

Supplementary Information

Lithium Salt Derived Artificial Near-surface Reconfiguration to Stabilize High-Voltage LiCoO₂

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1. Experimental section

Synthesis of B/F@LCO

The B/F@LCO was synthesized by solvothermal-assisted method and calcination treatment. The calculated amount of commercial LiCoO_2 (99%, Guangdong Canrd New Energy Technology Co.,Ltd) and LiDFOB (99%, Aladdin) dissolved in absolute ethanol until it was completely dried. The collected mixture was transferred to a tube furnace filled with Ar, and heated to 600 °C at a rate of 5 °C/min for 3 hours. Finally, the modified LCO samples were obtained, and named as B/F@LCO.

Material Characterizations

Crystal structure of the samples was performed on X-ray diffraction (XRD, Rigaku UltimaIV diffractometer), and the X-ray diffraction measurements were fitted with Cu-K α X-rays ($\lambda = 1.5406$ Å). Elemental oxidation state and composition were analyzed by X-ray photoelectron spectrometer (XPS, Thermo Fisher Scientific K-Alpha) with an Al-K α radiation. All spectra energies were calibrated by standard C 1s peaks at 284.8 eV. Morphologies of samples were obtained by scanning electron microscopy (SEM, ZEISS GeminiSEM 500) and transmission electron microscopy (TEM, F30). The content of Co in the sample was analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES, Spectroblue FMX36). X-ray Absorption Spectra (XAS) measurements were performed at the Shanghai Synchrotron Radiation Facility. The cross-section of the sample was processed with a three-ion beam cutting instrument (Leica EM TIC 3X).

Electrochemical Measurements

Active material, Super-P, and polyvinylidene fluoride (PVDF) at a weight ratio of 80:10:10 were mixed in N-methyl pyrrolidine (NMP) solvent evenly to form slurry. The prepared slurry was uniformly coated on an aluminum (Al) foil collector and dried in a vacuum oven at 100 °C for 12 hours. The mass loading of each electrode is about 3~5 mg cm⁻². The electrolyte composition is 1 M LiPF_6 in ethylene carbonate/dimethyl carbonate (EC/EMC, 3:7 in weight) with the addition of 10% fluoroethylene carbonate (FEC). The entire process of battery assembly takes place in a glove box filled with Ar. All the half-cells were evaluated using a Land CT3002A system at 30 °C. All electrochemical tests were performed in constant current mode. As for long-term cycling tests, the cells were charged and discharged at 0.1 C (1 C=200 mA g⁻¹) for the first two formation cycles within a voltage range of 2.7-4.5 V (vs. Li/Li^+) or 2.7-4.6 V (vs. Li/Li^+). Rate performance is accomplished at various currents of 0.1 C, 0.3 C, 0.5 C, 1 C, 3 C and 5 C. The galvanostatic intermittent titration technique (GITT) measurements were performed at a current density of 0.1 C for the first cycle under the current density of 0.1 C, with charging step of 600 s and relaxation step of 1 h. Electrochemical impedance spectroscopy (EIS) tests were measured on an electrochemical workstation (CHI760E, Shanghai Chenghua, China).

2. Figures

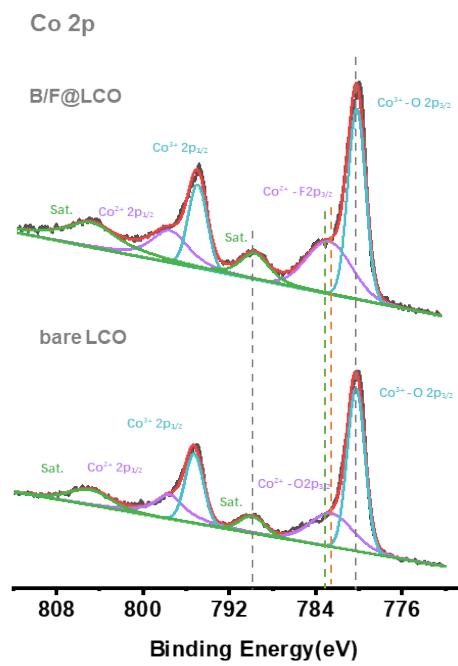


Fig. S1 XPS spectra of Co 2p in the bare LCO and B/F@LCO.

