Supporting Information

Enhancing high-temperature storage performance for the commercial lithium-ion battery via an effective additive strategy

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Table S1 Formulation of STD and after addition to STD

Main solvents (100%)				Lithium salt	Additives (Quality ratio)
Ethylene carbonate (EC)	Propylene carbonate (PC)	Propyl phenylacetate (PP)	Ethyl propionate (EP)	$LiPF_6$	MMDS
30%	10%	50%	10%	1.2mol/L	0%
30%	10%	50%	10%	1.2mol/L	0.5%
30%	10%	50%	10%	1.2mol/L	1%
30%	10%	50%	10%	1.2mol/L	1.5%

Table S2 Electrical performance data from different mass ratios of MMDS which are added to the STD after storage under 100%SOC

ratio (%)	Voltage (V)	Initial capacity (mAh)	Storage capacity (mAh)	Storage time (month)	Voltage (V)	Retained capacity (mAh)	Recovered capacity (mAh)	Capacity retention (%)	Capacity recovery (%)
STD	4.187	61.9	61.9	1	4.137	54.2	59.6	87.56	96.28
0.5	4.185	67.4	67.4		4.126	59.5	64.4	88.28	95.55
1.0	4.185	66.7	66.7		4.126	59.4	64.5	89.06	96.70
1.5	4.185	67.5	67.5		4.185	59.4	64.3	88.00	95.26
STD	4.19	62.3	62.3	2	4.114	52.5	58.1	84.27	93.26
0.5	4.185	67.4	67.4		4.108	56.9	63.2	84.42	93.77
1.0	4.185	67.2	67.2		4.108	56.7	63.1	84.78	93.90
1.5	4.185	67.3	67.3		4.108	56.6	62.9	84.10	93.46
STD	4.188	60.5	60.5	3	4.095	47.2	54.8	78.02	90.58
0.5	4.185	67.2	67.2		4.09	54.1	62.0	80.51	92.26
1.0	4.185	67.4	67.4		4.093	54.7	62.4	81.16	92.58
1.5	4.185	66.7	66.7		4.093	53.8	61.2	80.66	91.75

Table S3 Electrical performance data from different mass ratios of MMDS which are added to the STD after storage under 30%SOC

Ratio (%)	Voltage (V)	Initial capacity (mAh)	Storage capacity (mAh)	Storage time (month)	Voltage (V)	Retained capacity (mAh)	Recovered capacity (mAh)	Capacity retention (%)	Capacity recovery (%)
STD	4.187	61.9	61.9	1 month	4.137	54.2	59.6	87.56	96.28
0.5	4.185	67.4	67.4		4.126	59.5	64.4	88.28	95.55
1.0	4.185	66.7	66.7		4.126	59.4	64.5	89.06	96.70
1.5	4.185	67.5	67.5		4.185	59.4	64.3	88.00	95.26
STD	4.19	62.3	62.3	2 months	4.114	52.5	58.1	84.27	93.26
0.5	4.185	67.4	67.4		4.108	56.9	63.2	84.42	93.77
1.0	4.185	67.2	67.2		4.108	56.7	63.1	84.38	93.90
1.5	4.185	67.3	67.3		4.108	56.6	62.9	84.10	93.46
STD	4.188	60.5	60.5	3 months	4.0948	47.2	54.8	78.02	90.58
0.5	4.185	67.2	67.2		4.09	54.1	62.0	80.51	92.26
1.0	4.185	67.4	67.4		4.093	54.7	62.4	81.16	92.58
1.5	4.185	66.7	66.7		4.0927	53.8	61.2	80.66	91.75

Table S4 Battery performance with the STD and 1% MMDS after 900 cycles.

Electrolyte	Initial capacity	Capacity value after cycling	Coulombic efficiency (%)	Capacity retention (%)
STD	71.6	65.0	99.98	90.78
1% MMDS	71.6	66.4	99.99	92.74

Table S5 Electrical performance data of the batteries with and without MMDS additive

Initial capacity (mAh)	Storage capacity (mAh)	SOC	Electrolyte	Storage time (month)	Retained capacity/mAh	Recovered capacity/mAh	Capacity retention change ratio	Capacity recovery change ratio
61.9	61.9	100%	STD	1	54.2	59.6	87.56%	96.28%
62.3	62.3			2	52.5	58.1	84.27%	93.26%
60.5	60.5			3	47.2	54.2	78.02%	89.59%
66.7	66.7		1%MMDS	1	59.4	64.5	89.06%	96.70%
67.2	67.2			2	57.9	63.3	86.16%	94.20%
67.4	67.4			3	54.7	62.4	81.16%	92.58%
62.1	18.6	30%	STD	1	15	60	94.20%	96.62%
65.4	19.6			2	12.3	61.7	88.84%	94.34%
62.8	18.8			3	8.7	56.8	83.92%	90.45%
67.4	20.1		1%MMDS	1	16.6	65.7	94.81%	97.48%
67.4	20.1			2	14.1	64.5	91.10%	95.70%
66.9	20.1			3	11	62.5	86.40%	93.42%

