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Uracil-based Additives for Enabling Robust Interphases of High-Voltage Li-ion Batteries at Elevated Temperature

Fu Jie Yang†[a], Jing Bai†[c], Bing Shao†[b], Qing Feng Liu[a], Chong Mao[c], Yuan Qing Zhang[c], Xin Ming Fan*[d], Pi Pi Wang*[c] and Jing Huang*[b]

[a]College Chemistry and Chemical Engineering, Zhongkai University of Agriculture and Engineering, Guangzhou 510275, P. R. China

[b]College of Pharmacy, Guangxi Medical University, Nanning 530021, P. R. China.

[c]Zhuhai Smooth Way Electronic Material Co., Ltd, Zhuhai 519110, P. R. China

[d]Powder Metallurgy Research Institute, Central South University, Changsha 410083, Hunan, China

† These authors contributed equally to this work.

Corresponding author

E-mail: kakaxi95@163.com

E-mail: fanxinming@csu.edu.cn

E-mail: huangjin@mailbox.gxnu.edu.cn

MATERIALS AND METHODS

1.1 Preparation of Electrolytes and Cell Assembled

Uracil (UC) and 2-thiouracil (TUC), purchased from Shanghai Aladdin Biochemical Polytron Technologies Inc., were dried at 80 ^{o}C for 24 h in a vacuum before use. The baseline electrolyte was composed of 1.0 M lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (3:7, wt.%). Moreover, due to the solubility of UC and TUC in the baseline electrolyte only 0.3 wt% (see Figure S1), the electrolytes containing 0.3 wt% of UC and TUC were used as the functional electrolytes for studying their influence on the cell performances. All preparation of electrolytes was performed in an argon-filled glove box with O_2 and H_2O concentration below 0.1 ppm.

The $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC523)‖artificial graphite pouch cells were obtained from Li-Fun Technology (Zhuzhou, China) to conduct the electrochemical experiments, sealed without electrolyte. The anode electrodes were prepared by casting the mixing slurry, artificial graphite materials (Shenzhen BTR Energy Materials Co., Ltd), Super-P, styrene-butadiene rubber (SBR) and carboxymethyl cellulose (CMC) in a weight ratio of 94.8:1.2:2.5:1.5 dispersed in water on Al foil and pre-dried in an oven, and the excess of anode material is 15%. The areal loading and compaction density of the prepared anode were 10 mg cm^{-2}, and 1.5 g cm^{-3}, respectively. The cathode electrodes were prepared by casting the mixing slurry, pristine NMC532 materials (Xiamen Tungsten Industry Co., Ltd.), PVDF and carbon black, in a weight ratio of 94:3:3 dispersed in N-methyl-2-pyrrolidine one, on Al foil

and pre-dried in an oven, the areal loading and compaction density of prepared cathode were 16.4 mg cm^{-2} and 3.3 g cm^{-3} respectively. The separator between cathode and anode was used the polyethylene (PE) membrane coated with Al_2O_3 on one side.

Before injecting the liquid electrolytes, the cells were open and dried in the oven at 85 ^oC under vacuum for 12 h in a vacuum oven (pressure <1 mbar). For each cell, the electrolyte (4.5±0.05 g) was injected afterwards in a glovebox filled with argon. After filling the different electrolytes, the cells were sealed again at 165 ^oC under vacuum using a vacuum sealer (GN-HS200V, Gelon LIB Group).

1.2 Electrochemical Tests and Theory Calculation

The linear sweep voltammetry (LSV), together with the cyclic voltammetry (CV) measurements were tested on the electrochemical workstation (AUTOLAB PGSTAT128N) in a three-electrode system. Platinum (Pt) and two lithium pieces were used as the working electrode, the counter and reference electrodes, respectively. The scan rate was set to be 0.1 mV s^{-1}, and the voltage ranges from 3.0-7.0 V and 3.0-4.2V vs Li/Li^+ for the LSV and CV measurements, respectively.

