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Interfacial Design for a 4.6 V High-Voltage Single-Crystalline LiCoO₂ Cathode

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Single-crystalline cathode materials have attracted intensive interest in offering greater capacity retention than their polycrystalline counterparts by reducing material surfaces and phase boundaries. However, the single-crystalline LiCoO₂ suffers severe structural instability and capacity fading when charged to high voltages (4.6 V) due to Co element dissolution and O loss, crack formation, and subsequent electrolyte penetration. Herein, by forming a robust cathode electrolyte interphase (CEI) in an all-fluorinated electrolyte, reversible planar gliding along the (003) plane in a single-crystalline LiCoO₂ cathode is protected due to the prevention of element dissolution and electrolyte penetration. The robust CEI effectively controls the performance fading issue of the single-crystalline cathode at a high operating voltage of 4.6 V, providing new insights for improved electrolyte design of high-energy-density battery cathode materials.

1. Introduction

As a dominant commercial cathode material for lithium-ion batteries (LIBs), LiCoO₂ (LCO) successfully attracted academia and industrial attention.^[1–3] Although the price of cobalt continues to increase,^[4,5] LiCoO₂ cathode still dominates in portable electronic devices and consumer electronics,^[3,6] because LiCoO₂ possesses several critical advantages such as high theoretical capacity (274 mA h g⁻¹), high volumetric energy density, and good Li⁺/ electron conductivity. However, its practical discharge capacity with stable cycling performance is only about 170 mA h g⁻¹ due to the electrolyte limitation (4.4 V vs Li/Li⁺),^[3,6,7] Charging to

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higher voltage can potentially enhance the energy density for LIBs.^[8,9] However, the increased cutoff voltages also accelerate material dissolution and interfacial side reactions between LCO and electrolytes and even form cracking due to the phase change. Specifically, when the voltage is charged to 4.6 V, a phase transformation takes place from the O3 hexagonal phase to the hybridized O1-O3 hexagonal phase (also known as H1-3 phase, where O represents octahedral sites, 1 represents the stacking sequence of oxygen layers as ABAB, 3 represents ABCABC). The phase transformation generates internal strain inside the particles, which is harmful to the cycling stability of the battery.^[10–13] The lattice structure gliding will be less revers-

ible and crack will form in the cathode. As the internal strain accumulates, also, the electrolyte penetration into the cracks results in side reactions, which in turn accelerates the cracking generation. The LiCoO₂ cathode's surface instability is another key issue that plays a vital role in the electrode material's stability. When charging to voltages higher than 4.5 V, not only is the decomposition of electrolyte rapidly increased due to the high oxidation potential, but also serious surface structure decay along with oxygen loss and cobalt dissolution start from the surfaces to the cores of LiCoO₂ cathode, resulting in irreversible phase transition and fast capacity degradation.^[6,14]

Researchers have developed many strategies to suppress the side reaction between LiCoO2 and electrolytes and cater to the long-cycling stability of LiCoO₂ at high voltage. Element doping, surface coating, and electrolyte design are the most effective strategies.^[15-25] Element doping notably tunes the basic physical properties of materials, while the doping strategies introduced some inactive elements into the cathode, lowered the specific capacity and energy density of the cathode, which canceled the advantages of increased cutoff voltage. Surface coating can protect the electrode surface, by optimizing the coating surficial structure, reducing the activity of electrolyte, and suppressing the transition-metal-ion dissolution, numerous surface coating strategies have been put forward in the past several years.^[26-32] Although the coating method is properly effective in some cases to improve the electrochemical performance of LiCoO₂, the high interfacial resistance raised by the coating layer, and the lack of self-healing capability of the coating layer reduce the effectiveness after cycles.



Single-crystalline cathodes have attracted increasing attention for LIBs due to the reduced surface areas, phase boundaries, and more integrated crystal structures. Also, when composing the high-strength single crystals into the electrode, the compressed electrode density was enhanced, as well as the energy density improved. Single-crystalline cathodes have superior capacity retention compared with the conventional polycrystalline cathodes, due to the high structural stability in single-crystalline cathodes.^[12,33–36] As reported by Bi et al.,^[33] the reversible planar gliding and microcracking along the (003) plane in a single-crystalline Ni-rich cathode were observed. Although fractures along the (003) direction appear in single crystals during cycling, the cracks are stable if electrolyte does not penetrate into the cracks and will not initiate catastrophic reactions to produce a fracture zone that leads to pulverization of the entire single crystal. Following this train of thought, we believe the single-crystalline LiCoO₂ cathode should be a potential direction for the suppression of structure collapse during cycling if a robust cathode electrolyte interphase (CEI) can be formed on the surface of LiCoO₂. Formation of robust CEI is critical for reversible microcracking self-healing of single-crystal LiCoO2.[37] In addition, effective CEI can also reduce transition metal dissolution, and lattice oxygen instability.^[38] The design of an effective CEI layer on the cathode surface is vital for the cycling stability of single-crystal LiCoO₂ cathode at high cutoff voltage. It must be considered to completely isolate the active LiCoO₂ from electrolytes (at least after the initial several cycles), enhance the surface structure stability, and entirely avoid O transport, O2 release, and Co dissolution.

