Supporting Information

A phosphite derivative with stronger HF elimination ability as an additive for Li-rich based lithium-ion batteries at elevated temperatures

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Supplementary Figures

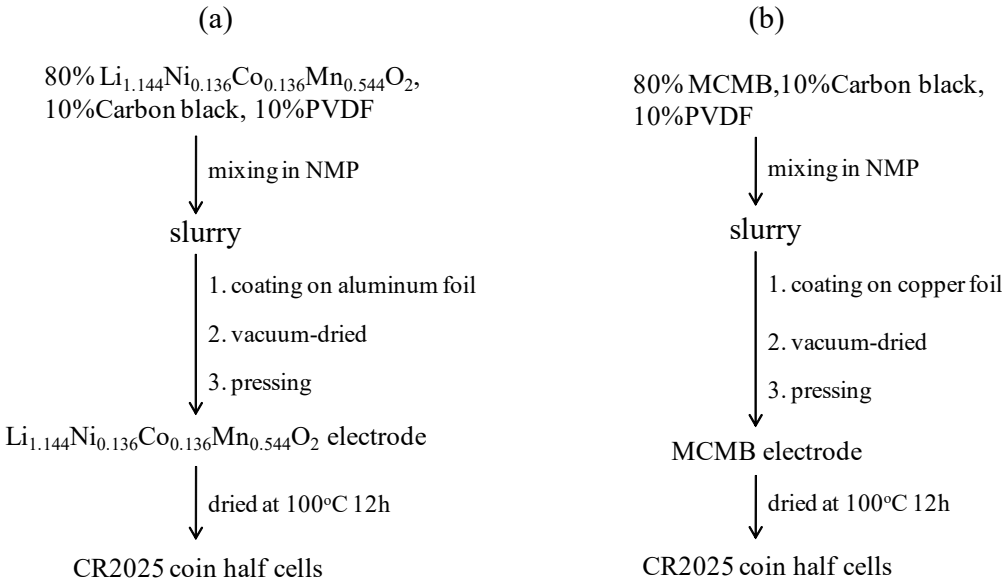

Fig. S1 The preparation process of (a) $Li_{1.144}Ni_{0.136}Co_{0.136}Mn_{0.544}O_2$ electrodes and (b) MCMB electrodes.

Table S1 Cartesian coordinates of the optimized structures of DMC and DMC^+.

DMC	X	Y	Z	DMC^+	X	Y	Z
C	-0.035873	0.533452	0.000042	C	-0.022381	0.439789	0.00006
O	-0.666624	1.57496	0.000123	O	0.625994	1.57121	-0.00007
O	1.300946	0.526488	0.000024	O	-1.291926	0.509705	0.000088
O	-0.565945	-0.69536	-0.000036	O	0.625578	-0.661547	0.000051
C	2.024512	-0.729259	-0.00009	C	-2.106963	-0.73716	-0.000067
H	1.786073	-1.304994	-0.89659	H	-1.875687	-1.295358	0.905257
H	3.075746	-0.442996	-0.000095	H	-3.126338	-0.362651	-0.000364
H	1.786119	-1.305128	0.896336	H	-1.875215	-1.295494	-0.905185
C	-2.011279	-0.768601	-0.000028	C	2.117107	-0.72358	-0.000016
H	-2.239916	-1.833535	-0.000195	H	2.31701	-1.790656	-0.000009
H	-2.409581	-0.287944	0.89573	H	2.478192	-0.242575	-0.907418
H	-2.409611	-0.287655	-0.895617	H	2.478293	-0.242505	0.907306

Table S2 Cartesian coordinates of the optimized structures of EC and EC^+.

EC	X	Y	Z	EC^+	X	Y	Z
C	-0.842138	0	0.000001	C	0.760756	0	-0.000002
O	-0.080916	1.109178	0.097178	O	0.117185	-1.105388	0.092558
O	-2.050826	0	-0.000002	O	2.056515	0	0.000004
O	-0.080915	-1.109178	-0.097174	O	0.117184	1.105387	-0.092567
C	1.312916	0.75853	-0.10785	C	-1.331571	-0.75841	-0.104509
H	1.912615	1.306648	0.617901	H	-1.877008	-1.31909	0.651272
H	1.586931	1.047524	-1.125346	H	-1.579369	-1.077699	-1.115377
C	1.312916	-0.758531	0.107847	C	-1.33157	0.75841	0.104514
H	1.586936	-1.04752	1.125344	H	-1.579357	1.0777	1.115384
H	1.912613	-1.30665	-0.617903	H	-1.87702	1.319093	-0.651259

Table S3 Cartesian coordinates of the optimized structures of EMC and EMC^+.

EMC	X	Y	Z	EMC^+	X	Y	Z
C	0.599061	0.547538	0.000047	C	0.537675	0.450062	0.000004
O	1.294236	1.548103	0.000132	O	1.235017	1.552428	-0.000006
O	-0.733969	0.621335	0.000024	O	-0.724987	0.581747	0.000004
O	1.056833	-0.711347	-0.000032	O	1.136361	-0.68094	0.000014
C	-1.549489	-0.592044	-0.000073	C	-1.627737	-0.645392	-0.000018
H	-1.300353	-1.175895	0.889849	H	-1.364317	-1.202522	0.89876
H	-1.300329	-1.17577	-0.89007	H	-1.364335	-1.202478	-0.898829
C	2.495025	-0.868029	-0.000008	C	2.622953	-0.792992	-0.000002
H	2.66177	-1.944458	-0.000027	H	2.789432	-1.865823	-0.000098
H	2.921232	-0.411302	-0.895545	H	3.001637	-0.324794	-0.907166
H	2.9212	-0.411337	0.895562	H	3.001633	-0.324955	0.907247
C	-2.999994	-0.152435	-0.000062	C	-3.038772	-0.12179	0.000009
H	-3.23187	0.441395	-0.8905	H	-3.245203	0.47232	-0.894438
H	-3.644168	-1.038796	-0.000141	H	-3.709497	-0.989226	-0.000011
H	-3.231899	0.441258	0.89046	H	-3.245187	0.472268	0.894494

Table S4 Cartesian coordinates of the optimized structures of TMSPi and $TMSPi^{+}$.