The charging/discharging cycling of the cells was conducted through NEWARE battery measurement device (CT-4008) in a constant current (CC) / constant voltage (CV) mode between a voltage range of 3.0~4.5 V (1C=180 mAh g^{-1}) at 25 ^oC and 45 ^oC. Before the test, the cells underwent four formation cycles with the increasing current density of C/20, C/10, C/5 and C/2 rate in order to form solid electrolyte

interface (SEI) films on the electrodes' surfaces. The electrochemical impedance spectroscopy (EIS) results were obtained from an electrochemical station in the frequency range of 1 MHz-10 mHz at an amplitude of 10 mV. The testing cells were performed at a half state of charge condition. The storage performances at 60 ^{o}C were investigated by the following steps. Firstly, the NMC532‖graphite pouch cells that have gone through the above-mentioned four formation cycles were charged to 4.5 V at 1.0 C in the CC / CV mode. Subsequently, the cells were discharged to 3.0 V at the same current density for detecting the initial discharged capacity. Both the above steps were performed at 25 ^{o}C. The cells were recharged to 4.5 V to reach 100 % charge state, and then put in an oven for storing 15 days at 60 ^{o}C. After that, the cells were transferred into the room-temperature environment to cool down for 1 h and discharged to 3.0 V at 1.0 C rate, wherein the discharge capacity is defined as retained capacity. The recovery capacity was the discharge capacity of the preceding cells that went through a CC/CV charge/discharge to 4.5 V and 3.0 V. The corresponding capacity retention rate and the capacity recovery rate can be decided in the following formulas: Capacity retention rate (%) = Retained capacity / initial capacity×100%; Capacity recovery rate (%) = Recovery capacity / initial capacity×100%.[28]

Density functional theory (DFT, Materials Studio) with DMol3 module was employed to calculate the highest occupied molecular orbital (HOMO) / lowest unoccupied molecular orbital (LUMO) of EC, EMC and UC-based additives at the double numerical plus d-functions (DND) basis set. The structural optimization was performed for ensuring the energy of the optimized conation with the lowest energy.

DFT was also used for the density of states calculation. TUC and UC molecules were set into a 20 Å×20 Å×20 Å vacuum box for calculation. The truncation energy and the convergence criterion for each atomic force are set to 400 eV and 0.02 eV/Å, respectively. *k*-points are set to 1×1×1. When calculating the density of states, *k*-points should be readjusted and set to 2×2×2. The combination energies between Ni^{3+}/Mn^{2+} and the additive are calculated by the following: $\Delta E = E(AB)-E(A)-E(B)$, in which AB, A and B represent the combined compound, the additive, and Ni^{3+}/Mn^{2+}, respectively.

1.3 Material Characterization

For physical and chemical characterization, the NMC523‖graphite pouch full cells before and after high-voltage cycling were disassembled in the argon-filled glove box. The retrieved anodes and cathodes were rinsed several times with dimethyl carbonate (DMC) and dried at room temperature for a series of structural characterization. Morphology images of the dried samples were acquired on the scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, FEI Talos F200S). The chemical components were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo-VG Scientific ESCALAB 250) equipped with Al Kα radiation (excitation energy = 1468.6 eV). The amount of transition metal ions (Mn, Ni and Co ions) dissolved from cycled NCM523 cathode was detected by Inductively Coupled Plasma-Mass Spectrometry (ICP-OES, PerkinElmer Optima8000, USA). To detect the transition metal contents, the graphite anode was immersed in the 60 vol% HNO_3 solution at 250 ^oC for dissolving the

elements completely. Subsequently, the prepared solution was analyzed by ICP-OES.

Gas chromatography mass spectrometry (GC-MS) was utilized to analyze the gas decomposition products of NMC532 graphite pouch cells. Before the test, the pouch cells underwent the initial four formation cycles with the increasing current density of C/20, C/10, C/5 and C/2 rate. The gas products were taken directly from the pouch cells using a "gas-tight" type chromatography syringe, and the collected gas products were injected directly into the column. The oven was maintained at 50^{o}C for a carrier gas flow rate set at 0.5 mL min^{-1}.