In this work, we seek to understand the electrolyte design principle for the formation of a robust and thin CEI layer on single-crystalline LiCoO₂ cathode. The single-crystalline LiCoO₂ materials have fewer phase boundaries and material surfaces compared with the polycrystalline counterparts. The specially designed all-fluorinated electrolyte (1 M LiPF₆ in fluoroethylene carbonate/methyl (2,2,2-trifluoroethyl) carbonate/1,1,2,2tetrafluoroethyl-2,2,3,3-tetrafluoropropylether (FEC/FEMC/ TTE) [denoted as AFE] + 2 wt% tris(trimethylsilyl)borate (TMSB) [denoted as AFTB]) formed a robust inorganic-rich CEI, extending anodic potential up to 5.5 V. The single-crystalline LiCoO₂ cathode maintained excellent cycling stability when cycled in the AFTB electrolyte, achieving high Coulombic efficiencies (CEs) of 99.85% in LiCoO₂//Li half-cells. The fabricated 4.5 V high loading (4 mA h cm⁻²) LiCoO₂//graphite full cell delivered an energy density of 430 W h kg⁻¹ (based on the cathode and anode active materials) with excellent cycle stability of 80% capacity retention after 500 cycles. The comprehensive transmission electron microscopy (TEM), time-of-flight secondary-ion mass spectroscopy (TOF-SIMS), and X-ray photoelectron spectroscopy (XPS) characterizations confirmed that a robust, dense, and thin CEI layer formed on the cycled LiCoO₂ cathode in the AFTB electrolyte. The CEI layer is composed of B- and Si-compounds and F-rich inorganic composition. The as-designed CEI layer facilitates the surface structure stability of the cathode, maintains the bulk structure stability at high cutoff voltage, and inhibits the dissolution of Co/O elements. The observed planar gliding and microcracking in single-crystalline LiCoO₂ cathode is reversible, which can be demonstrated by the reversible charge-discharge capacity at a high-voltage range from 4.5 to 4.6 V. This work provides a rational design of electrolytes for high-voltage cathode materials to form a stable CEI layer, which protects the structural stability of cathode materials.

2. Results and Discussion

2.1. Electrolyte Design for High-Voltage Cathodes

The electrolyte property closely influences the surface stability, thermal stability, and kinetics of Li-ion transfer at the electrode/electrolyte interface. Current carbonate-based electrolytes cannot form effective CEI at a high-voltage cathode surface. We developed an all-fluorinated electrolyte (1 м LiPF₆ in FEC/ FEMC/TTE), which demonstrated stability to high voltage by forming LiF-rich CEI on the high-voltage cathode with sufficient ionic conductivity (Figure S1a,b, Supporting Information).^[39,40] To further enhance the robustness of CEI, we added TMSB into 1 м LiPF₆ in FEC/FEMC/TTE as an additive, and used single-crystal LiCoO₂ to demonstrate the electrolyte design for the high-voltage cathode. The all-fluorinated electrolyte forms a stable solid electrolyte interphase (SEI) on the anode surface and a robust CEI on the high-voltage cathode as demonstrated before.^[40,41] The TMSB additive can be oxidized before 4 V.^[42-44] The oxidation product of TMSB including some B-O and Si-O chemical bonds stick to the cathode surface. The bond energy of B-O (806(5) kJ mol⁻¹) and Si-O (798(8) kJ mol⁻¹) is much higher than Co–O (368(21) kJ mol⁻¹), which stabilizes the LiCoO₂ bulk structure.^[6]

Three electrolytes (ethylene carbonate (EC)-diethyl carbonate (DEC), AFE, AFTB) are prepared with detail presented in the Experimental Section. The corresponding electrochemical anodic stability was evaluated using a linear sweep voltammetry (LSV) at a slow scan rate of 0.1 mV s⁻¹. As shown in Figure S1a,b (Supporting Information), the oxidation current of the AFE and AFTB electrolytes during the anodic scan is extremely small up to 5.5 V versus Li⁺/Li, while the oxidation current of the EC-DEC electrolyte presents a rapid increase at potentials above 4.5 V. Moreover, there is a small peak observed in the AFTB electrolyte at around 3.5 V, which is originated from the oxidation of the TMSB additive. The decomposition of TMSB will form the corresponding CEI components on the surface of cathodes. As shown in Table 1, according to the firstprinciple calculations, the highest occupied molecular orbital (HOMO) level of TMSB is the highest among all the molecules or anions, demonstrating that it will be the first to be oxidized before solvent or salt anion when voltage increases in the cell.^[44]

2.2. Characterization and Performance of Single-Crystal ${\rm LiCoO_2}$ in AFTB Electrolytes

Figure 1a presents the Rietveld refinement of the powder X-ray diffraction (XRD) pattern of single-crystalline LiCoO₂, it can be fitted to a 3*R*-type layered rhombohedral system (space group: $R\overline{3}m$) with a hexagonal unit cell, the lattice parameters *a* and *c* are 2.817(3) and 14.062(8) Å, respectively. Detailed structural information of the single-crystal LiCoO₂ is shown in

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Molecule	Structure	HOMO [a.u.]	LUMO [a.u.]
EC		-0.3111	-0.0104
DEC	$\sim 0 \downarrow 0 \sim$	-0.2959	0.0024
FEC	° F	-0.3296	-0.0143
FEMC	F F F	-0.3267	-0.1412
TTE		-0.2605	-0.2312
TMSB	~si_o o_B_o_si_ -si_	-0.2430	-0.0595

 Table 1. Chemical structures and energies of various organic solvents.