Table S6. Data of EIS of 30%SOC and 100%SOC stored for 3 months of the batteries

Samples	$R_s(\Omega)$	$R_f(\Omega)$	$R_{ct}(\Omega)$
STD-30%SOC	0.38	0.572	1.19
STD-100%SOC	0.483	0.528	1.13
1% MMDS-30% SOC	0.348	0.622	1.81
1% MMDS -100% SOC	0.436	0.607	1.72

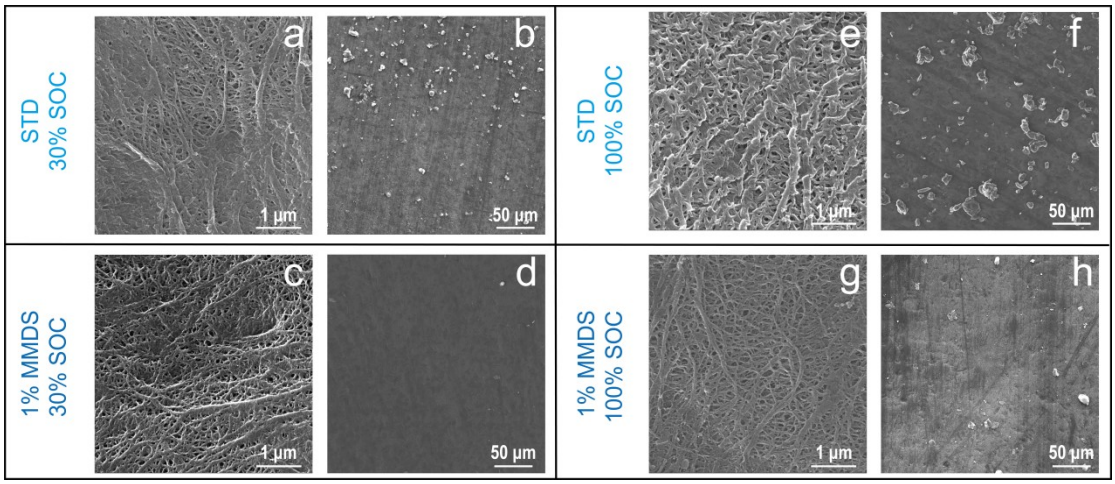

Figure S1 (a,b) Scanning electron microscopy of separator in 1µm and 50 µm under 30%SOC stored for 3 months in STD. **(c,d)** SEM of separator in 1µm and 50 µm under 30%SOC stored for 3 months after addition to STD. **(e,f)** Under 100%SOC stored for 3 months in STD. **(g,h)** Under 100%SOC stored for 3 months after addition to STD.

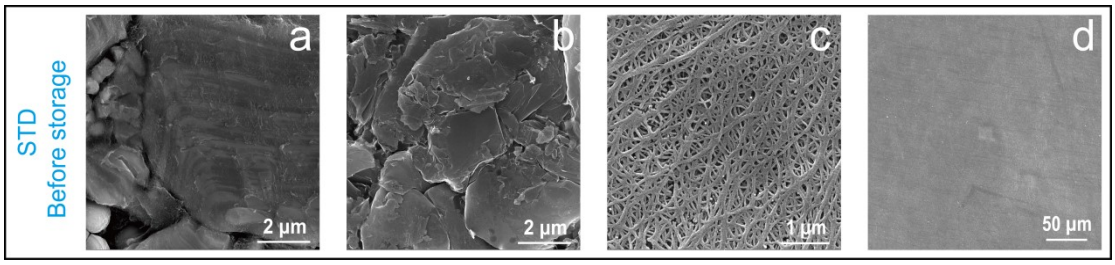

Figure S2 a,b,c,d: Cathode, anode, separator in 1µm and 50 µm in STD before storage.