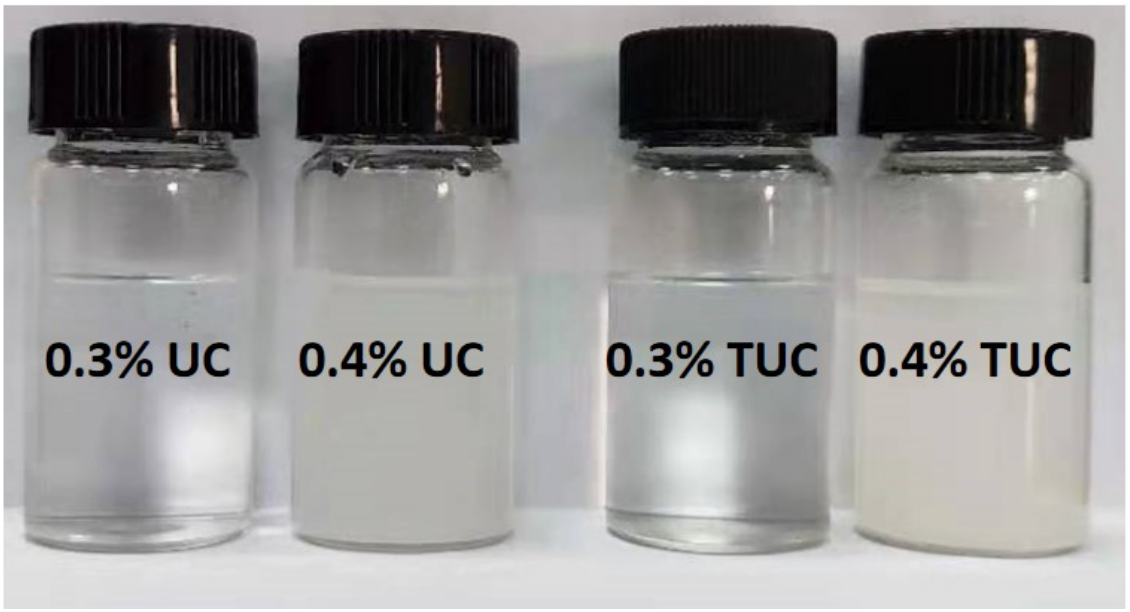

Figure S1. The photographs of the functional electrolytes with different contents of UC and TUC.