Table S1 (Supporting Information) and the schematic views of the atomic structures are illustrated in the inset of Figure 1a. Synthesized single-crystalline LiCoO₂ has a microsized particle size of 5–20 μ m (Figure 1b). Co and O elements are homogeneously distributed in LiCoO₂, as demonstrated by the elemental mapping (Figure S2, Supporting Information). Pure phases of 3*R*-type layered structures are confirmed by selected area electron diffraction (SAED; Figure 1c). The typical crystal plane of (1120) is observed in the SAED. The distinct lattice fringes of 4.6 Å shown in the high-resolution transmission electron microscopy (HRTEM) image demonstrate high crystallinity (Figure 1d).

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The electrochemical performance of single-crystalline LiCoO₂ cathode was evaluated under a high charge cutoff voltage of 4.6 V in three different electrolytes: EC-DEC, AFE, and AFTB, where the optimized amount of TMSB additive in the fluorinated electrolyte (2%) was used, as shown in Figure S3a,b (Supporting Information). As presented in Figure 2a-c, the singlecrystal LiCoO2 presents a high reversible discharge capacity of 225 mA h g⁻¹. And 74.8% capacity retention (compared with the fourth cycle) is achieved in AFTB electrolyte after 300 cycles at a current rate of 0.5 C (1 C = 274 mA g^{-1} ; note that all cells were cycled at 0.1 C for the formation process at the first three cycles). While the capacity retention of LiCoO₂ is 68.1% in AFE and 3.4% in EC-DEC electrolytes. The Coulombic efficiency was measured during cycling. The first cycle Coulombic efficiency in AFTB electrolyte (97.2%) is slightly lower than that in AFE electrolyte (97.6%) owing to the decomposition of TMSB during the first charging process. While both of them were higher than that in EC-DEC



Figure 1. Characterization of single-crystalline LiCoO₂. a) Synchrotron XRD and Rietveld refinement pattern. b) SEM image of single-crystalline LiCoO₂. c) Electron diffraction pattern of a selected area of single-crystalline LiCoO₂. d) High-resolution TEM image of single-crystalline LiCoO₂.







Figure 2. Electrochemical performance of single-crystalline $LiCoO_2$. a–c) Cycling stability of single-crystalline $LiCoO_2$ in half-cells with 1 \bowtie LiPF₆ in ethylene carbonate and diethyl carbonate [denoted as: EC–DEC] electrolyte (a), 1 \bowtie LiPF₆ in FEC/FEMC/TTE [denoted as: AFE] electrolyte (b), and 1 \bowtie LiPF₆ in FEC/FEMC/TTE + 2 wt% TMSB [denoted as: AFTB] electrolyte (c). d,e) The normalized galvanostatic charge–discharge curves and voltage fade comparison of single-crystalline LiCoO₂ in commercial EC–DEC electrolyte (d), and AFTB electrolyte (e). f) The rate capability of single-crystalline LiCoO₂ in AFTB electrolyte.

electrolyte (87.5%). Also, the electrochemical performance of polycrystalline LiCoO₂ is much worse than the single-crystalline in Figure S3c,d (Supporting Information). The charge–discharge profiles at selected cycle numbers are presented in Figure S4 (Supporting Information). Significantly degraded voltage profiles can be seen in EC–DEC electrolytes after 10 cycles, indicating the severe structural degradation in LiCoO₂ cathode and worse CEI layer on LiCoO₂ cathode surface. The normalized 5th and 50th charge–discharge curves (Figure 2d,e) reveal that the LiCoO₂ cathode in EC–DEC electrolyte exhibits a large voltage fade in the whole discharge and high-voltage plateau of O3 to H1–3 at 4.5 V disappeared after 50 cycles, while the LiCoO₂ cathode in

AFTB electrolyte exhibits very little voltage fade in the whole discharge profile after 50 cycles. Interestingly, when we compare the specific capacity within the voltage range from 4.5 to 4.6 V (Figure S5, Supporting Information), there is barely capacity fade in AFTB electrolyte after 50 cycles in the high-voltage range from 4.5 to 4.6 V. This means that the phase transformation from O3 to H1–3 in LiCoO₂ cathode is fully reversible. However, this phase transformation gradually disappeared in EC–DEC electrolyte, meaning it is not fully reversible in EC–DEC electrolyte, hence, the robust CEI formed on LiCoO₂ cathode surface in AFTB electrolyte played an important role for the reversible of O3 to H1–3 phase transformation.

Figure 2f presents the rate performances of single-crystalline LiCoO₂ cathode in AFTB electrolyte with different rates from 0.1 C to 10 C (1 C = 274 mA g^{-1}). The corresponding discharging capacities of LiCoO₂ cathode at 0.1, 0.2, 0.5, 1, 2, 5, and 10 C are 225, 222, 213, 200, 176, 140, and 98 mA h g⁻¹ with high average CE of >99.9%, suggesting the excellent rate capability of single-crystalline LiCoO2 cathode within AFTB electrolyte. The quasiequilibrium potential and overpotential of LiCoO₂ cathode in AFTB electrolyte were investigated in LiCoO2//Li coin cell using the galvanostatic intermittent titration technique (GITT). As shown in Figure S4c (Supporting Information), single-crystalline LiCoO2 cathode presents a low quasiequilibrium potential hysteresis of <0.2 V and ultrasmall overpotential of <30 mV during the charge and discharge processes at 1/15 C (18 mA g^{-1}), demonstrating the good ionic diffusion ability of the single-crystalline LiCoO₂ cathode.