Table S7 The errors of the Atomic Absorption Spectrometer method in the quantitative determination of lithium content

Number of samples	Sample composition	Purity quotient	Lithium content in samples	Measured Li content by atomic absorption spectrometer method	Test error of atomic absorption spectrometer method
Number 1				18.66%	0.67%
	Li_2CO_3	99.99%	18.7855%		
Number 2				18.87%	0.45%

Table S8 Date of dead lithium and cobalt in the anode stored for 3 months at 45 ℃ in STD and after addition to STD

SOC	Storage time	Electrolyte	Weight of anode piece /mg	Weight of copper foil/ mg	Net weight of anode/ mg	Constant volume/ mL	Li mass in the anode/ mg	Co mass in the anode/ mg	The proportion of dead Li in the anode	The proportion of Co in the anode
30 %	3 months	STD	52.7	16.44	36.26	100mL	0.448	0.018	1.450 %	0.066%
100 %			52.2		35.76		0.454	0.02	1.490 %	0.074%
30 %		After addition	45.6		29.16		0.267	0.01	1.074 %	0.045%
100 %			55		38.56		0.358	0.014	1.089 %	0.048%

The detail theoretical calculation process is as follows:

The geometry optimization, frequencies and density functional theory (DFT) chemical description for the molecular structures of all title compounds were performed using Gaussian09 program[1] package with M062X exchange-correlation functional and 6-311+G** basis set[2,3] for all atoms. In this work, temperature (45℃) were considered to calculate the thermodynamic data. Harmonic vibration frequency calculations were performed for all stationary points to confirm them as a local minima (zero imaginary frequencies). Orbital composition analysis employed by Multiwfn program[4,5]. The thermochemical corrections for the Gibbs free energies were derived at 298.15 K and 318.15 K (45℃) using Shermo_2.4[6]. The interaction energy of species (EC, EP, PP, PC, and MMDS) and $LiPF_6$ is given as:

$$\Delta Eint = Ecomplex - Especies - ELiPF_6$$

Where the Ecomplex, Especies, $ELiPF_6$ represents for the energy of species-$LiPF_6$ complexes, EC, PC and MMDS etc, and $LiPF_6$.

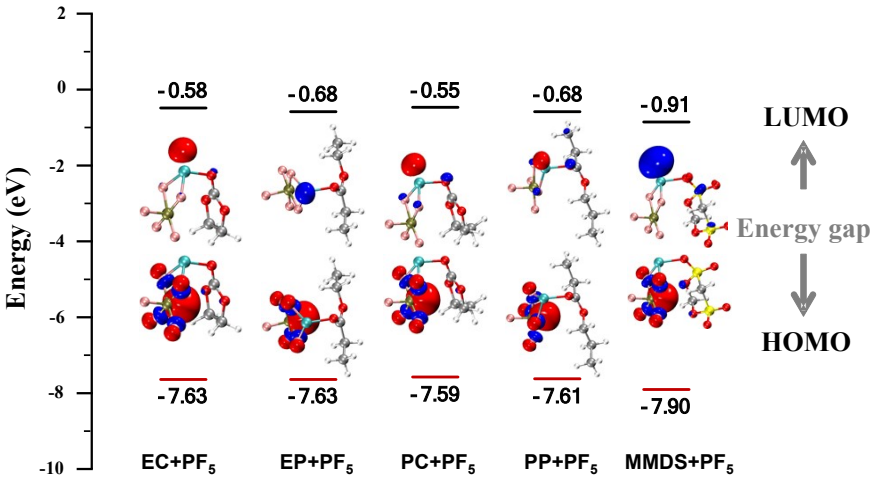

Fig. S3 LUMO and HOMO energy level analysis of EC+PF_5, EP+PF_5, PC+PF_5, PP+PF_5, and MMDS+PF_5.

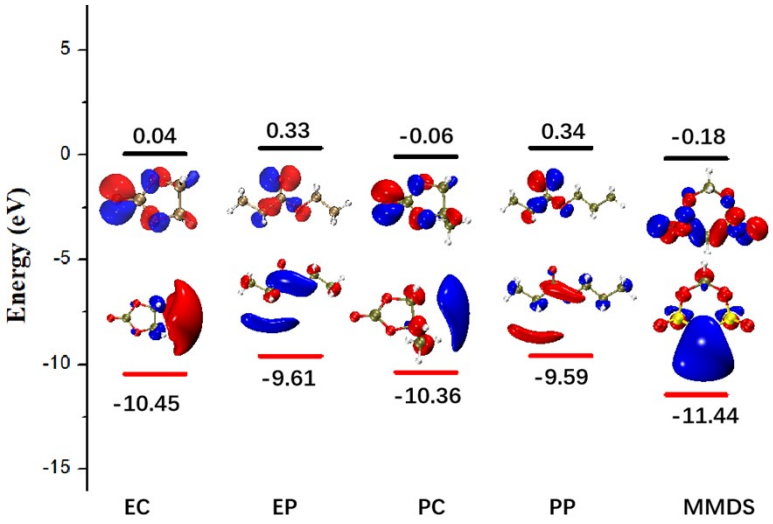

Fig. S4 LUMO and HOMO energy level analysis of EC, EP, PC, PP, and MMDS.

References:

[1] Gaussian 09, Revision A.02; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. Gaussian, Inc.: Wallingford, CT, 2009.

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