TMSPi	X	Y	Z	$TMSPi^{+}$	X	Y	Z
P	-0.017301	0.046272	0.384759	P	-0.010718	0.028474	-0.48984
O	0.006057	-1.410582	-0.383629	O	0.655012	-1.291617	0.020697
O	1.185385	0.797071	-0.458668	O	-1.467748	0.133895	0.069155
O	-1.303561	0.717202	-0.393073	O	0.829786	1.258674	-0.01613
Si	0.694076	-2.930095	-0.03922	Si	0.421029	-3.042789	0.044233
Si	2.272791	2.042257	-0.040764	Si	-2.902583	1.163353	0.041823
Si	-2.962354	0.877542	-0.042219	Si	2.485412	1.871298	0.046771
C	0.715143	-3.211302	1.824483	C	-0.974224	-3.431513	-1.143125
H	1.097576	-4.215492	2.049858	H	-1.13392	-4.51681	-1.177734
H	1.358754	-2.48703	2.338585	H	-1.91611	-2.966405	-0.830414
H	-0.291851	-3.132653	2.25243	H	-0.740522	-3.09724	-2.161013
C	-0.413084	-4.178207	-0.906405	C	2.077492	-3.713498	-0.506325
H	-0.030197	-5.197565	-0.767651	H	2.061859	-4.81074	-0.496133
H	-1.435261	-4.145124	-0.509793	H	2.318002	-3.388608	-1.525273
H	-0.461264	-3.981488	-1.98458	H	2.881072	-3.381708	0.161186
C	2.440979	-2.970647	-0.741508	C	0.012238	-3.419513	1.831383
H	2.43839	-2.780282	-1.821894	H	0.813676	-3.085244	2.500287
H	3.081153	-2.217102	-0.266526	H	-0.920818	-2.933224	2.138266
H	2.899645	-3.95407	-0.574448	H	-0.10986	-4.501948	1.965411
C	-3.190487	1.25292	1.790679	C	3.471487	0.954486	-1.2544
H	-4.252871	1.417421	2.013804	H	4.500942	1.33527	-1.266581
H	-2.842612	0.425626	2.421329	H	3.517127	-0.120959	-1.04827
H	-2.642564	2.156619	2.08505	H	3.050278	1.10112	-2.256107
C	-3.543593	2.310703	-1.111369	C	2.276251	3.692721	-0.320798
H	-4.618063	2.487613	-0.973199	H	3.248755	4.199905	-0.282082
H	-3.013649	3.235847	-0.853275	H	1.854018	3.848961	-1.32022
H	-3.370608	2.106232	-2.175181	H	1.616689	4.171451	0.412175
C	-3.838597	-0.72252	-0.509517	C	3.045385	1.513199	1.796794
H	-3.676677	-0.969598	-1.565978	H	2.393656	2.001783	2.530332
H	-3.480547	-1.565987	0.093566	H	3.05046	0.436574	2.001092
H	-4.920531	-0.629804	-0.347577	H	4.065362	1.890305	1.94617
C	3.416805	1.425792	1.323454	C	-3.276593	1.491586	-1.762872
H	4.162508	2.191027	1.575984	H	-4.198259	2.080744	-1.850472
H	2.859774	1.188465	2.238347	H	-2.47191	2.058516	-2.24617
H	3.955391	0.522636	1.010595	H	-3.422008	0.555917	-2.315062
C	3.223255	2.395813	-1.623349	C	-4.179106	0.090626	0.888482
H	3.963969	3.189495	-1.461192	H	-5.138694	0.620994	0.937558

H	3.756957	1.503157	-1.972125	H	-4.337494	-0.845046	0.340075
H	2.548778	2.722395	-2.424375	H	-3.876228	-0.15493	1.912701
C	1.304265	3.553009	0.533249	C	-2.455935	2.704263	1.005817
H	0.603383	3.893667	-0.238721	H	-2.157835	2.458807	2.031691
H	0.728944	3.34001	1.44294	H	-1.63583	3.253531	0.52922
H	1.986641	4.383159	0.758134	H	-3.324012	3.374049	1.057877

Table S5 Cartesian coordinates of the optimized structures of TMSPE and $TMSPE^{+}$.

TMSPE	X	Y	Z	$TMSPE^{+}$	X	Y	Z
P	-0.036941	0.593924	-1.068094	P	0.007389	0.532783	-0.509112
O	-0.886498	-0.488089	-0.173236	O	-1.017703	-0.475047	0.088531
O	-0.023445	1.821205	0.075525	O	-0.465078	1.99106	-0.068027
O	1.469189	-0.028234	-0.938997	O	1.442018	0.272846	0.042312
Si	-2.545932	-0.776161	0.098847	Si	-2.723227	-0.953842	0.050347
Si	2.452402	-0.938264	0.12243	Si	2.786803	-0.880011	0.070775
C	0.571209	3.081522	-0.303585	C	0.340286	3.214779	-0.284871
H	1.661819	2.998814	-0.213897	H	1.343358	3.025165	0.103019
H	0.334072	3.303896	-1.353493	H	0.384237	3.38988	-1.362195
H	0.037138	4.173683	0.6081	H	-0.35568	4.341014	0.447857
C	0.269103	3.954189	1.656299	C	-0.408132	4.139132	1.522149
H	0.498567	5.1338	0.347816	H	0.218336	5.262181	0.296306
H	-1.049126	4.272815	0.504865	H	-1.367453	4.496945	0.061116
H	-2.686122	-2.633312	0.355801	H	-2.638637	-2.820226	0.097886
C	-3.725904	-2.91755	0.56304	C	-3.652314	-3.239663	0.120763
H	-2.357341	-3.18289	-0.534747	H	-2.128221	-3.21769	-0.786921
H	-2.073029	-2.96305	1.203606	H	-2.108483	-3.17083	0.990834
H	-3.536506	-0.211572	-1.401282	H	-3.439941	-0.271215	-1.538719
C	-3.444652	0.868809	-1.567633	C	-3.413844	0.824536	-1.559196
H	-3.20929	-0.724386	-2.314092	H	-2.903035	-0.649658	-2.416603
H	-4.601199	-0.435502	-1.254404	H	-4.488889	-0.58081	-1.629808
H	-3.062573	0.166928	1.643323	H	-3.450341	-0.188198	1.595097
C	-4.115907	-0.030339	1.881953	C	-4.508658	-0.465169	1.68353
H	-2.459797	-0.132481	2.509584	H	-2.932969	-0.540657	2.494778
H	-2.944154	1.248415	1.506454	H	-3.388631	0.905649	1.565616
H	2.096549	-2.761893	-0.183589	H	2.348312	-2.267094	-1.107191
C	1.057752	-3.010547	0.063378	C	1.449418	-2.805388	-0.78572
H	2.268635	-3.02445	-1.234901	H	2.18838	-1.895375	-2.126196
H	2.751271	-3.393005	0.431571	H	3.174068	-2.989247	-1.142445
H	4.214153	-0.501913	-0.374862	H	4.251079	0.139326	-0.486847
C	4.415443	0.565858	-0.223743	C	4.407897	1.003727	0.168686
H	4.936644	-1.068756	0.226598	H	5.162616	-0.471256	-0.463982
H	4.398411	-0.736137	-1.430642	H	4.113985	0.502095	-1.512164
C	2.128304	-0.470402	1.917555	C	2.864829	-1.410674	1.862869
H	2.807985	-1.027194	2.576398	H	3.702234	-2.104676	2.009744
H	2.296811	0.599757	2.08725	H	3.017896	-0.551352	2.525699
H	1.100535	-0.704274	2.217184	H	1.943963	-1.922491	2.164951