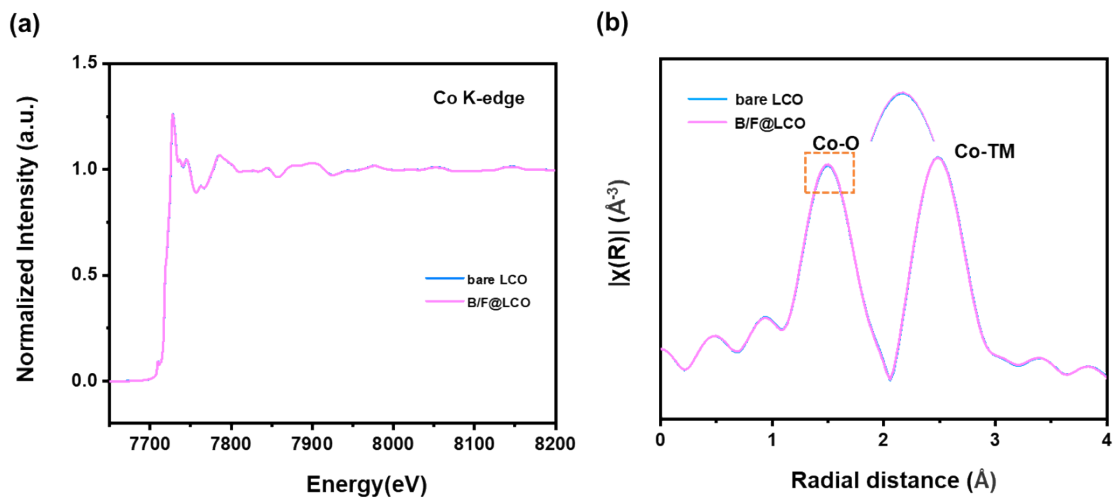


Fig. S2 (a) The Co K-edge XAS spectra and (b) Radial distribution functions (RDF) derived from EXAFS data of bare LCO and B/F@LCO sample.

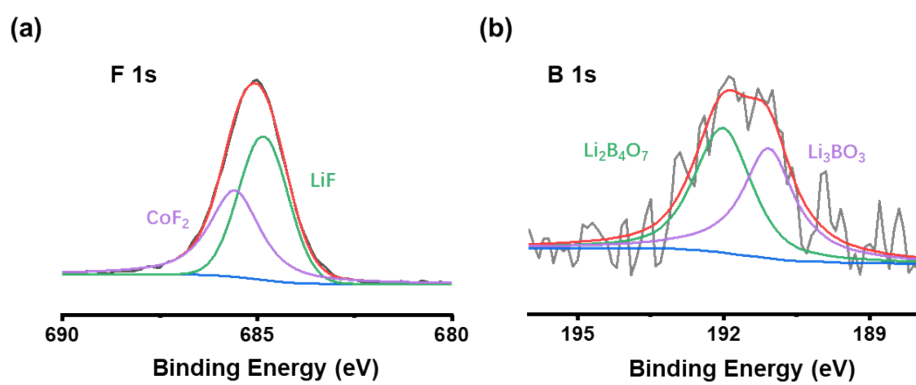


Fig. S3 (a) F 1s and (b) B 1s XPS spectra of B/F@LCO.

