

Supporting Information for

1,3,5-Trifluorobenzene, an electrolyte additive with high thermal stability and superior film-forming property for Lithium-ion batteries

Xinlan Wang,^{ab} Ziqi Zeng,^{*a} Han Zhang,^b Mingsheng Qin,^b Yanli Zhu^{*c} and Jia Xie^{*a}

^a State Key Laboratory of Advanced Electromagnetic Engineering and Technology, School of Electrical and Electronic Engineering, Huazhong University of Science and Technology, Wuhan 430074, China.

^b State Key Laboratory of Materials Processing and Die and Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China.

^c State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, China.

*Corresponding author.

E-mail: xiejia@hust.edu.cn; ziqizeng@hust.edu.cn; zhuyanli1999@bit.edu.cn

Experimental section

Electrolyte preparation. Lithium hexafluorophosphate (LiPF_6 , 99.5%), lithium perchlorate (LiClO_4 , 99.5%), ethylene carbonate (EC, 99.9%), diethyl carbonate (DEC, 99.9%) and fluoroethylene carbonate (FEC, 99.9%) were purchased from Dodo Chem (Suzhou, Jiangsu Province, China). 1,3,5-trifluorobenzene (F_3B , 98%) was provided by Aladdin. The electrolytes were formulated according to the ratio of conventional carbonate electrolytes as 1 M lithium salt dissolved in EC/DEC (1:1 by weight). And the amount of additives was 10 wt. %. All the electrolyte preparation was done in the glove box.

Electrode preparation and battery assembly. The graphite anodes were prepared by mixing graphite, super-P and carboxymethylcellulose sodium (CMC) in a mass ratio of 8:1:1. The slurry was coated onto the copper foil and dried at 80°C overnight. The NCM65 cathodes were made by blending $\text{LiNi}_{0.65}\text{Co}_{0.2}\text{Mn}_{0.15}\text{O}_2$ (NCM65), super-P, and poly(vinylidene fluoride) (PVDF) with a mass ratio of 8:1:1. The obtained slurry was coated on Al foil and dried at 110°C overnight. Separators (Celgard 2400), Li foil ($\Phi 14$ mm, thickness: 400 μm) were obtained from China Energy Lithium Co., Ltd. The capacity ratio (N/P ratio) of graphite/NCM65 was 1.1:1. All coin cells (CR2032) were assembled in glove box with Argon atmosphere. And a fixed volume of electrolyte (30 μL) was used to assemble the coin cells.

Electrochemical measurements and characterizations. All cells were tested on Neware battery test system (CT-4008Tn-5V10mA-164, Shenzhen, China). Linear sweep voltammetry (LSV) curves and cyclic voltammetry (CV) curves of the cells were tested by CHI 600D. Electrochemical impedance spectrometry (EIS) was conducted from 100 KHz to 0.1 Hz with voltage amplitude of 10 mV. The micromorphology of NCM65 electrodes were characterized by scanning electron microscope SEM (Nova NanoSEM 450). The X-ray photoelectron spectroscopy (XPS) was carried out on an AXISULTRADLD-600W. X-ray diffraction (XRD) patterns of graphite electrodes were collected by X-ray Powder diffractometer (Rigaku MiniFlex600).

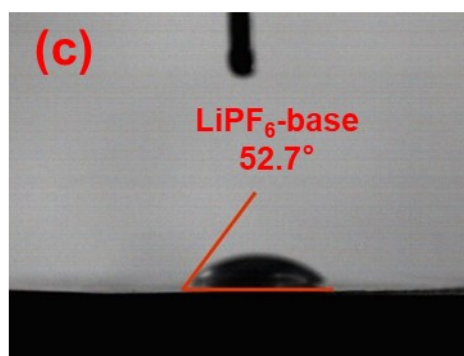
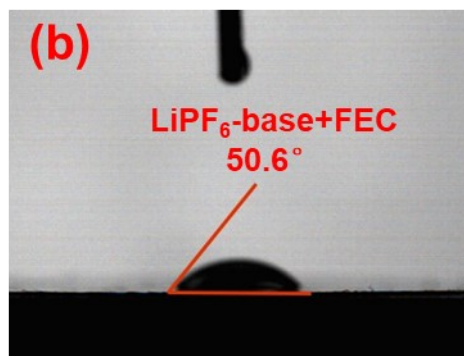
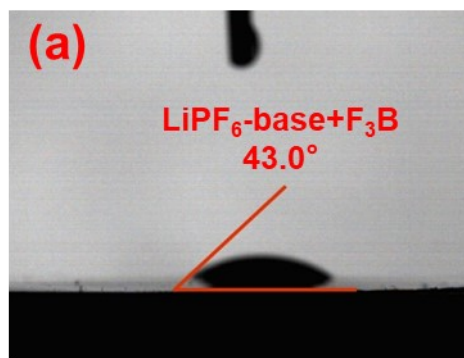