Table S6 Cartesian coordinates of the optimized structures of TEP and TEP^{+}.

TEP	X	Y	Z	TEP^{+}	X	Y	Z
P	0.080101	0.054834	1.182173	P	0.022935	0.005858	0.818416
O	-0.415686	1.122265	-0.004786	O	-0.424701	1.349998	0.092828
O	-0.690031	-1.344717	0.742154	O	-0.93214	-1.213276	0.55641
O	1.643512	-0.1038	0.694955	O	1.455662	-0.356355	0.257941
C	-0.821485	-1.878332	-0.601557	C	-0.885922	-2.160405	-0.606787
H	-0.908128	-1.05132	-1.313632	H	-1.064256	-1.55904	-1.500257
H	0.086766	-2.446462	-0.831365	H	0.118678	-2.583477	-0.628126
C	-2.047013	-2.77468	-0.651795	C	-1.955349	-3.19943	-0.374739
H	-2.956986	-2.205286	-0.432619	H	-2.948159	-2.742608	-0.32272
H	-2.145354	-3.211637	-1.652833	H	-1.941216	-3.900214	-1.21784
H	-1.962573	-3.591801	0.07312	H	-1.766581	-3.762495	0.544312
C	-1.728916	1.717152	0.119262	C	-1.760488	1.993866	0.21453
H	-1.921043	1.967337	1.17124	H	-1.849159	2.349203	1.242557
H	-2.481111	0.985232	-0.19958	H	-2.512449	1.228359	0.014268
C	-1.782179	2.962049	-0.749055	C	-1.797675	3.122196	-0.791221
H	-2.777467	3.417161	-0.683044	H	-2.772251	3.617698	-0.715396
H	-1.041755	3.699463	-0.420261	H	-1.01751	3.860941	-0.584443
H	-1.586971	2.713967	-1.798304	H	-1.679492	2.74661	-1.812054
C	2.163031	-0.106691	-0.663729	C	2.58579	0.593932	0.066444
H	2.01572	-1.10654	-1.085989	H	2.208912	1.425276	-0.531412
H	1.602951	0.616515	-1.26176	H	2.876735	0.945011	1.058276
C	3.639001	0.246487	-0.610269	C	3.692595	-0.169713	-0.623667
H	4.19215	-0.470382	0.006624	H	3.369753	-0.535435	-1.603062
H	4.059275	0.224946	-1.622979	H	4.539109	0.510682	-0.770386
H	3.786009	1.250403	-0.19694	H	4.029594	-1.013986	-0.014744

Table S7 HOMO energies, LUMO energies, and oxidation potential of EC, DMC, EMC, and P-based additives.

Compound	HOMO / au.	LUMO / au.	Oxidation potential / V
EC	-0.3087	-0.00835	7.08
EMC	-0.2954	0.00098	6.79
DMC	-0.2983	0.00008	6.75
TMSP	-0.278	-0.0175	5.99
TMPSi	-0.2327	-0.0137	4.28
TMSPE	-0.2403	-0.01115	4.41
TEP	-0.2555	0.00086	4.73

The molecular structures of EC, EMC, DMC and P-based additives were optimized by means of nonlocal density functional theory (DFT) using the B3LYP function with the 6-311g (d) level basis set (Gaussian 09 package). The frontier molecular orbital energy of each organic molecule was calculated with this program. The bulk solvent effect (dielectric constant = 20.5) was included via polarized continuum models (PCM).

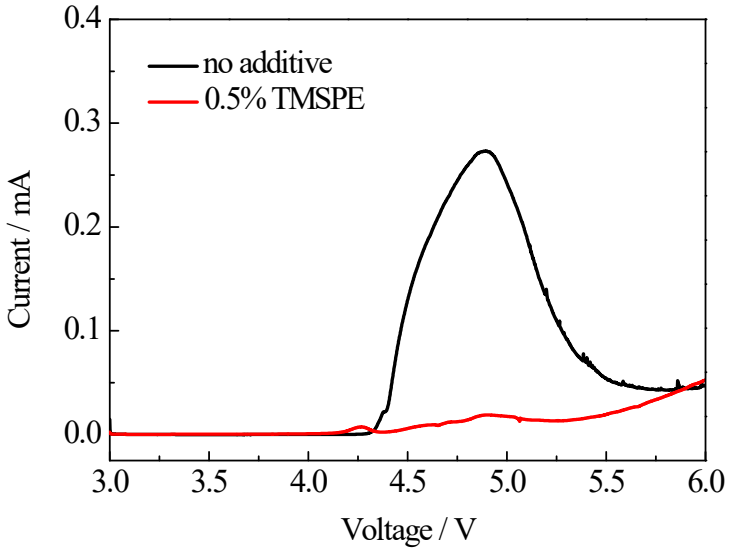

Fig. S2 Linear sweep voltammograms of Pt electrode in 1 mol L^{-1} $LiPF_6$-EC/DMC/EMC (1:1:1, wt.%) with and without TMSPE at 0.1 mV s^{-1} from 3.0 to 6.0V.

