyte system was based on the density measured by experiments, and then a certain number of DEC, Li and ClO_4^- were randomly placed according to different molar ratios of the system. The AIMD trajectory of the final 10 ps of each system was used to obtain the radial distribution function of Li-O pairs. The result of PDOS was calculated by taking points every 0.5ps for the last 10ps of simulation, and obtained by statistical average.

Spectroscopic Characterization: DEC was purchased from DoDoChem and $LiClO_4$ was purchased from Sigma-Aldrich. The electrolytes were prepared in an argon-filled glovebox by adding $LiClO_4$ into DEC with different molar ratio of salt to solvent in the vials and stirring until homogeneous solutions were obtained. FT-IR measurements were conducted on Thermo Nicolet IR iS50 spectrometer. The spectra were obtained in ATR mode with a resolution of 8cm^{-1} and 32 total scans.

Chemical stability and electrochemical experiments: The chemical stability experiment of electrolytes can be visually observed by immersing Li pieces in $LiClO_4$/DEC electrolytes with various MRs in room temperature. The interfacial compatibility experiments of electrolyte with graphite (Gr) in different MR electrolytes were measured by using the CR2032 coin half cell with above working electrodes, Li foil as counter electrode, polypropylene microporous membrane (Celgard 2400) as the separator and different MR $LiClO_4$/DEC or traditional EC-based (1 M $LiPF_6$ EC-EMC) as electrolyte. The graphite working electrode is composed of 85 % graphite, 6 % Super P, 4.5 % sodium carboxymethyl cellulose (CMC-Na, dissolved in water) and 4.5 % styrene butadiene rubber (SBR, mixed with water). The mixed slurry was casted on a Cu foil and then dried at 100 °C under vacuum overnight. All the coin cells were assembled in Argon-filled glove box with H_2O and O_2 content less than 0.1 ppm. The charge-discharge tests were conducted by Neware battery cycler (CT-4008T-5V10mA-164, shenzhen, China) in a voltage range of 0.01-1.5 V at room temperature.

Results and Discussion

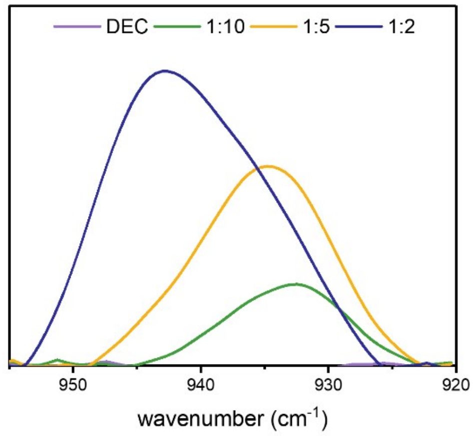

Fig. S1 FTIR spectra of ClO_4^- in $LiClO_4$/DEC solutions.

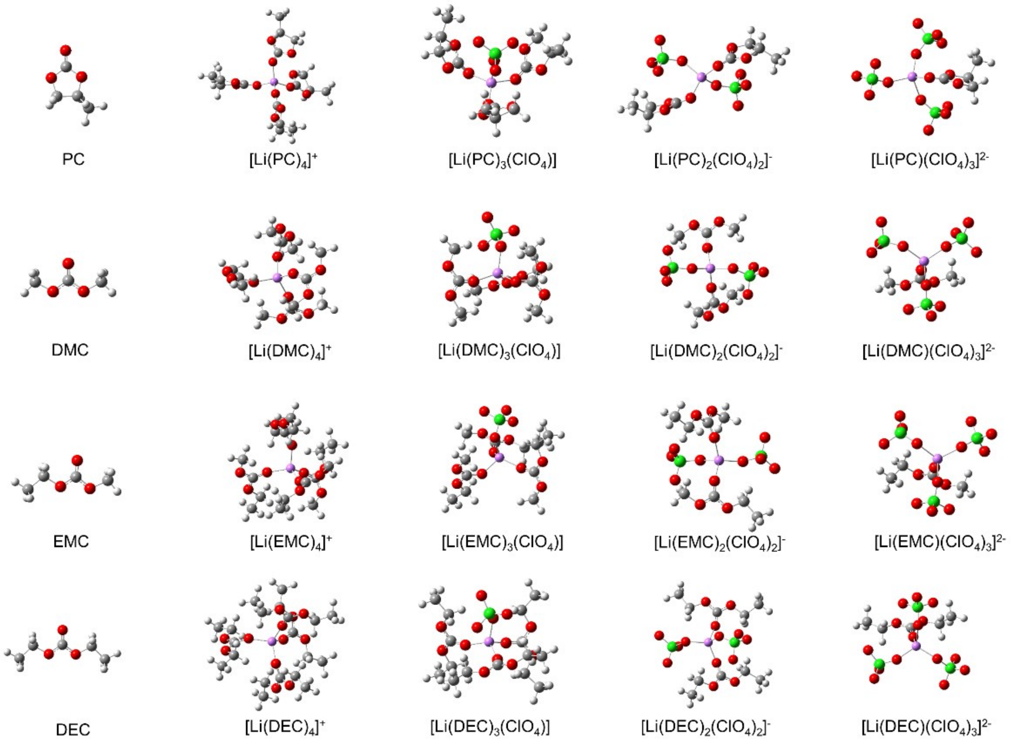

Fig. S2 The optimized geometrical structures of solvent and ion-solvent-coordinated structures of DFT calculations. Purple, Li; green, Cl; red, O; white, H; silver, C.