Fig. S1 Contact angle of (a) LiPF₆-base+F₃B, (b) LiPF₆-base+FEC, and (c) LiPF₆-base with PP separator.

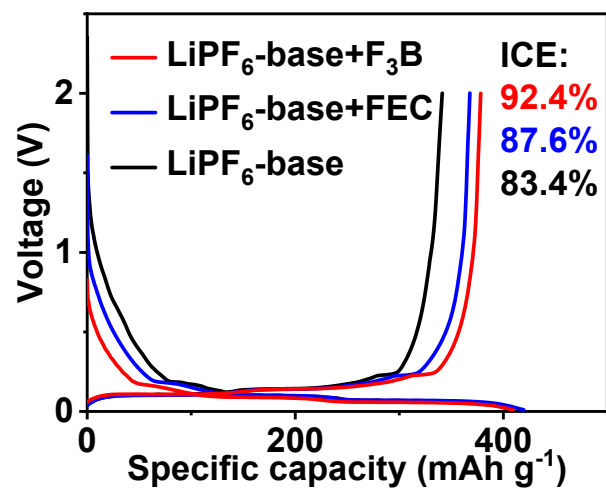


Fig. S2 Initial charge-discharge curves of Li/graphite cells in the voltage range of 0.05 - 2 V with LiPF₆-based electrolytes.

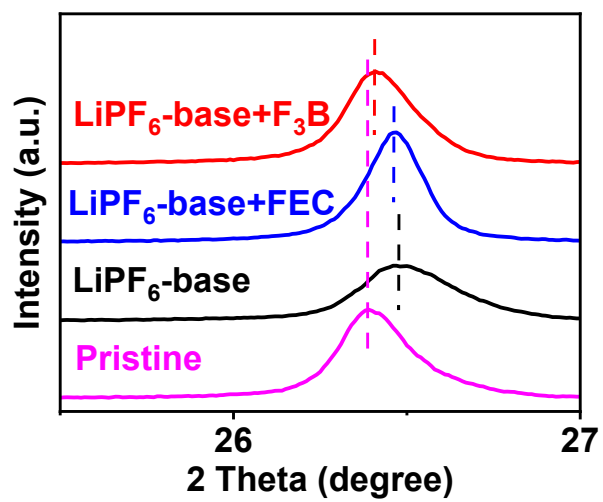


Fig. S3 XRD spectrum of graphite uncycled and after cycling with LiPF₆-based electrolytes.

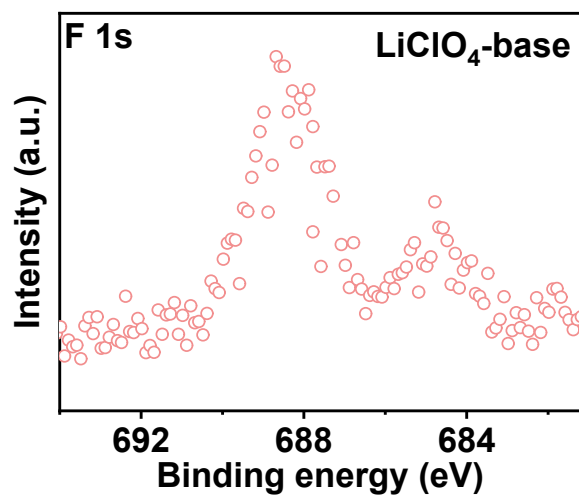


Fig. S4 XPS spectra of F 1s for the graphite electrode after 30 cycles in LiClO₄-base electrolyte.