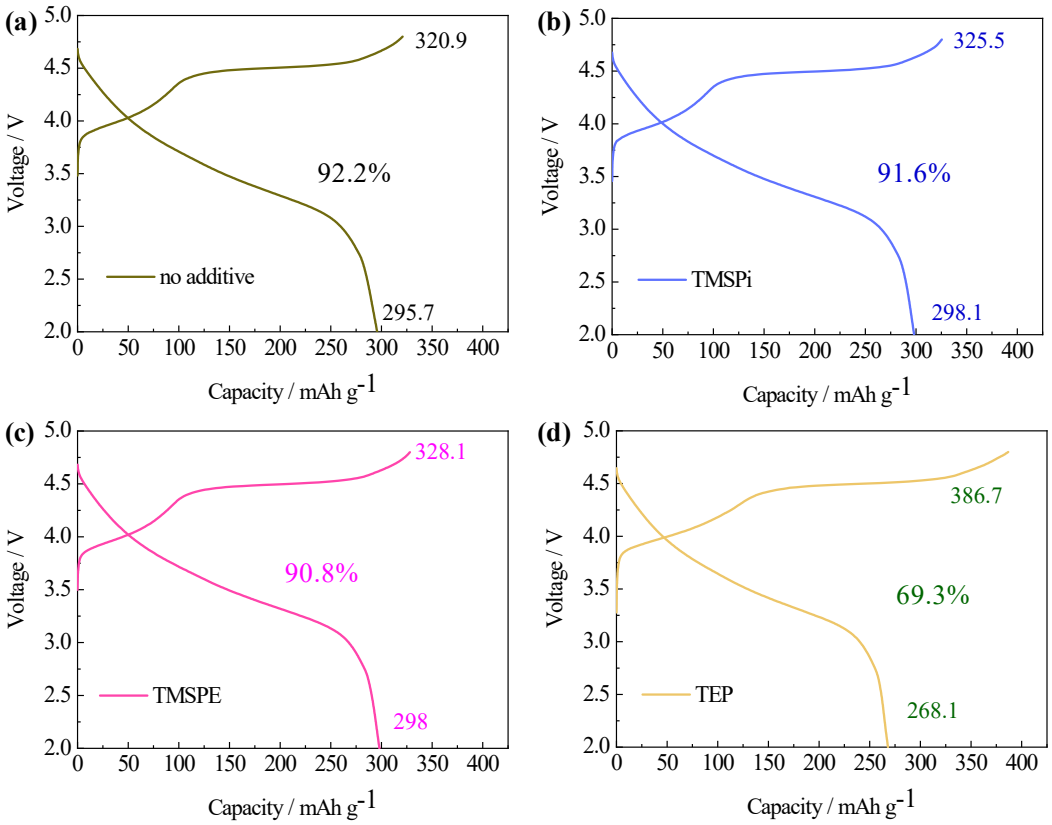

Fig. S3 The initial charge-discharge curve performance of $Li_{1.144}Ni_{0.136}Co_{0.136}Mn_{0.544}O_2$/Li cells with different additive at 45℃.

Table S8 The initial charge and discharge capacities of P-based additives in different concentrations additive.

Material	Concentration / %	Charge capacity / mAh g^{-1}	Discharge capacity / mAh g^{-1}	Efficience / %
TMSP	0.5	322.2	301.3	93.5
	1.0	332.3	293.7	88.4
	2.0	332.9	277.1	83.3
TMSPi	0.5	325.5	298.1	91.6
	1.0	334.5	295	88.2
	2.0	349.1	268.7	77
TMSPE	0.5	328.1	298	90.8
	1.0	366.9	310.5	84.6
	2.0	379.5	290.8	76.6
	3.0	382.4	295.7	77.3
TEP	0.5	331.2	288.0	87.0
	1.0	341.2	276.3	81.0
	3.0	386.7	268.1	69.3

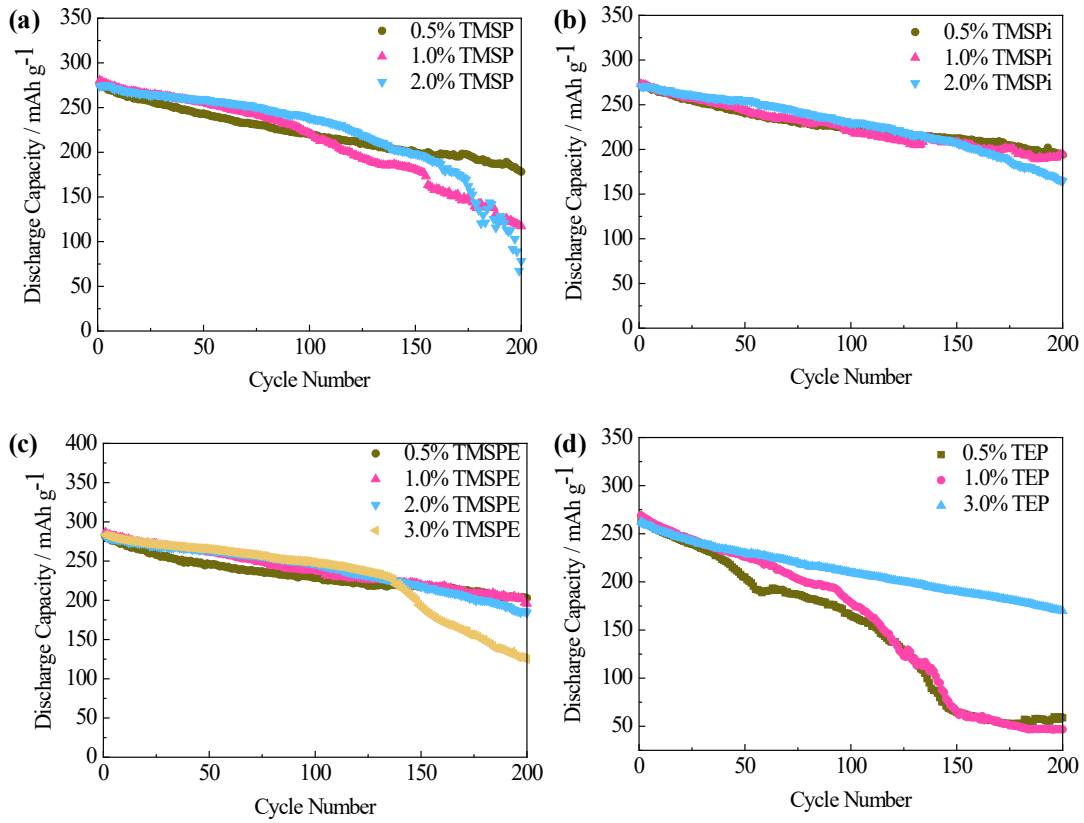

Fig. S4 Cycling performance of $Li_{1.144}Ni_{0.136}Co_{0.136}Mn_{0.544}O_2$/Li cells with electrolytes in the different concentration of additive. The current is 0.2 C.