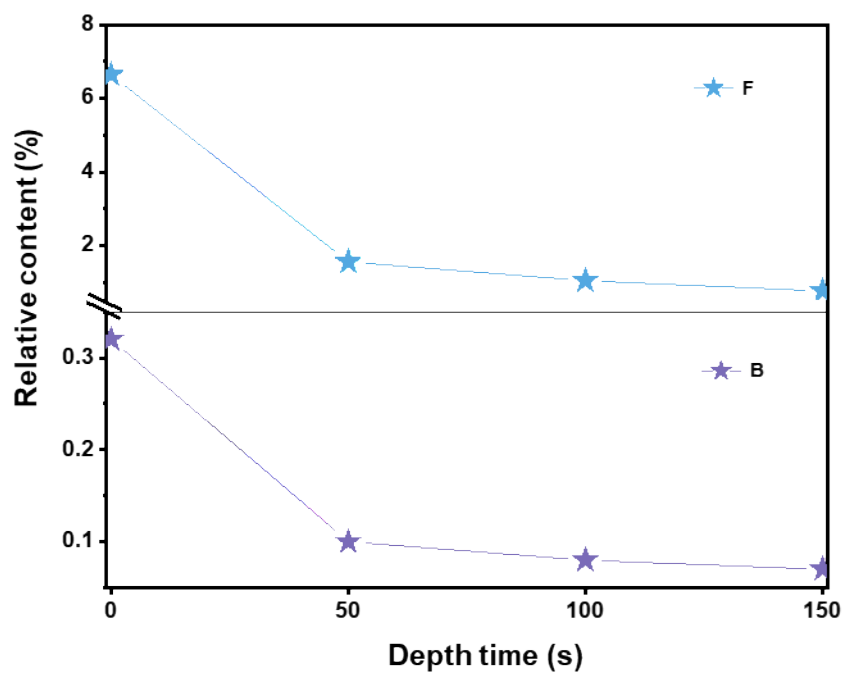


Fig S4 Illustration of the relative content of F and B as a function of the etching time.

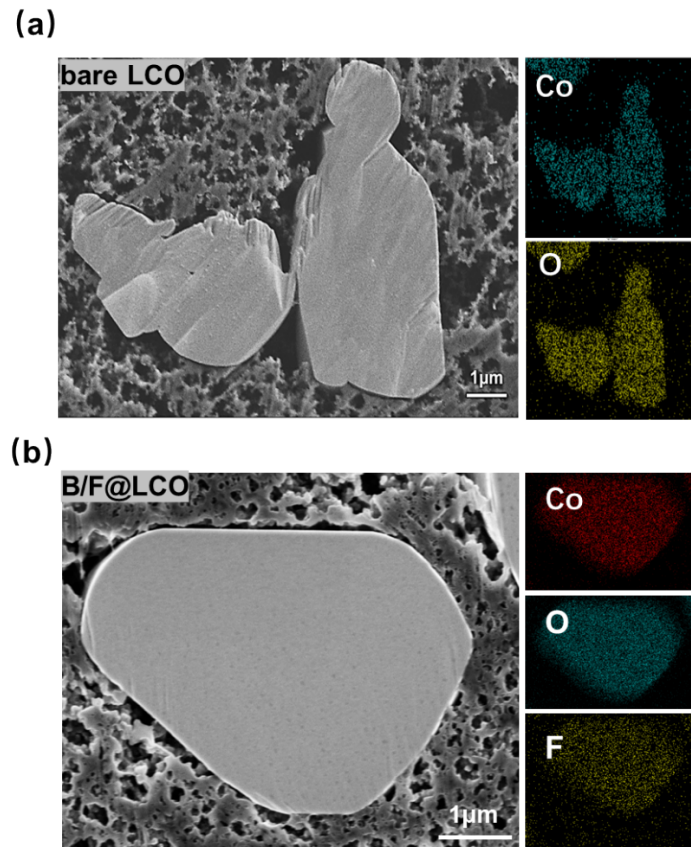


Fig. S5 The EDS elemental mappings of the cross section for (a) bare LCO and (b) B/F@LCO.

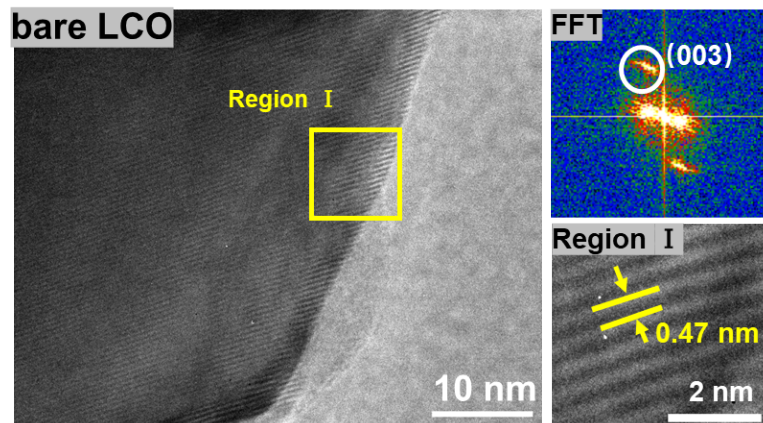


Fig. S6 HRTEM images and FFT results in region I of bare LCO.