The thin CEI formed in the AFTB electrolyte has better stability compared with the EC-DEC electrolyte, as evidenced by the interfacial resistance in the electrochemical impedance spectroscopy (EIS) spectra (Figure S6, Supporting Information). The Nyquist plots of the LCO cathode measured using a three-electrode cell with a strip of lithium metal as the reference electrode were measured at 50% of the state-of-charge (SOC) after 1 and 10 cycles in EC-DEC and AFTB electrolytes. The high frequency semicircle represents the interfacial resistance and charge transfer resistance of LCO.^[45,46] Impressively, the resistance of the LCO cathode cycled in AFTB almost remains the same value after 10 cycles. However, it quickly increased from 20 Ω after 1st cycle to 58 Ω after 10 cycles when cycled in EC-DEC. The continuous increase of interfacial resistance in EC-DEC electrolyte demonstrates the continuous decomposition of electrolyte and the thickening of the CEI layer, and poor kinetics in the electrode. The stable resistance for the cell cycled in AFTB electrolyte indicates the high stability of the AFTB electrolyte and the CEI layer, as well as good kinetics of the electrode cycled in AFTB electrolyte. Furthermore, the cyclic voltammetry (CV) curves of LiCoO2 cathode in AFTB electrolyte and EC-DEC electrolyte were also compared in Figure S7 (Supporting Information). The first two CV curves in two electrolytes are almost overlapped, respectively, suggesting the excellent reversibility for the LiCoO2 cathode at the beginning of cycles. However, the CV curves after 50 cycles exhibit a huge difference between the AFTB electrolyte and the EC-DEC electrolyte. There was huge hysteresis of the redox reaction for LiCoO₂ cathode, and the O3 to H1-3 (4.5-4.6 V) redox reaction was even disappeared in the EC-DEC electrolyte. While the hysteresis of the redox reaction for LiCoO₂ cathode in AFTB electrolyte is very small, and the O3 to H1-3 (4.5-4.6 V) redox reaction was still in good reversible condition, demonstrating that the effective and robust CEI layer formed on LiCoO₂ cathode facilitates the structural stability of the bulk phase and holds the reversibility of the high-voltage phase transformation.

2.3. Structural and Phase Analysis of Cycled Single-Crystal ${\rm LiCoO_2}$

As the cycling stability of $LiCoO_2$ is strongly associated with its structural evolution, the dynamic evolution of the phase and

structure of single-crystalline LiCoO₂ cathode in AFTB electrolyte during the delithiation process was monitored by ex situ XRD measurement (Figure 3a,c). The (003) peak indicates the variation the of *c*-value, and Amatucci et al.^[47] have reported that the c-value changes significantly when Li ions were extracted from the LiCoO₂ cathode. Figure 3c shows the (003) peak evolution during the charging process to different voltages. The (003) peak was located at 18.4° , when the LiCoO₂ cathode was charged to 4.6 V, a small peak occurred at 19.3°, indicating that the LiCoO₂ cathode undergoes a phase transition from O3 to H1-3 between 4.5 and 4.6 V. As the voltage was charged to 4.8 V, the (003) peak shifted to 19.8°, indicating that the whole LiCoO₂ cathode changed into O1 phase. This irreversible hexagonal to cubic spinel phase transition, leading to the density of dislocation and internal strain increase, is detrimental to the reversibility of LiCoO₂ cathode at high voltage. The crystal structure evolutions of the LiCoO2 cathode during Li intercalation/extraction to different voltages (Figure S8, Supporting Information) were characterized using the ex situ XRD patterns, as presented in Figure S9 (Supporting Information). Details of the structural evolutions during cycling were monitored via the shifts of the selected peak at (003) (Figure S10, Supporting Information). As shown in Figure S10 (Supporting Information), the diffraction peak of (003) planes located at 18.4° first shift to a lower degree when charged to 4.3 V, and then shift to a higher degree when the cell was charged to 4.6 V, and a small peak occurred at 19.3°. Then, after discharge the cell, the diffraction peak of (003) planes gradually shift back to 18.4°, demonstrating good reversibility of the LiCoO₂ structure. Combining the electrochemical performance above in Figure 2, the LiCoO₂ cathode presents good reversibility when charged to 4.6 V in the AFTB electrolyte. The structure change of the LiCoO2 cathode at different cycles in EC-DEC and AFTB electrolytes was characterized using the XRD patterns. As presented in Figure 3b,d, the small peak at 19.3° occurred for the samples cycled in AFTB electrolyte after 10 and 50 cycles, while there is no peak at 19.3° for the samples cycled in EC-DEC electrolyte after 10 and 50 cycles, which reconfirmed that LiCoO₂ cathode cannot transfer to the H1-3 phase after cycling in the EC-DEC electrolyte.