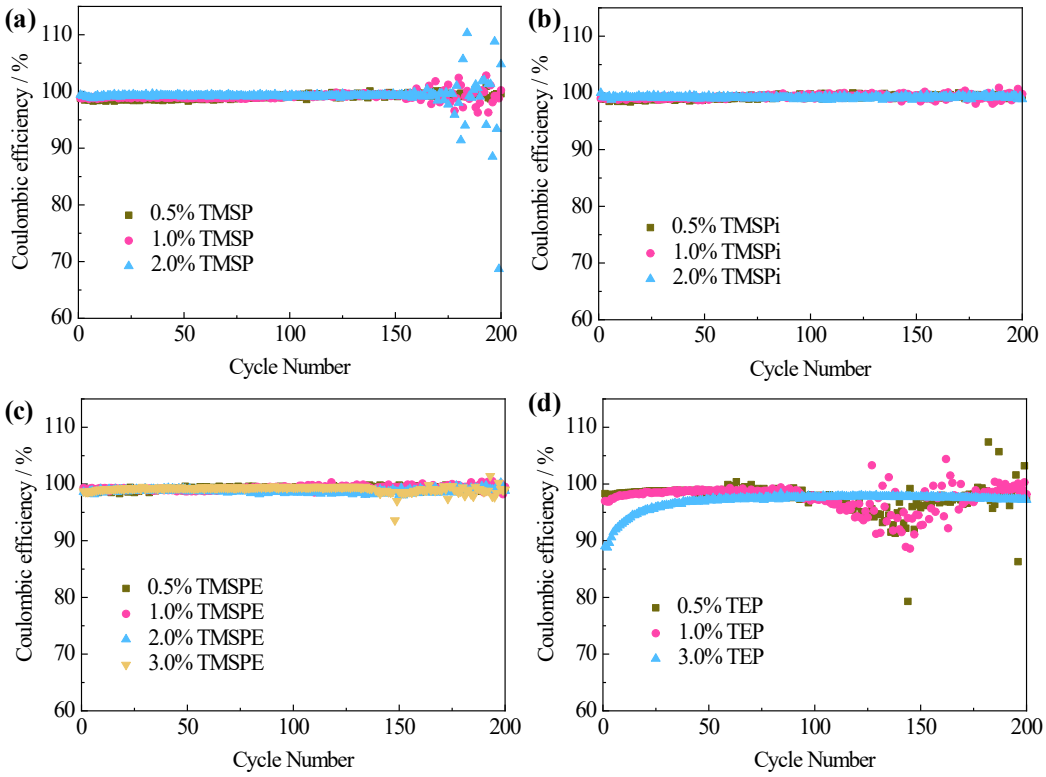

Fig. S5 Coulombic efficiency of $Li_{1.144}Ni_{0.136}Co_{0.136}Mn_{0.544}O_2$/Li cells with electrolytes in the different additive.

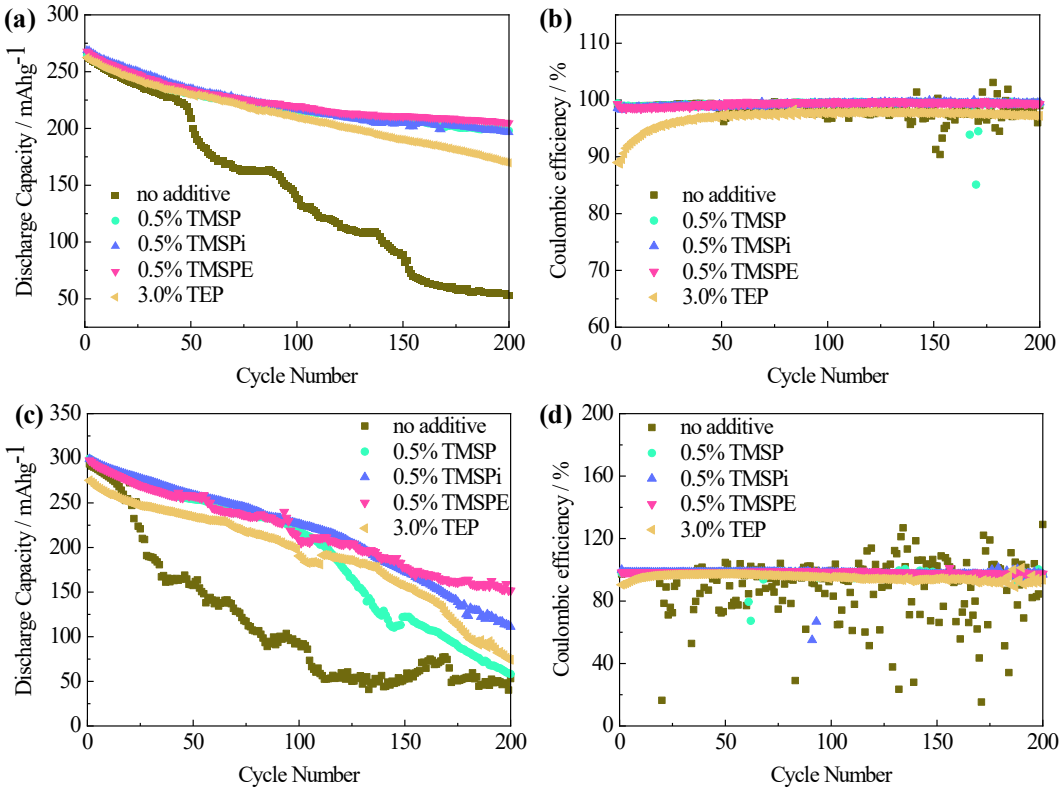

Fig. S6 Cycling performance (a, c) and coulombic efficiency (b, d) of $Li_{1.144}Ni_{0.136}Co_{0.136}Mn_{0.544}O_2$/Li cells with electrolytes in the different additive at 25 °C (top) and 45 °C (bottom).