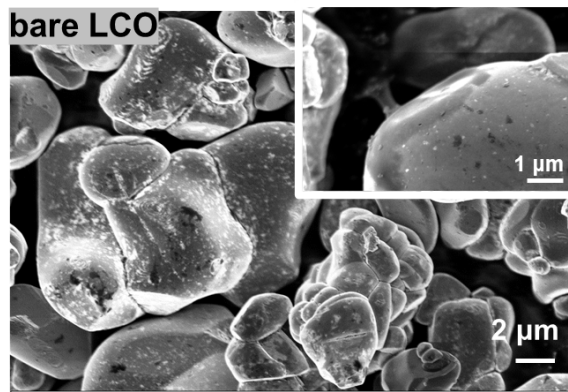


Fig. S7 SEM images and corresponding enlarged images of bare LCO.

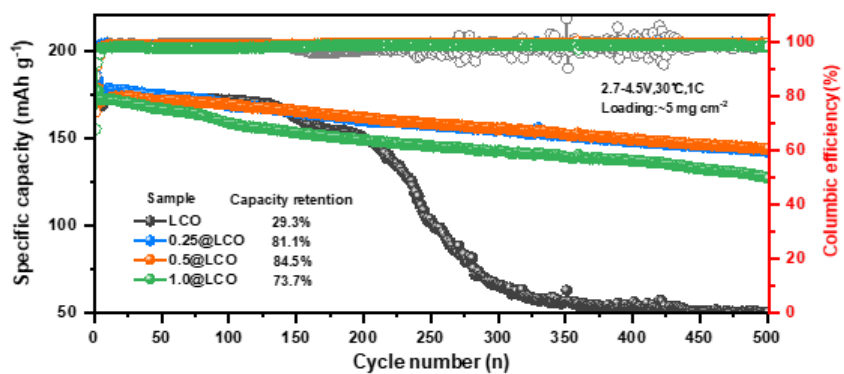


Fig. S8 Comparison of the cycle stability curves of LCO with different coating weigh at 1 C in the voltage range of 3.0–4.5 V (vs. Li/Li⁺) at 30 °C.

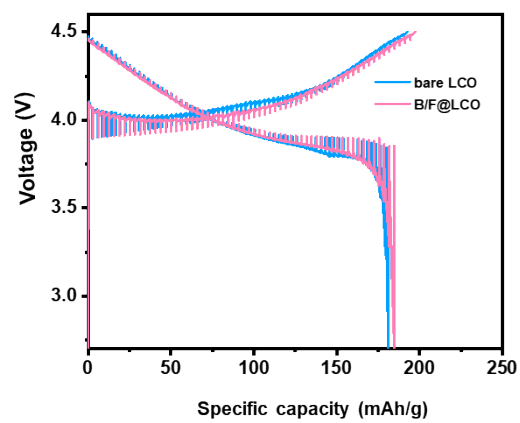


Fig. S9 GITT curves of LCO and B/F@LCO.

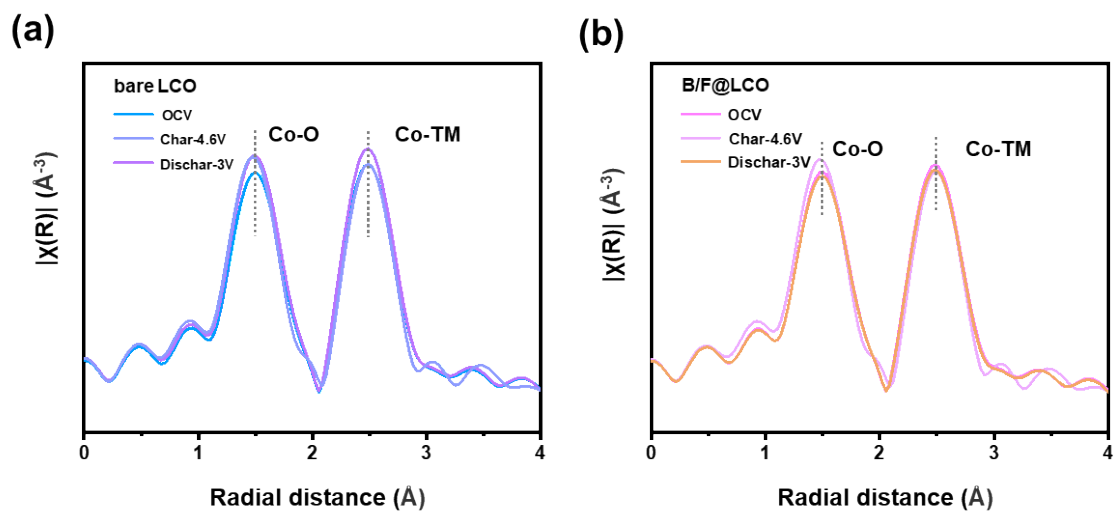


Fig. S10 Co K-edge EXAFS R space curves of (a) bare LCO and (b) B/F@LCO at different states.