Co dissolution is associated with the capacity decay in the LiCoO₂ cathode when it was charged to above 4.2 V. The transition metal dissolution is related to the stability of the CEI and cathode structure.^[48] The dissolved Co contents in EC-DEC and in AFTB electrolytes after different cycles were detected using an inductively coupled plasma atomic emission spectrometer (ICP-AES) (Figure 3e). Both electrolytes were collected after the LiCoO₂ cathode was charged/discharged 10, 50, and 100 times. The Co content is 105 ppm in the EC-DEC electrolyte, while only 7.2 ppm of the Co content is in the AFTB electrolyte. The high Co content in the EC-DEC electrolyte reveals the serious structural damage of LiCoO₂ cathode after cycling. There is very little Co content tested in the AFTB electrolyte, suggesting that the LiCoO₂ structure maintained good stability after 100 cycles. Oxygen loss is one of the critical reasons to trigger structural degradation from surface to core of the LiCoO₂ cathode.^[49] The gas evolution during cycling was investigated by operando monitoring cell pressure change using a home-built system. The cell pressure increased around 5% after 20 cycles in the EC-DEC electrolyte, while there were few increases for the www.advancedsciencenews.com

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Figure 3. Structure and phase study of single-crystalline $LiCoO_2$. a) The ex situ XRD patterns were collected during the 4th charging process of LCO electrode under 0.2 C. b) The XRD patterns of LCO electrode cycled in different electrolytes and different cycles. c) Selected region of the (003) planes collected in the charging process in (a). d) Selected region of the (003) planes collected in the patterns in (b). e) Contents of transition metal Co ions in different electrolytes after different cycle numbers. f) Pressure evolution of $LiCoO_2/Li$ cells containing different electrolytes cycled at 0.5 C in the voltage range of 3.0–4.6 V.

cell cycled in the AFTB electrolyte (Figure 3f). Further GC–MS experiments were carried out to detect gas composition after cycling. As displayed in Figure S11 (Supporting Information), a large amount of O_2 was detected for the cell cycled in EC–DEC electrolyte, while only a few detected for the cell cycled in AFTB electrolyte, suggesting the serious loss of lattice oxygen in the LiCoO₂ cathode when cycled in the EC–DEC electrolyte. Meanwhile, the CO₂ intensity of the cell cycled in the EC–DEC electrolyte is very strong, meaning that the EC–DEC carbonate electrolyte experienced intense decomposing during the cycling process. In summary, the robust and efficient CEI layer formed on the LiCoO₂ cathode surface in the AFTB electrolyte largely avoided Co element dissolution and O₂ gas release during cycling, enhanced the surface structure stability, and stabilized the LiCoO₂ cathode structural stability.

2.4. Characterization of CEI on the Single-Crystal LiCoO2

When charged to a high voltage of 4.6 V, the $LiCoO_2$ cathode will be exposed to the risk of accumulation of high stress inside the bulk phase, and even lead to structural damage and cracks. To prevent the electrolyte penetration into the cracks enabling reversible structural change of the single-crystalline $LiCoO_2$, a robust and efficient CEI layer has to be formed on the $LiCoO_2$ surface. The surface of $LiCoO_2$ cathodes before and after 100 cycles in the potential range of 3.0–4.6 V were characterized by scanning electron microscopy (SEM) and TEM (Figure 4a–f

and Figure S12 (Supporting Information)). The surface of pristine LiCoO₂ particles before cycling is clean and smooth (Figure S12, Supporting Information). After 100 cycles in the EC–DEC electrolyte, serious cracks are observed in the SEM pattern, the thickness of CEI layer is more than 20 nm in the TEM pattern, and the cycled LiCoO₂ cathode shows deteriorated crystallinity in the SAED pattern (Figure 4a–c). While for the LiCoO₂ cathode that was cycled in AFTB electrolyte for 100 cycles, there are no cracks presented in the SEM, the CEI layer thickness is only 8.5 nm in the TEM, and the cycled LiCoO₂ cathode presents good crystallinity in the SAED (Figure 4d–f).

The more detailed morphology and structure of the CEI formed in the AFTB electrolyte was further characterized by TOF-SIMS. As presented in Figure 4g, the edge surface of the crater shows an explicit etching layer of around 252.6 nm thickness after sputtering with a Ga⁺ ion beam (5 μ m × 5 μ m area). The negative species were chosen to analyze the components of the CEI layer, including F (m/z = 19), and O (m/z = 16). The chemical mappings are displayed in Figure 4h and Figure S13 (Supporting Information). The F signal was found within the top 10 nm surface layer, and the O signal was increased with the depth of the etching layer. Figure 4i presented the depth profiles of the negative modes. The decrease of the F signal indicates the thickness of the CEI layer, which contained the LiF component. The low O signal intensity at the beginning of sputtering originated from the oxygen compounds in the CEI layer, indicating the low content of organic oxygen compounds in the CEI layer, while the O signal reaches a steady state after

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Figure 4. Morphology of the cycled single-crystalline $LiCoO_2$ and characterization of CEI layer. a,d) SEM images of LCO electrode after 100 cycles in EC–DEC electrolyte (a) and in AFTB electrolyte (d). b,e) TEM images of LCO electrode after 100 cycles in EC–DEC electrolyte (b) and in AFTB electrolyte (e). c,f) SAED images of LCO electrode after 100 cycles c) in EC–DEC electrolyte and f) in AFTB electrolyte. The interface analysis of the LCO cathode after 100 cycles in AFTB electrolyte by TOF-SIMS. g) Crater image of around 252.6 nm by a Ga⁺ ion beam, and h) the corresponding F⁻ element distributions in the sputtered cross section. i) TOF-SIMS depth profiles of F⁻ and O^{2–} species in CEI layer.