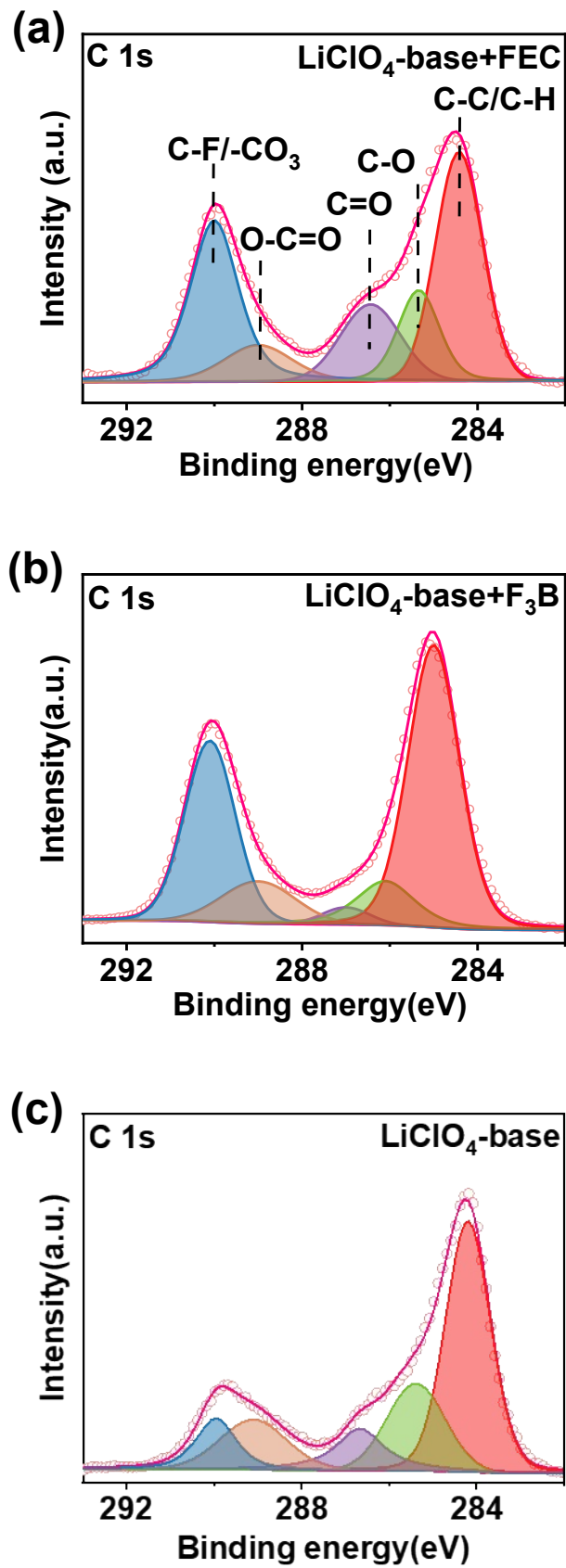


Fig. S5 XPS spectra of C 1s for the graphite electrodes after 30 cycles in (a) LiClO₄-base+FEC, (b) LiClO₄-base+F₃B, and (c) LiClO₄-base electrolyte.

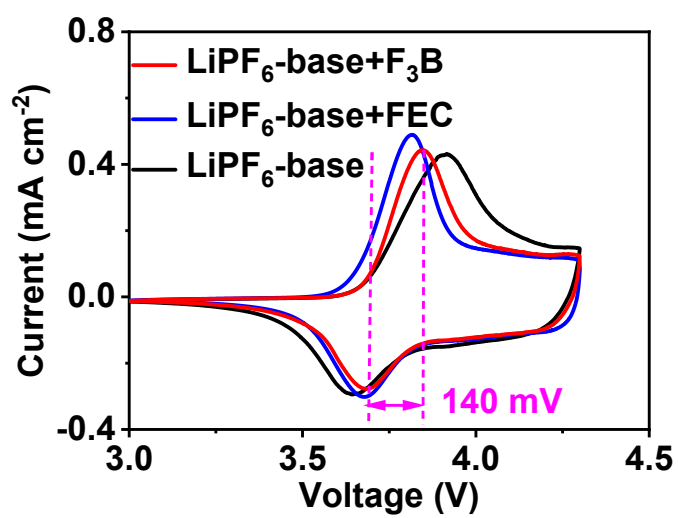


Fig. S6 CV curves of Li/NCM65 cells in the voltage range of 3 - 4.3 V with LiPF₆-based electrolytes.