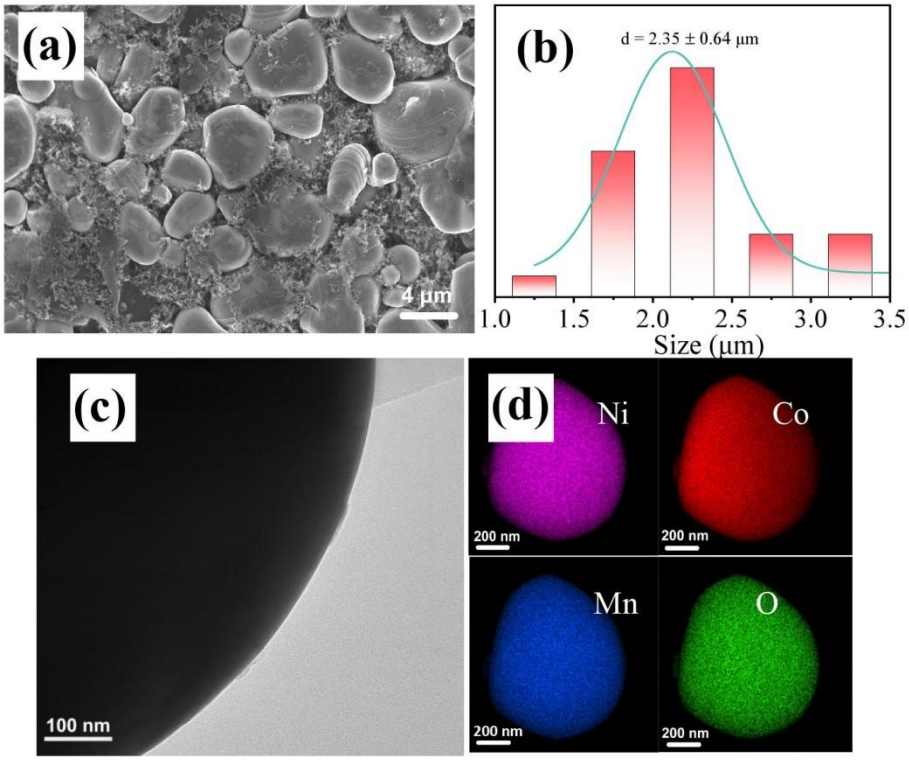

Figure S2. Morphological characterization of fresh NCM523 cathodes. (a) and (b) presented SEM images and associated particle size distribution of the cathode; (c) and (d) revealed TEM images and EDS analysis (Ni, Co, Mn, O), respectively.

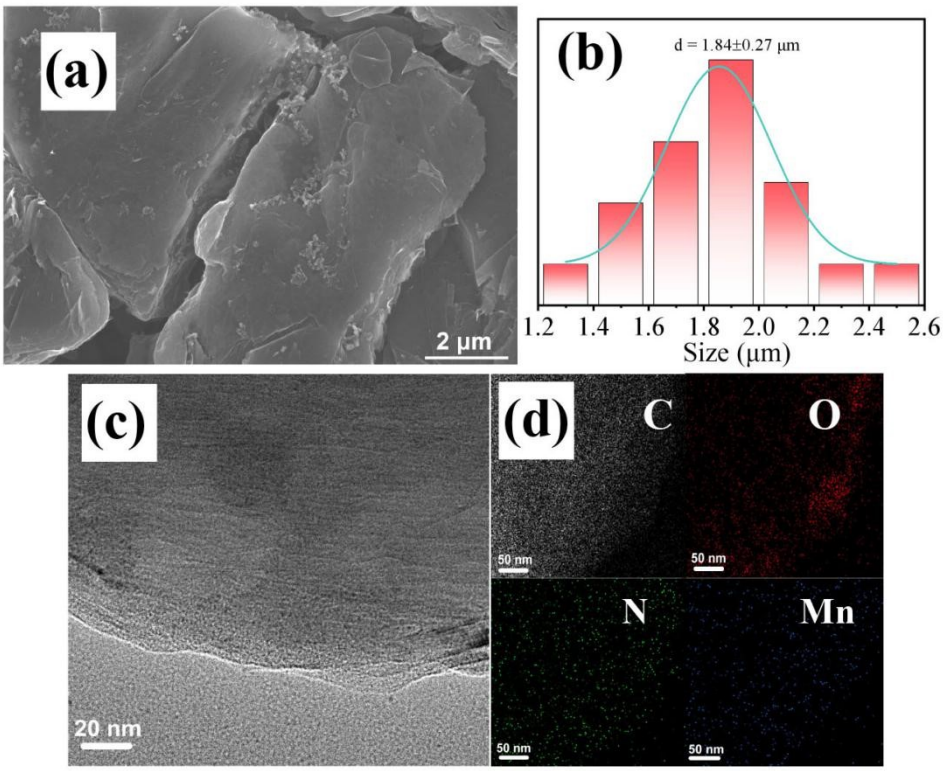

Figure S3. Morphological characterization of fresh graphite anodes. (a) and (b) presented SEM images and associated particle size distribution of the anode; (c) and (d) revealed TEM images and EDS analysis (C, O, N, Mn), respectively.