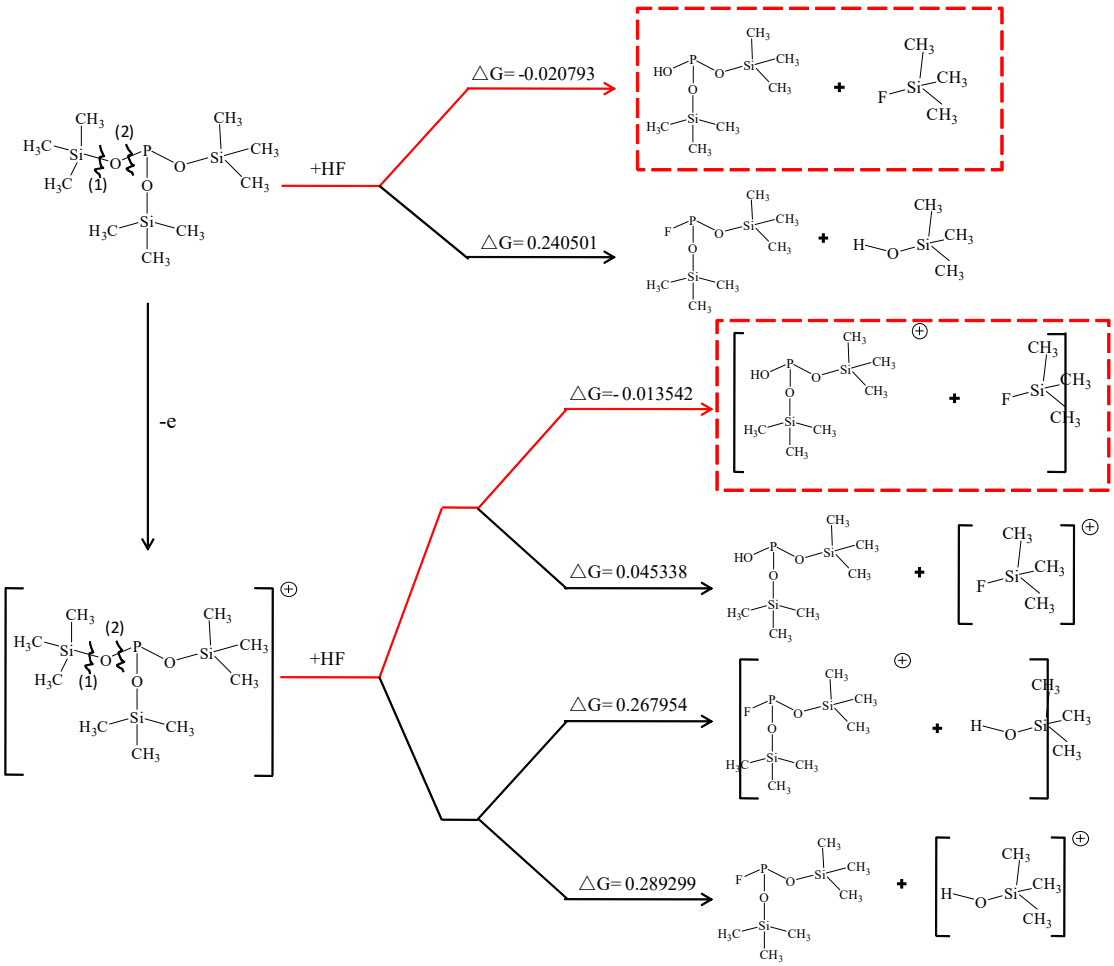

Fig. S7 Reaction energies (△G in au.) of TMSPi and $TMSPi^{+}$ with a HF molecule.

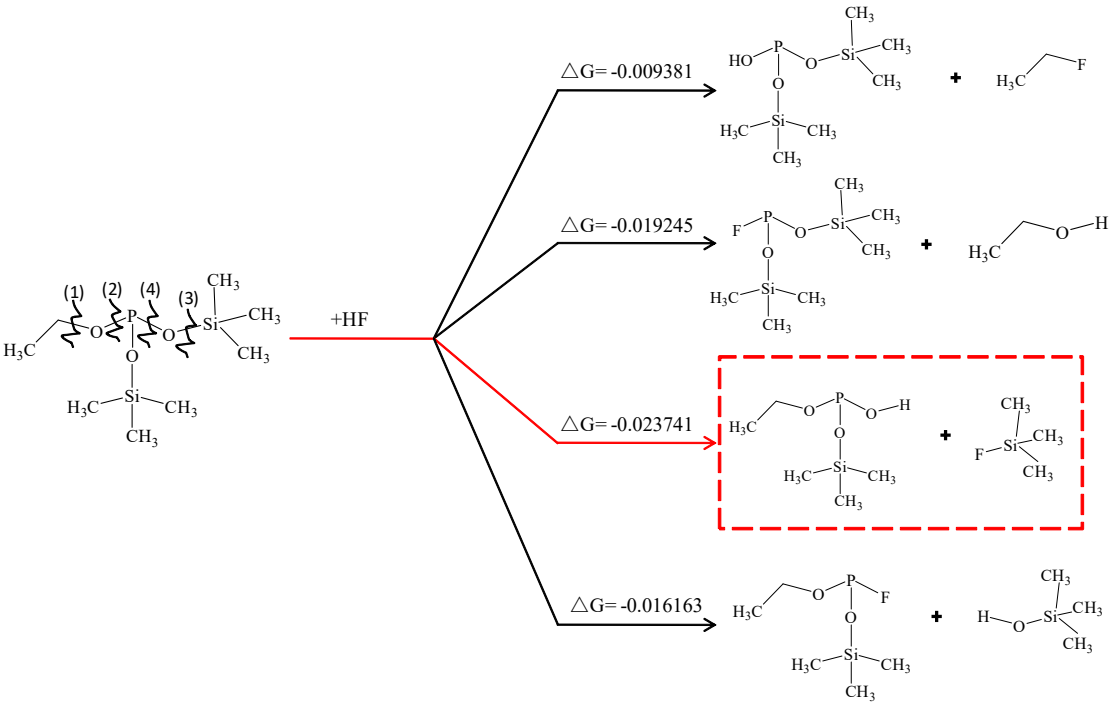

Fig. S8 Reaction energies (△G in au.) of TMSPE with a HF molecule.