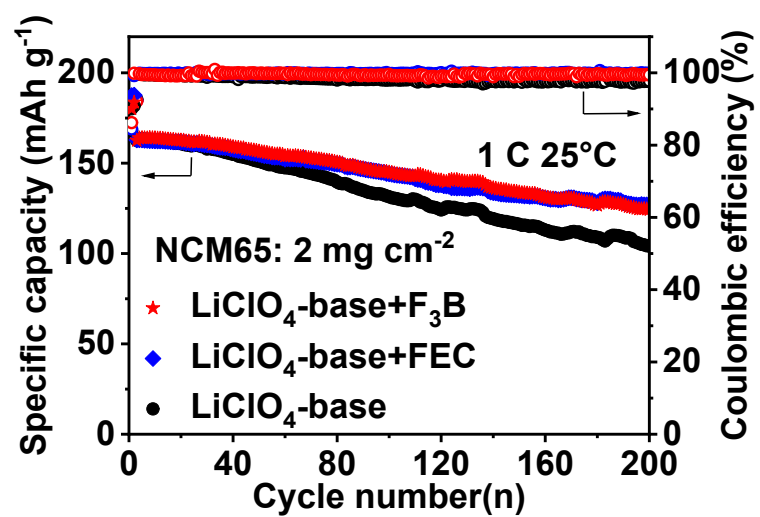


Fig. S7 Cycling performances of Li/NCM65 cells in the voltage range of 3 - 4.3 V with LiClO₄-based electrolytes.

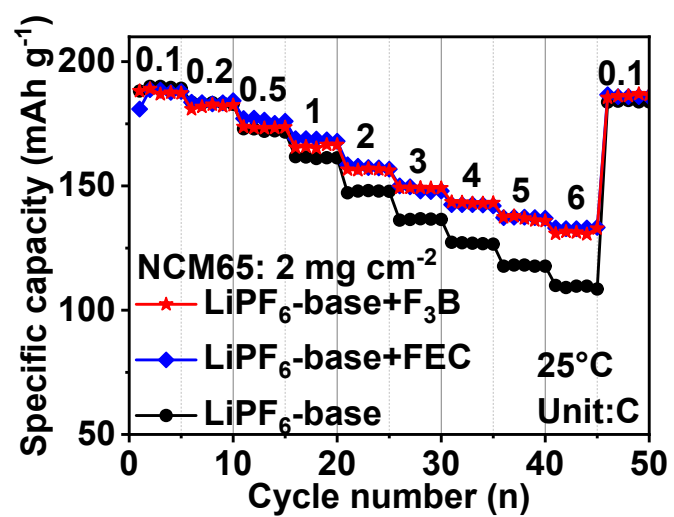


Fig. S8 Rate performance of Li/NCM65 cells in the voltage range of 3 - 4.3 V with LiPF₆-based electrolytes.

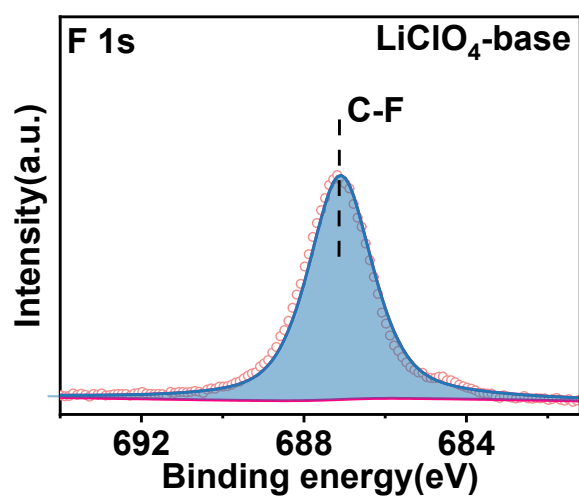


Fig. S9 XPS spectra of F 1s for the NCM65 after 30 cycles in LiClO₄-base electrolyte.