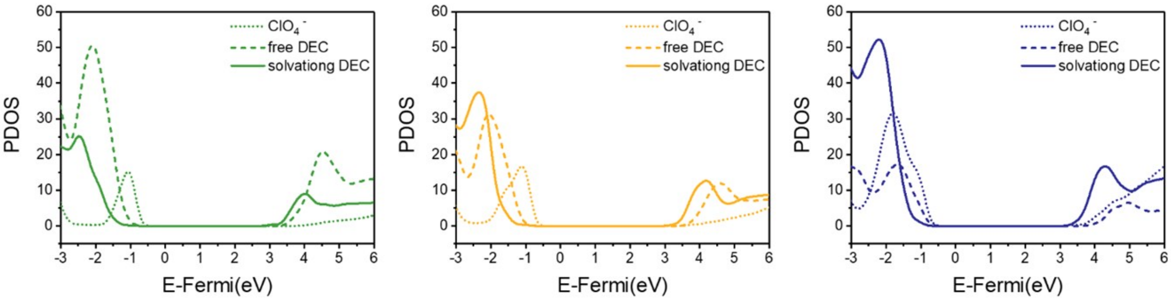

Fig. S3 Simulation of projected density of states for (a) 1:10-LiClO$_4$/DEC, (b) 1:5-LiClO$_4$/DEC and (c) 1:2-LiClO$_4$/DEC electrolytes from density functional theory molecular dynamics (DFT-MD).

Table S1. Properties of four simulated solution systems.

molar ratio $LiClO_4$: DEC	density [g/cm^3]	unit cell size [Å x Å x Å]	molecules in unit cell $LiClO_4$: DEC
1:10	1.00	16.1x16.1x16.1	2:20
1:5	1.03	15.0x15.0x15.0	3:15
1:2	1.06	15.1x15.1x15.1	8:16

Table S2. Calculated Thermodynamic Values for Selected Solvation Reactions at 298.15 K.

reaction	ΔH°(kJ/mol)	ΔS° (J/mol·K)	ΔG°(kJ/mol)
$Li^+ + 4PC \rightarrow Li(PC)_4^+$	-522.9	-444.0	-390.5
$Li^+ + 3PC + ClO_4^- \rightarrow Li(PC)_3(ClO_4)$	-794.6	-518.0	-640.2
$Li^+ + 2PC + 2ClO_4^- \rightarrow Li(PC)_2(ClO_4)_2^-$	-822.9	-503.5	-672.8
$Li^+ + PC + 3ClO_4^- \rightarrow Li(PC)(ClO_4)_3^{2-}$	-627.7	-453.1	-492.7
$Li^+ + 4DMC \rightarrow Li(DMC)_4^+$	-435.6	-460.9	-298.2
$Li^+ + 3DMC + ClO_4^- \rightarrow Li(DMC)_3(ClO_4)$	-766.0	-500.6	-616.8
$Li^+ + 2DMC + 2ClO_4^- \rightarrow Li(DMC)_2(ClO_4)_2^-$	-843.0	-485.7	-698.2
$Li^+ + DMC + 3ClO_4^- \rightarrow Li(DMC)(ClO_4)_3^{2-}$	-656.1	-449.8	-522.0
$Li^+ + 4EMC \rightarrow Li(EMC)_4^+$	-448.9	-490.5	-302.6
$Li^+ + 3EMC + ClO_4^- \rightarrow Li(EMC)_3(ClO_4)$	-769.6	-518.8	-614.9
$Li^+ + 2EMC + 2ClO_4^- \rightarrow Li(EMC)_2(ClO_4)_2^-$	-840.4	-496.4	-692.4
$Li^+ + EMC + 3ClO_4^- \rightarrow Li(EMC)(ClO_4)_3^{2-}$	-655.1	-448.1	-521.5
$Li^+ + 4DEC \rightarrow Li(DEC)_4^+$	-460.5	-451.1	-326.0
$Li^+ + 3DEC + ClO_4^- \rightarrow Li(DEC)_3(ClO_4)$	-772.5	-500.9	-623.1
$Li^+ + 2DEC + 2ClO_4^- \rightarrow Li(DEC)_2(ClO_4)_2^-$	-841.8	-486.7	-696.7
$Li^+ + DEC + 3ClO_4^- \rightarrow Li(DEC)(ClO_4)_3^{2-}$	-656.6	-450.2	-522.4

References

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Journal*, 2016.
2. P. C. Hariharan and J. A. Pople, *Theoretica chimica acta*, 1973, **28**, 213-222.
3. T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580-592.
4. G. Kresse and J. Furthmüller, *Physical Review B*, 1996, **54**, 11169-11186.
5. G. Kresse and D. Joubert, *Physical Review B*, 1999, **59**, 1758-1775.
6. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
7. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
8. S. Nosé, *Mol. Phys.*, 1984, **52**, 255-268.