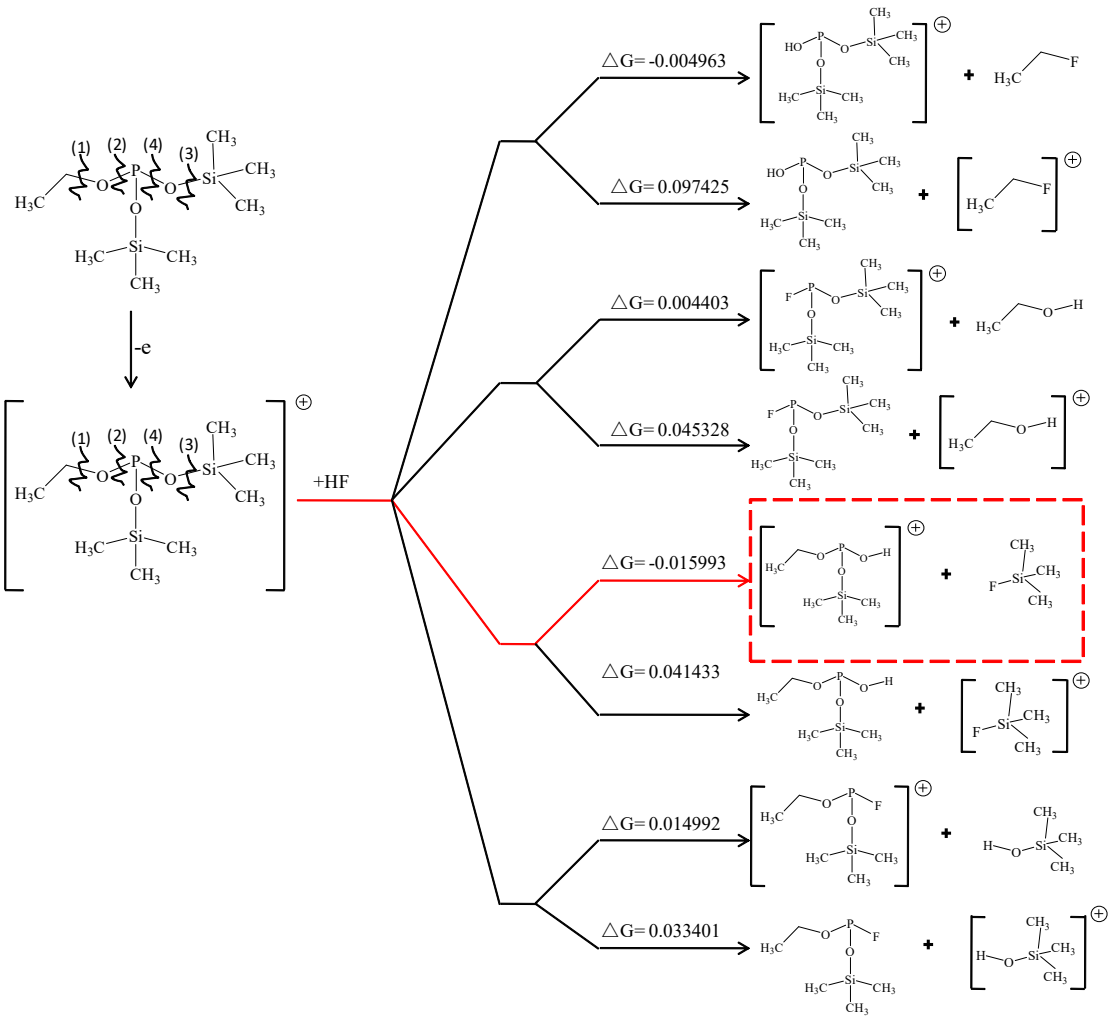

Fig. S9 Reaction energies (△G in au.) of $TMSPE^{+}$ with a HF molecule.