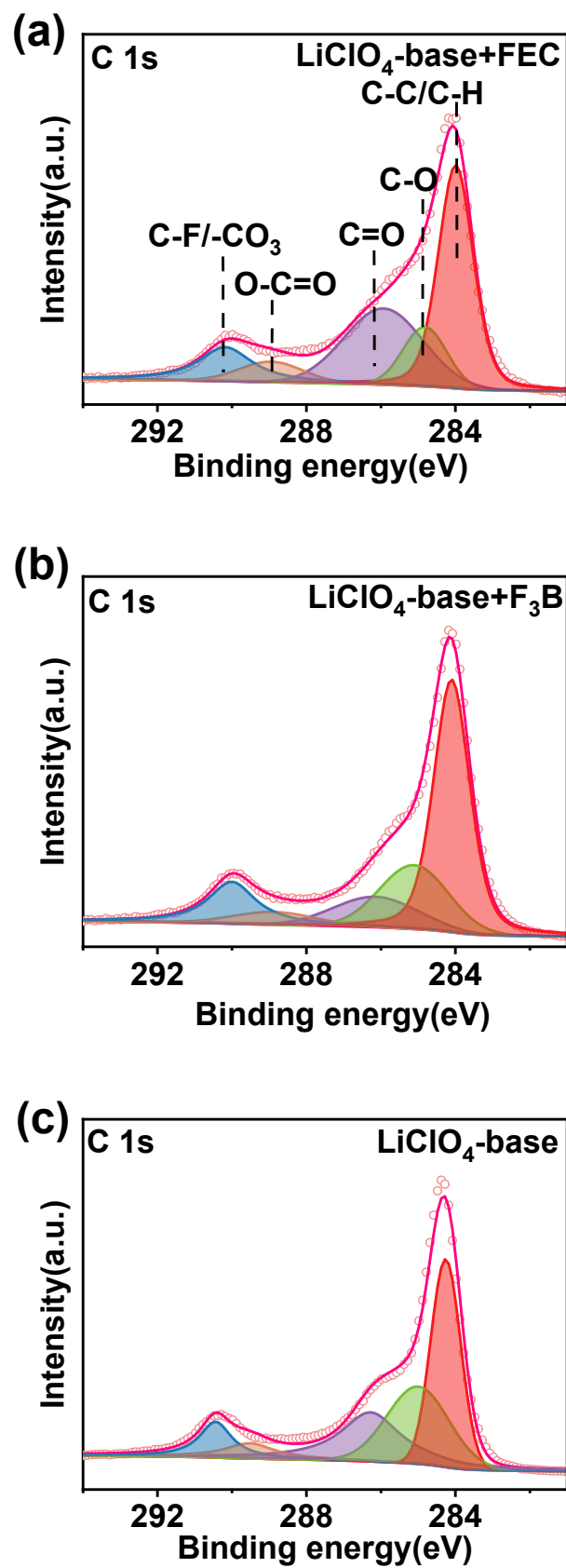


Fig. S10 XPS spectra of C 1s for the NCM65 after 30 cycles in (a) LiClO₄-base+FEC, (b) LiClO₄-base+F₃B, and (c) LiClO₄-base electrolyte.

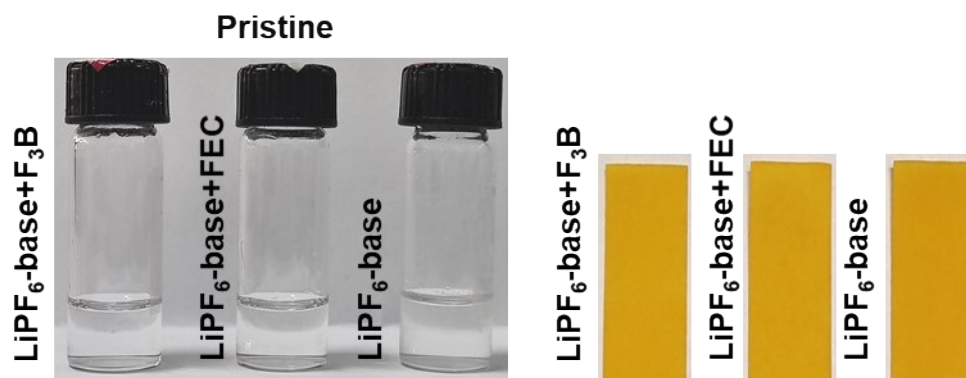


Fig. S11 Photographs and pH results of $\text{LiPF}_6\text{-base+F}_3\text{B}$, $\text{LiPF}_6\text{-base+FEC}$, and $\text{LiPF}_6\text{-base}$ electrolyte before storage.