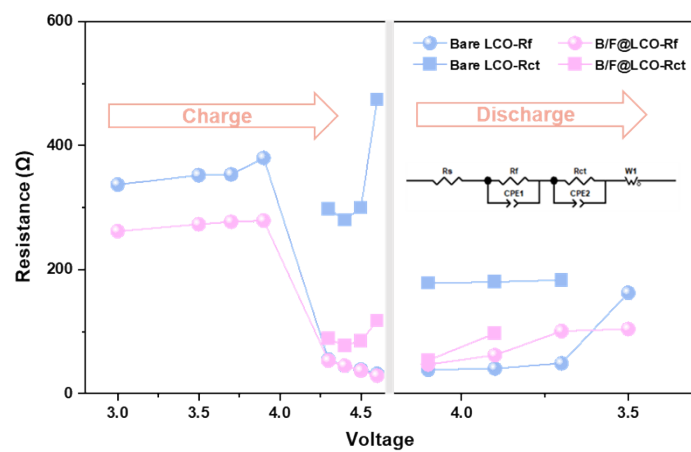


Fig. S11 Corresponding fitting of R_f and R_{ct} according to the in-situ EIS results, and the small diagram is equivalent circuit.

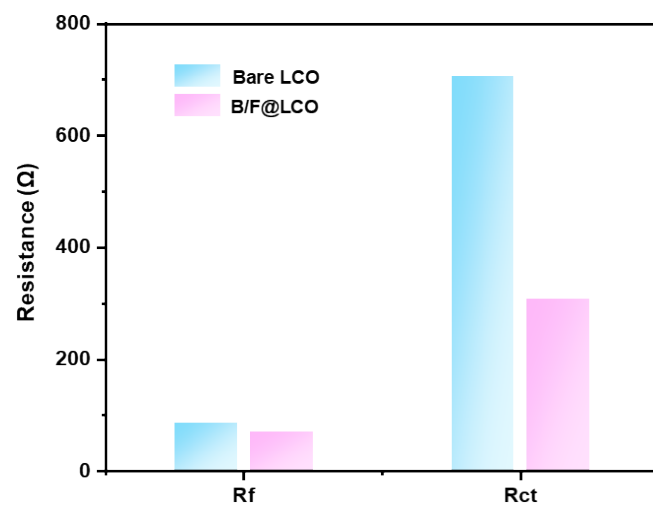


Fig. S12 Corresponding fitting of R_f and R_{ct} according to the EIS result.

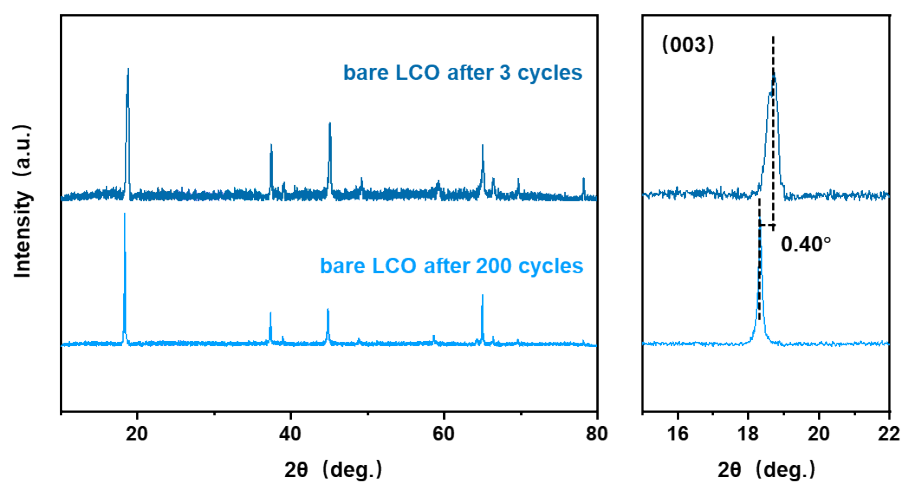


Fig. S13. XRD patterns for bare LCO after 3rd and 200th cycled.