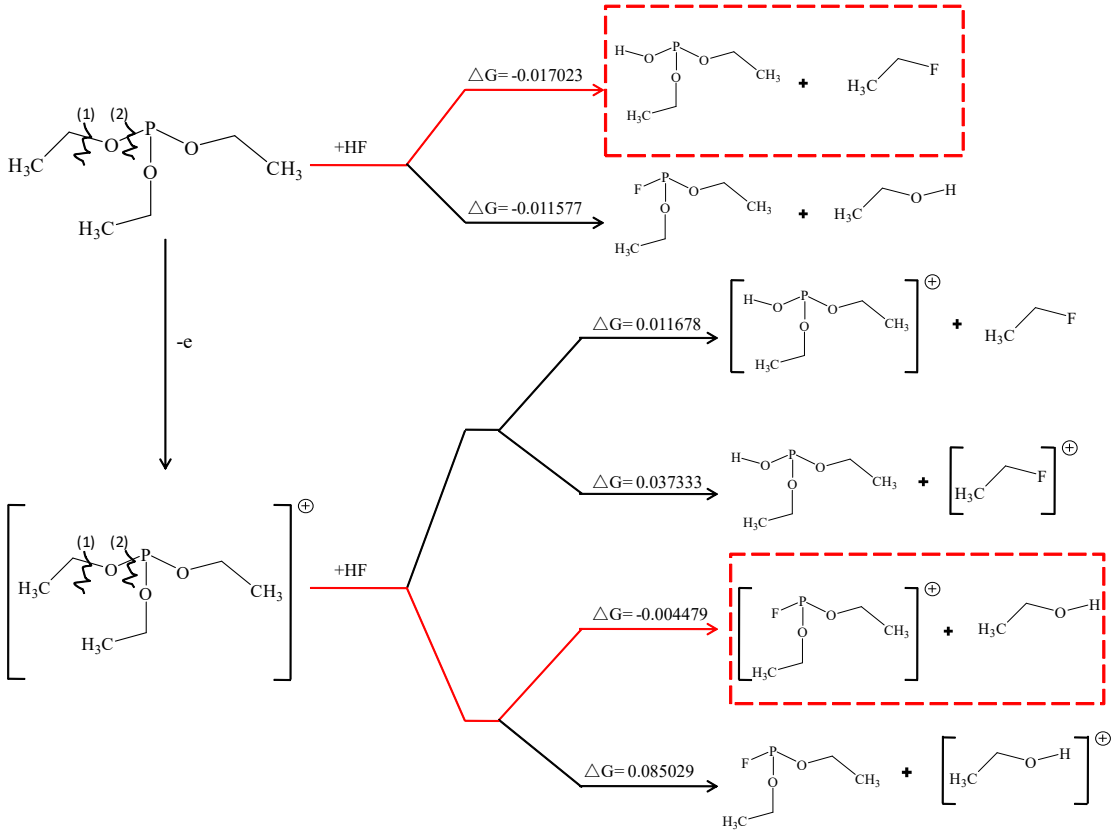

Fig. S10 Reaction energies (△G in au.) of TEP and TEP^{+} with a HF molecule.

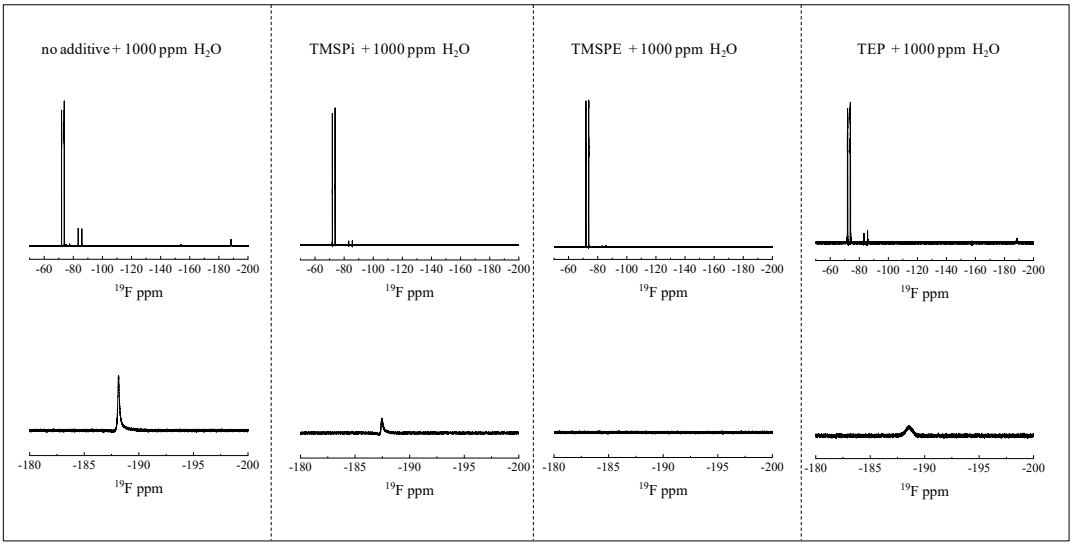

Fig. S11 ^{19}F NMR spectra of the electrolytes with and without adding different additive after storage under 25 °C for 24 h.

Fig. S12 Optimized structures and the relative combination energies (Δ E, KJ mol^{-1}) between HF and solvents or electrolyte additives: DMC/EC/EMC/TMSPi/TMSPE/TEP-HF.

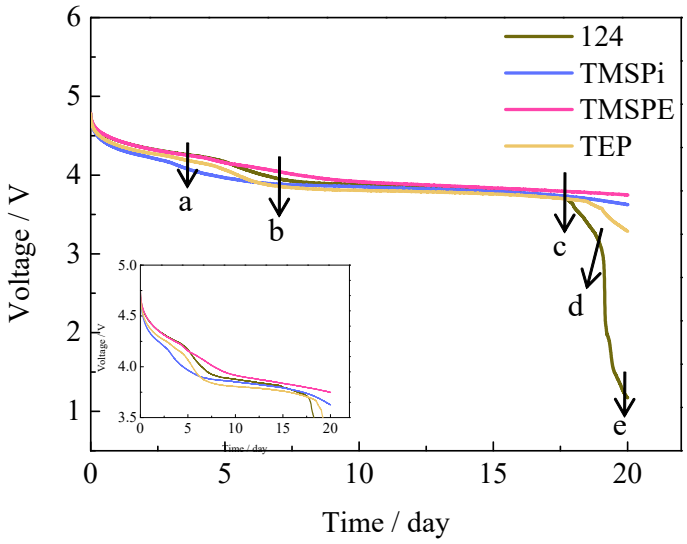

Fig. S13 OCV variation of $Li_{1.144}Ni_{0.136}Co_{0.136}Mn_{0.544}O_2$/Li cells with different additive during storage for 20 days at 45 °C.

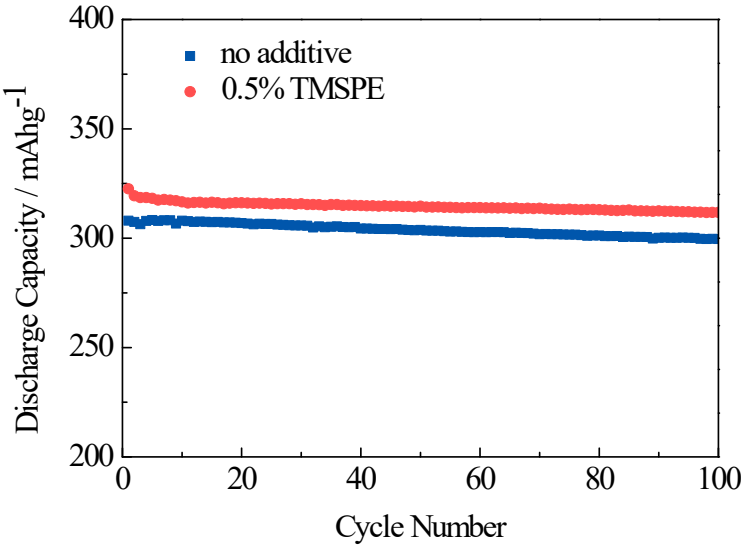

Fig. S14 Cycling performance of MCMB/Li cells with electrolytes in the different additives.