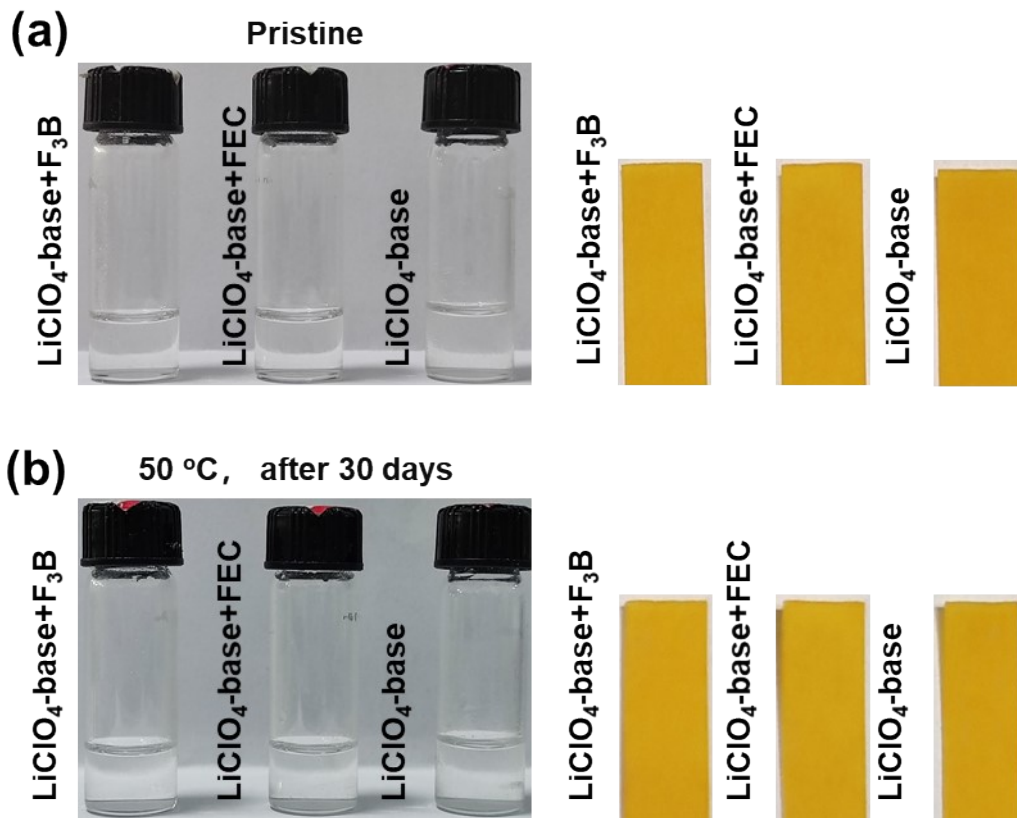


Fig. S12 Photographs and pH results of LiClO₄-base+F₃B, LiClO₄-base+FEC, and LiClO₄-base electrolyte (a) before and (b) after storage at 50°C for 30 days.

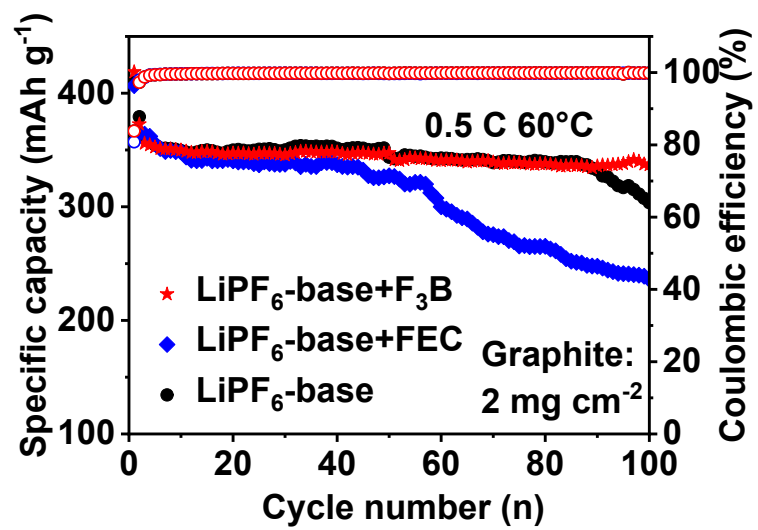


Fig. S13 Cycling performances of Li/graphite cells with different electrolytes at 60°C in the voltage range of 0.05-2 V.