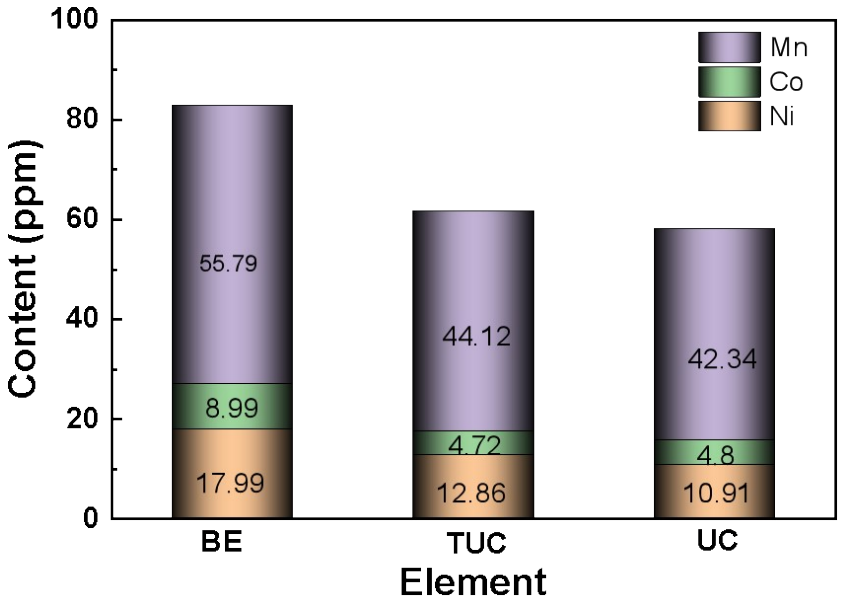

Figure S4. The concentration of transition metal ions in the graphite anodes with different electrolytes after 185 cycles.

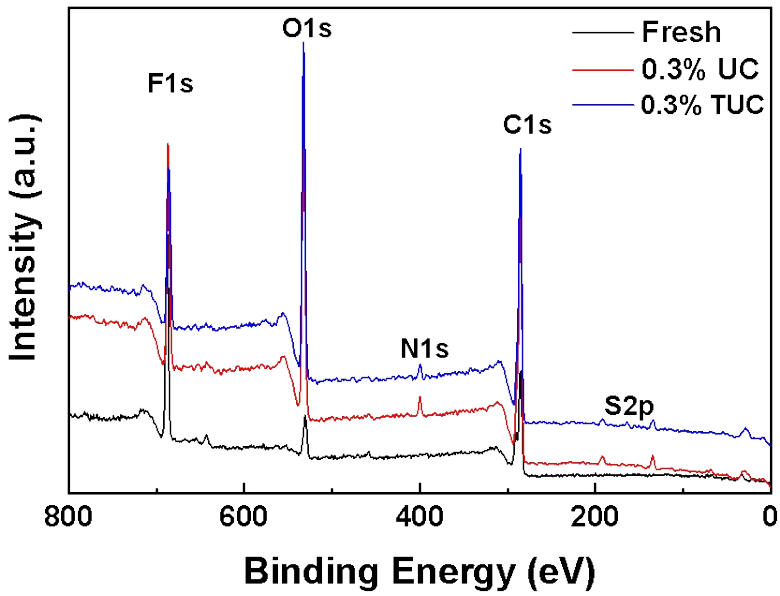

Figure S5. XPS analysis of fresh cathode and cycled cathodes with 0.3wt% UC and TUC.