50 nm of sputtering. All of the O signals come from the lattice oxygen in the LiCoO₂ cathode bulk phase.

The CEI compositions formed in the EC-DEC and AFTB electrolytes were characterized by in-depth XPS with continuous Ar-ion sputtering from the CEI surface to the bottom. Figure 5a-f displays the CEI composition on the LiCoO₂ cathodes after 100 cycles in the potential range of 3.0-4.6 V in EC-DEC and AFTB electrolytes before sputtering. For the CEI formed in AFTB electrolyte, a strong LiF bond (686.1 eV) is observed, and the atomic ratio change of LiF is steady at 23% during the sputtering process, demonstrating the robust and effective composition of LiF in the CEI layer. Also, the organic fluorides (CF_x and $Li_x PF_v O_z$, organic-F bond) decrease quickly during the sputtering process (Figure 5h), illustrating that the outlayer of CEI has a higher ratio of organic composition due to the decomposition of solvent. Meanwhile, for the F signal in the EC-DEC electrolyte, the typical LiF peak is much lower than the organic-F bond. Moreover, the C spectrum ratio in EC-DEC electrolyte (55%) is much higher than that in AFTB electrolyte (42%), which means that a high organic composition in the CEI was formed in EC-DEC electrolyte. This is because the EC-DEC carbonates are oxidized at a high potential and contribute more organic compounds to the CEI layer compared with the designed AFTB electrolyte. Furthermore, the fitted B 1s spectra and Si 2p spectra are presented in Figure S15 (Supporting Information), demonstrating the decomposition of the TMSB additive. Its corresponding products were contributed to the CEI of the LiCoO₂ cathode. Also, the bond energy of B-O (806(5) kJ mol⁻¹) and Si-O (798(8) kJ mol⁻¹) is much higher than Co-O (368(21) kJ mol⁻¹),^[6] indicating that the decomposed TMSB additive stabilizes the structure of LiCoO₂ during the cycling process. Combining the TEM, TOF-SIMS, and XPS results, a robust, dense, and thin CEI layer formed on the cycled LiCoO₂ cathode in the AFTB electrolyte. The CEI layer is composed of B- and Si-compounds and F-rich inorganic composition. Such a kind of in situ-formed CEI layer will not reduce the ion-transport kinetics, owing to the lower energy barrier for Li+ surface diffusion (0.17 eV)^[50] and the thin thickness CEI layer







Figure 5. The CEI chemical composition on the single-crystalline $LiCoO_2$ cathode surface. a–f) The typical elemental F 1s, O 1s, and C 1s spectra by XPS measurement of the CEI layer formed in the EC–DEC electrolyte (a–c) and the AFTB electrolyte (d–f). g,h) The atomic composition ratios by XPS measurement of the CEI layer formed in the EC–DEC electrolyte (g) and the AFTB electrolyte (h). The cycled $LiCoO_2$ cathodes were transferred under an inert Ar atmosphere to avoid any contamination by air or moisture.

(Figure 4e) as well as its intimate contact with $LiCoO_2$ cathode. As a result, this robust, dense, and thin LiF-rich CEI cooperated with B- and Si-compounds facilitate the reversible phase transformation of $LiCoO_2$ cathode, maintaining good cycling stability when charged to a high voltage of 4.6 V, and inhibit the Co dissolution and O loss during the cycling process.

2.5. LiCoO₂//Graphite Full Coin Cell and Pouch Cell Performance

Figure 6a presents the galvanostatic charge–discharge profiles of the graphite anode at different cycles in the AFTB electrolyte. The areal capacity of the graphite electrode is around 4 mA h cm⁻². In the AFTB electrolyte, graphite delivered \approx 345 mA h g⁻¹ reversible capacity in G/Li half-cells at the current density of 0.5 C (1 C = 372 mA g⁻¹; note that all cells were cycled at 0.1 C for the formation process at the first three cycles) with a high CE of 99.8% after 3 cycles. Moreover, extremely high capacity retention of 98.5% after 200 cycles was exhibited (Figure 6b), and a capacity retention of 90.5% was achieved after 400 cycles (Figure S16, Supporting Information). The optimized AFTB electrolyte presented good stability to the graphite anode.

The LiCoO₂//graphite coin cells were fabricated at a low N/P capacity ratio of 1.1 based on the specific capacities of LiCoO₂ and graphite as 225 and 345 mA h g⁻¹, respectively. As presented in Figure 6c, the LiCoO₂//graphite full cell delivered a specific capacity of 111 mA h g⁻¹ after 3 cycles of formation, calculated based on the total active materials of both the LiCoO₂ cathode and graphite anode. The initial Coulombic efficiency of the LiCoO₂//graphite full cells reaches 875%. The





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Figure 6. Electrochemical performance of the single-crystalline $LiCoO_2//graphite$ full cells. a) Galvanostatic charge–discharge profiles of graphite electrode with different cycles at 0.5 C in the AFTB electrolyte. b) Cycle performance of the graphite electrode at 0.5 C in the AFTB electrolyte. c,e) The galvanostatic charge–discharge curves of single-crystalline $LiCoO_2//graphite$ full cells in the AFTB electrolyte with coin cell (c), and pouch cell (e). d,f) Cycle performance of the single-crystalline $LiCoO_2//graphite$ coin cell (d) and pouch cell (f) in the AFTB electrolyte. The coin cell capacity for (c,d) is calculated based on the total active materials of both the $LiCoO_2$ cathode and graphite anode.