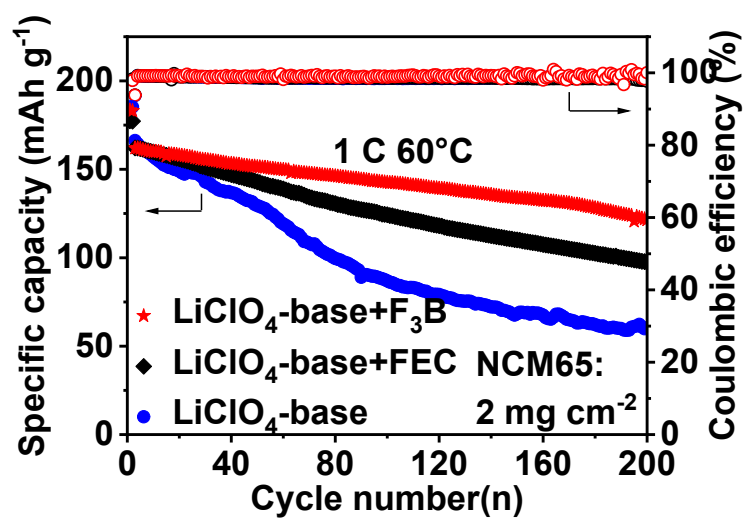


Fig. S14 Cycling performance of Li/NCM65 cells with LiClO₄-based electrolytes at 60°C.

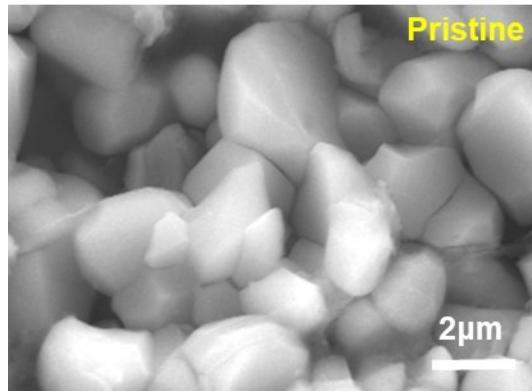


Fig. S15 SEM image of unicycled NCM65.