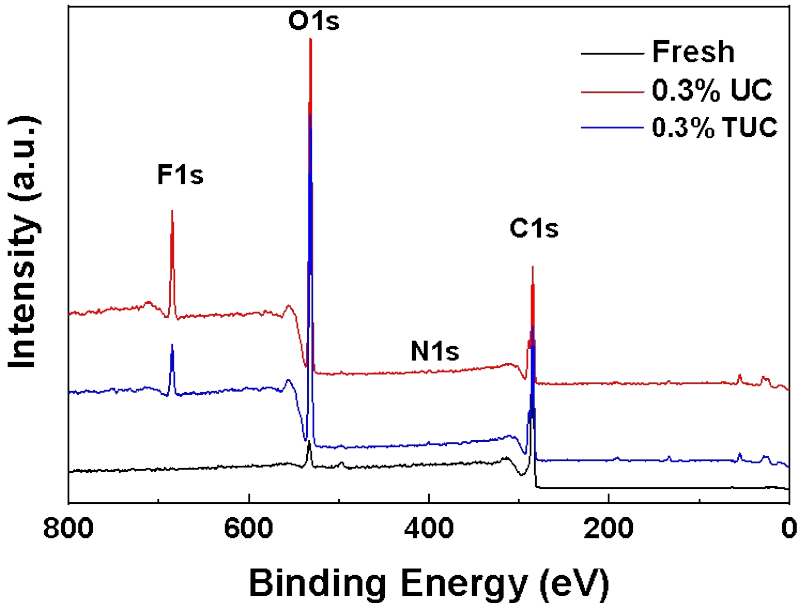

Figure S6. XPS analysis of fresh anode and cycled anodes with 0.3wt% UC and TUC.

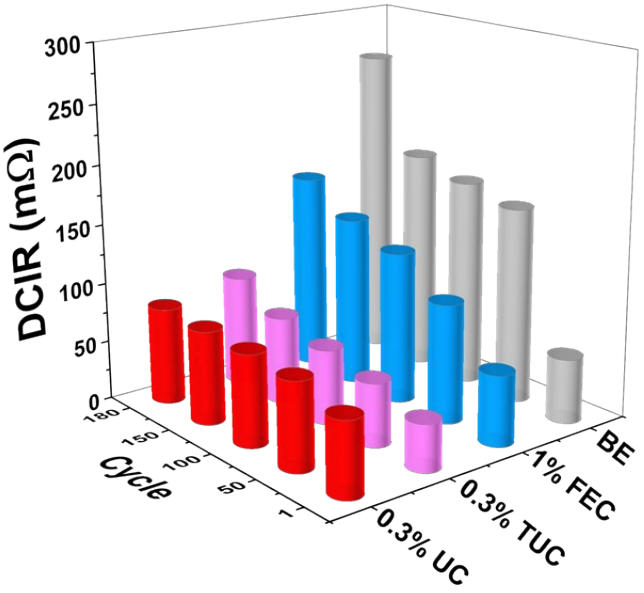

Figure S7. The direct-current resistance (DCR) data in different cycles for NMC532 graphite cells containing various electrolytes at 50% SOC.

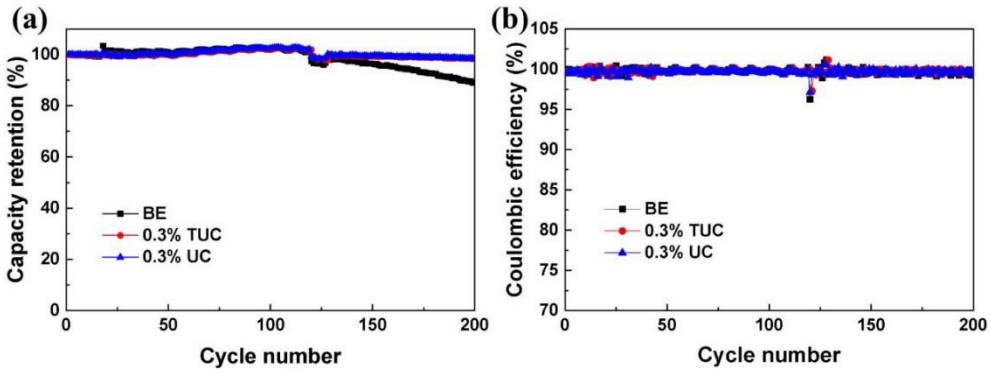

Figure S8. Cycle performance of the NMC532 graphite pouch cells with and without UC-based additives with 1 C current density between 3.0 V and 4.5 V at 25 ^{o}C.