high operating voltage (3.86 V) and high capacity of $LiCoO_2//$ graphite cells ensure a high energy density of 430 W h kg⁻¹ (active materials of anode and cathode) with excellent cycle stability of 80% capacity retention after 500 cycles (Figure S17a, Supporting Information). Moreover, the average CE from 10 to 500 cycles is 99.91%, indicating that the side reaction was inhibited during the cycles. The galvanostatic charge–discharge profiles of the $LiCoO_2//graphite$ full cell at the rate of 0.5 C based on coin cell are presented in Figure 6d. The normalized 5th

and 50th charge–discharge curves overlap well in Figure S17b (Supporting Information), exhibiting high structural stability and phase transformation reversibility in the whole charge–discharge process. The much higher cycling stability of the $LiCoO_2//graphite$ full cells compared with the $LiCoO_2//Li$ half-cells in Figure 2b also indicates that Li metal will reduce the cycling stability at a high cathode loading due to the unsatisfied Coulombic efficiency which consumes the Li and electrolyte.^[51] We also examined the cycled $LiCoO_2$ cathode morphology with



SEM. As presented in Figure S18 (Supporting Information), only a small gliding is observed in the large $LiCoO_2$ particles, and no obvious fracture in the particles is observed in this electrode. Therefore, the single-crystalline $LiCoO_2$ electrode is also reversible when charged to 4.5 V (vs graphite). Moreover, the gliding of the $LiCoO_2$ particles is also reversible, and there is no obvious detrimental effect from this small gliding of the $LiCoO_2$ particle on the cycling performance of the full cell.

For practical applications, full pouch cells (≈120 mA h) with the areal capacity of 4 mA h cm⁻² were assembled and cycled at room temperature in the voltage range of 3.0-4.5 V. As shown in Figure S19 (Supporting Information), the capacity of the LiCoO₂//graphite pouch cell in EC-DEC electrolyte fades quickly with only 27.3% of the capacity retention after 100 cycles. The average Coulombic efficiency is less than 99%. By contrast, as presented in Figure 6f, the same pouch cell cycled in AFTB electrolyte kept 77.5% of the capacity after 200 cycles, which is higher than the reported pouch cells in Table S2 (Supporting Information). The pouch cell cycled in AFTB electrolyte presents a much higher Coulombic efficiency (99.81%) than that (99%) of the cell cycled in EC-DEC electrolyte. Also, the galvanostatic charge-discharge profiles of the LiCoO₂//graphite pouch cell at the rate of 0.3 C are presented in Figure 6e, the clear charging platform at 4.45 V is due to the slow rate of 0.3 C and higher test pressure in pouch cell. The normalized 5th and 50th charge-discharge curves overlap well in Figure S17c (Supporting Information). Furthermore, the discharge mid voltage remains almost unchanged at around 3.85 V for the cell cycled in AFTB electrolyte, while it gradually drops to 3.58 V for the cell cycle in EC-DEC electrolyte (Figure S20, Supporting Information). The seriously degraded cycle performance of the LiCoO₂//graphite full cell in EC-DEC electrolyte can be attributed to the side reactions and structural degradation of the active materials induced by surface reaction and electrolyte penetration into the crack during the cycling process. While cycled in AFTB electrolyte, a robust, dense, and thin CEI layer formed on the surface of LiCoO₂ cathode as well as an effective SEI formed on the surface of the graphite anode to prevent the side reaction. The more robust SEI on graphite and CEI on LCO in AFTB electrolyte than those in EC-DEC electrolyte also evidenced less gas emission in AFTB electrolyte than in EC-DEC electrolyte during the cycling process (Figure S21, Supporting Information). In addition, the dissolution of Co into the electrolyte is also well suppressed, demonstrating that the LiCoO₂ structure is well preserved. Therefore, the robust CEI and SEI enable LiCoO₂//graphite cell in AFTB electrolyte to achieve super-electrochemical performance than that in EC-DEC electrolyte in a large cutoff voltage.

3. Conclusions

All-fluorinated electrolytes (1 \mbox{M} LiPF₆ in FEC/FEMC/TTE + 2 wt% TMSB) with TMSB additive enable single-crystalline LiCoO₂ to form a robust, dense, and thin CEI layer on the single-crystalline LiCoO₂ particle surface. The CEI layer is composed of B- and Si-compounds and has F-rich inorganic composition, which enables reversible planar gliding and microcracking in the single-crystalline LiCoO₂ cathode at a

high voltage of 4.5–4.6 V, and inhibits the Co/O element loss during cycling. The fabricated 4.5 V high loading (4 mA h cm⁻²) LiCoO₂//graphite full cell delivered an energy density of 430 W h kg⁻¹ (based on the cathode and anode active materials) with an excellent capacity retention of 80% after 500 cycles. This work proves that a stable CEI facilitates structural stability of the cathode materials even at a high cutoff voltage, providing a pathway to the design of high-performance cathode materials.