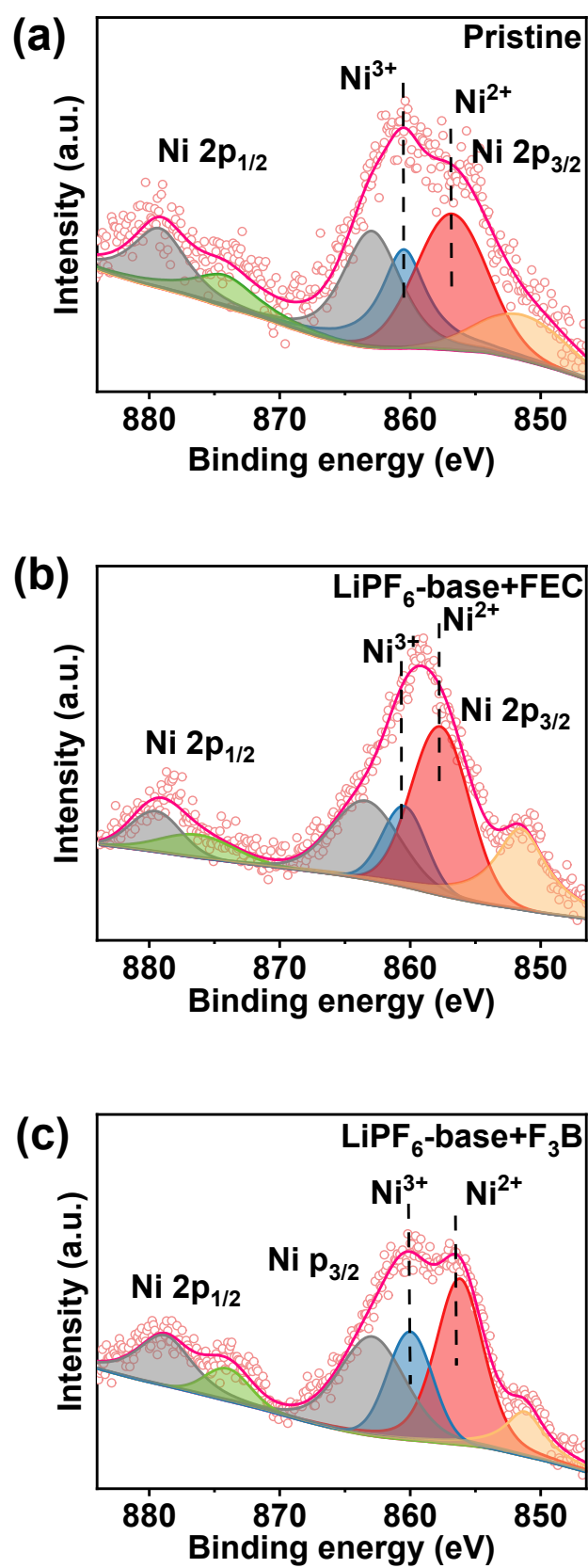


Fig. S16 XPS spectra of Ni 2p for the NCM65 (a) uncycled and after cycling at 60°C with (b) LiPF₆-base+FEC, (c) LiPF₆-base+F₃B.

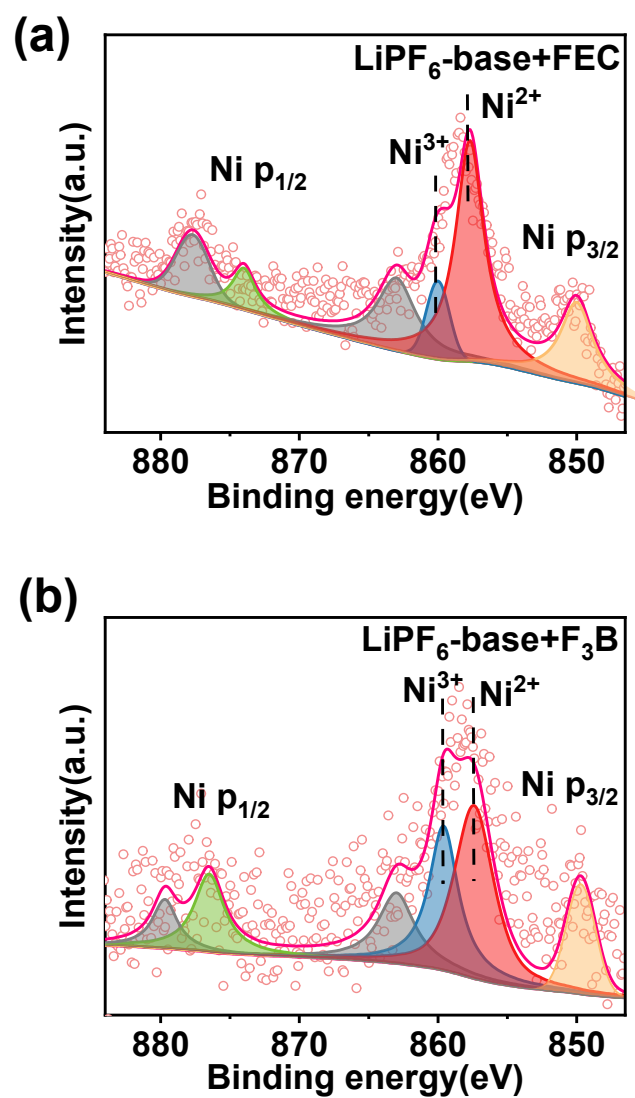


Fig. S17 XPS spectra of Ni 2p for the separator closed to anode side after cycling at 60°C with (d) LiPF₆-base+FEC and (e) LiPF₆-base+F₃B electrolyte.