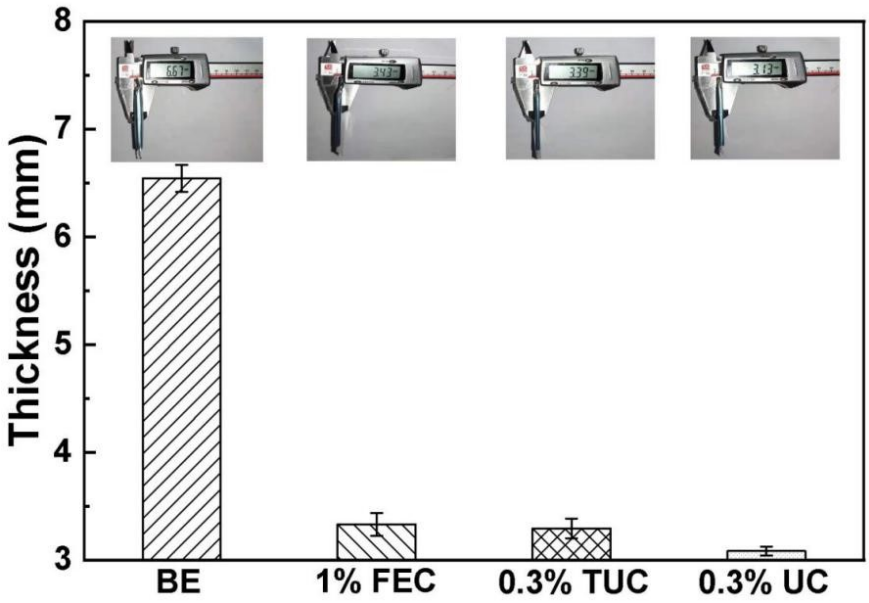

Figure S9. The thickness of the NMC532 graphite pouch cells containing different additives after high-voltage cycling at 45 °C, comparing to BE.

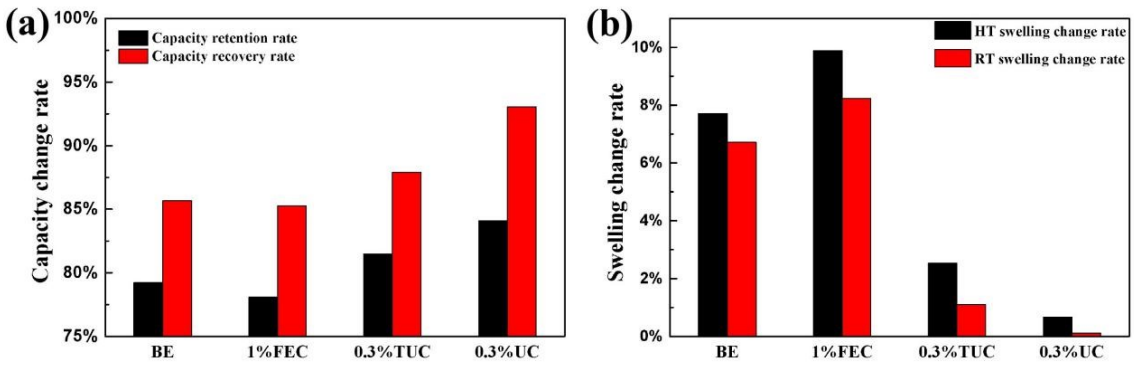

Figure S10. High-temperature storage performance of the pouch full cells with and without various additives at 60 °C for 15 days: (a) comparison of capacity retention rate (black) and capacity recovery rate (red); (b) swelling change rate for the pouch cells tested at 25 °C (RT) and 60 °C (HT), respectively.

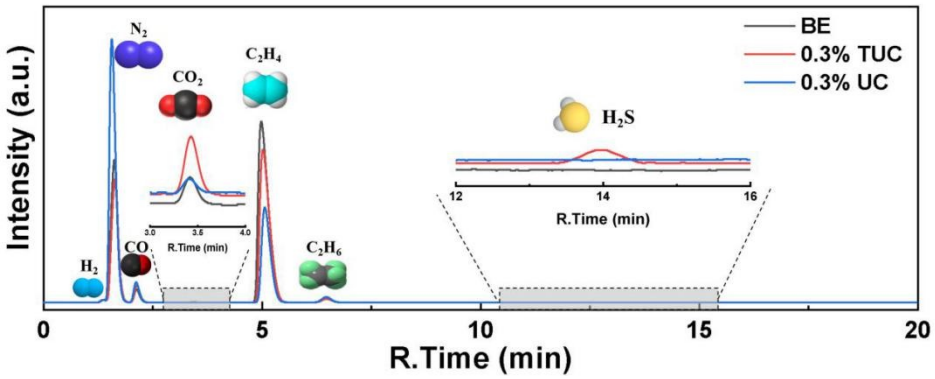

Figure S11. GC-MS chromatogram characterizations for analyzing the gaseous decomposition products of the NCM523/graphite pouch cells without and with UC-based additives.