4. Experimental Section

Material Preparation and Electrode Preparation: The single-crystal LiCoO₂ was purchased and used as obtained. A slurry was prepared at room temperature by mixing of active material, carbon black, and binder (poly(vinylidene fluoride)) with a mass ratio of 90:5:5, and dissolved in N-methyl-1,2-pyrrolidone solution. The slurry then was coated in a current collector (aluminum or copper foil) and dried at 100 °C overnight in a vacuum oven. The loading masses of the active materials for the electrode were \approx 18 mg cm⁻² (LiCoO₂ cathode) and 12 mg cm⁻² (graphite anode), respectively. The all-fluorinated electrolyte solution comprised 1 м LiPF₆ in fluoroethylene carbonate/methyl (2,2,2-trifluoroethyl) carbonate/1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropylether (FEC/ FEMC/TTE) (2:6:2 by volume) with TMSB (purchased from Sigma) additive (the optimized electrolyte was denoted as AFTB). The conventional electrolyte solution comprised 1 м LiPF₆ in EC/DEC (1:1 by volume) [denoted as EC-DEC]. The LiCoO2//graphite pouch cells were fabricated at a low N/P capacity ratio of 1.1 based on the specific capacities of LiCoO₂ and graphite as 225 and 345 mA h g^{-1} , respectively. The electrolyte amount added to the pouch cell was 3 g $(Ah)^{-1}$, the pouch cell was fixed in the fixture with a pressure loading as 1 MPa.

Material Characterization: The phases and crystallographic structures of the materials were characterized by powder XRD on a Bruker Smart1000 diffractometer (Bruker AXS Inc., USA) using Cu K α radiation. Rietveld refinement was performed using the TOPAS software. The morphologies of the sample were examined using a Hitachi SU-70 fieldemission scanning electron microscope and a JEOL 2100F field-emission transmission electron microscope. The ICP-AES was used to measure the Co content in the different electrolytes, they were determined by an ICPE-9000 (ICP Atomic Emission Spectrometer). The manufacturer is Shimadzu ICPE-9000. The GC-MS test was measured with JEOL JMS-700 MStation. It is a double-focusing magnetic sector mass spectrometer and is coupled with an Agilent 6890N GC system. The surface chemistry of the electrodes after cycling was examined by XPS with a Kratos Axis 165 spectrometer. The cycled coin cells were disassembled, and the electrodes were washed by 1,2-dimethoxyethane 3 times and dried under vacuum overnight before testing. The above operations were performed in the glove box. The XPS samples were transferred into the XPS chamber under argon-filled transformation bag to avoid any contamination by air. XPS data were collected with a monochromated Al K α X-ray source (1486.7 eV). The working pressure of the chamber was lower than 6.6×10^{-9} Pa. All reported binding energy values were calibrated to the C 1s peak at 284.8 eV. Quantification was done using casaXPS with relative sensitivity factors from the Kratos vision library. According to the casaXPS guideline, the FWHM was set as 2.0, and the range of full width at half maximum (FWHM) constraint was (1.9, 2.1). Some variation (≈10% of the FWHM) might be justified among different peaks due to small secondary effects.^[52] The TOF-SIMS attached with a Ga⁺ focused ion beam (FIB)/scanning electron microscope (Tescan GAIA3) was employed to analyze the elemental distributions in-depth and the accelerated voltage for FIB/SEM was 30 kV.

Density Functional Theory (DFT) Calculation: DFT calculations of the HOMO and the lowest unoccupied molecular orbital (LUMO) were performed with the GAUSSIAN 09 software package with a basis set of 6-311++G(d,p).

Electrochemical Measurements: The cells were assembled with a polypropylene microporous film (Celgard 3501) as the separator.





The electrochemical tests were performed with a coin-type cell (CR 2032), which was assembled in an argon-filled glove box with O_2 and moisture content lower than 1ppm. The pouch cells were assembled with an area of 30 cm². Electrochemical performance was tested with a Land testing system (Wuhan China). The half-cells (full cells) were charged/discharged between a voltage range of 3.0-4.6 V (3.0-4.5 V) and three formation cycles at C/10 were first conducted before a long-term cycling at a higher current density of C/2. For the full cells, the voltage of anode graphite was usually 0.1 V versus Li/Li⁺, therefore, 4.5 V was used as the cutoff voltage of the full cell. The LSV, CV, and EIS with different scan rates or voltage ranges were all conducted on a CHI 600E electrochemical workstation (CH Instruments Inc. USA). The GITT was tested at 0.1 C for 0.5 h with 10 h relaxation time between each pulse.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

J.Z. and P.-F.W. contributed equally to this work. J.Z., P.-F.W., and C.W. conceived the idea of the study. J.Z. and P.-F.W. prepared the materials and conducted the electrochemical experiments. P.-F.W. performed the TEM and scanning transmission electron microscopy (STEM) tests, X.P. helped with the HOMO and LOMO calculations, S.H. helped with the ICP tests, J.X. helped with the in situ gas pressure test. P.B., H.W., S.L., J.X., W.Z., Z.W., B.N., X.Z., and J.X. analyzed the data and discussed the results. J.Z., P.-F.W., J.X., and C.W. wrote and revised the paper, and all the authors contributed to the interpretation of the results.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

high-voltage $\rm LiCoO_2$ cathodes, inorganic-rich cathode electrolyte interphase, nonflammable electrolytes, single-crystalline cathodes

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