Table S1. Equivalent circuit data of the NCM523/Li and graphite/Li half cells without and with UC-based additives.

Samples		R_s / Ω	R_{SEI} / Ω	R_{ct} / Ω
NCM523/Li	BE	1.96	4.88	7.64
	UC	1.96	9.89	6.07
	TUC	3.28	8.89	8.67
Graphite/Li	BE	2.48	2.95	15.3
	UC	2.14	12.8	8.07
	TUC	1.38	6.13	19.1

R_s represents the total resistance of the cell, R_{SEI} refers to the solid-electrolyte-interface (SEI) resistances on anode or cathode at high frequency, and R_{ct} represents the charge-transfer resistance at medium-frequency regions.

Table S2. The corresponding results of EIS for high-voltage graphite/NCM523 pouch cells before and after 185 cycles.

Samples		R_s / mΩ	R_{SEI} / mΩ	R_{ct} / mΩ
Before cycling	BE	114	5.38	19.0
	UC	79.3	11.0	23.3
	TUC	77.8	10.0	9.23
After 185 cycles	BE	132	251	56.2
	UC	94	41.4	9.42
	TUC	117	85.8	14.5

Table S3. Comparison of the cycled performance of high-voltage Li-ion batteries

Electrolyte additive	Cell	Cut-off Voltage	Temperature	Capacity retention	References
BA	Li/NCM811 half cell	4.5 V	Room temperature	69 % after 200 cycles at 1C	*ChemSusChem* **2021**, DOI: 10.1002/cssc.202100061.
MTE-TMS	Graphite/NCM851005 full cell	4.3V	Room temperature	84% after 100 cycles at 0.2C	*Energy Storage Mater.* **2020**, 33, 216-229.
TBB	Graphite/NCM622 full cell	4.5V	25 °C	94.9% after 120 cycles at 1C	*Electrochimica Acta* **2020,** *354*, DOI: 10.1016/j.electacta.2020.136722.
UC	Graphite/NCM523 full cell	4.5 V	45 °C	93.1% after 180 cycles at 1C	***This work***
TUC	Graphite/NCM523 full cell	4.5 V	45 °C	90.3% after 180 cycles at 1C	***This work***
IAn	Graphite/NCM523 full cell	4.5 V	45 °C	92.3% after 200 cycles at 1C	*Journal of Power Sources* **2021**, 509, 230361
ADN	Graphite/NCM523 full cell	4.4V	Room temperature	85.2% after 100 cycles at 1C	*Solid State Ionics* **2019,** *337*, 63-69.
PACA	Graphite/NCM523 full cell	4.35V	Room temperature	91.84% after 100 cycles at 1C	*Electrochimica Acta* **2015,** *166*, 190-196.
LiDFP	Graphite/NCM111	4.5V	Room	78.2%	*Acs Applied Energy*

	full cell		temperature	after 200 cycles at 1C	*Materials* **2018,** *1* (6), 2647-2656.
EDPN	Graphite/NCM111 full cell	4.5V	Room temperature	83.9% after 100 cycles at 1C	*Acs Applied Materials & Interfaces* **2017,** *9* (11), 9630-9639.
Dopamine	Graphite/NCM111 full cell	4.5V	25 ^{o}C	90.1% after 100 cycles at 1C	*Acs Appl Mater Inter* **2016,** *8* (33), 21366-21372.
APTS	Li/$Li_{1.2}Mn_{0.55}Ni_{0.15}Co_{0.1}O_2$ half cell	4.8V	Room temperature	83% after 300 cycles at 1C	*Journal of Materials Chemistry A* **2018**, 6 (36), 17642-17652.