

## Electronic Supplementary Information (ESI)

# Janus *In-Situ* Formed CoO/Li<sub>2</sub>CO<sub>3</sub>/LiF Interlayer Between LiCoO<sub>2</sub> and Li<sub>6</sub>PS<sub>5</sub>Cl Solid Electrolytes Boosting the 4.5 V Performance of Sulfide-Based All-Solid-State Batteries

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## **Experimental details**

### ***Preparation of the Materials***

Xiamen Tungsten Co., Ltd (XTC) supplied the LiCoO<sub>2</sub>. Polyvinylidene fluoride (PVDF) was purchased from Shenzhen Kejing Zhida Technology Co., Ltd. Indium foils (0.05 mm in thickness) were purchased from Tengfeng Metal Materials Technology Co., Ltd. Solid electrolytes (Li<sub>6</sub>PS<sub>5</sub>Cl (LPSCl)) were purchased from Hefei Kejing Materials Technology Co., Ltd. Lithium (99.99% purity, 50 mm in thickness) was brought from China Energy Lithium Co., Ltd.

### ***Electrochemical tests***

Using the battery testing system (LAND, Wuhan) at room temperature (25 °C), the galvanostatic discharge/charge tests of ASSLBs with LCO cathodes were conducted within a potential range of 2.6-4.3 V vs. Li<sup>+</sup>/Li, with 1C defined as 120 mA g<sup>-1</sup>. For high voltage test conditions, potential ranges of 2.6-4.5 V vs. Li<sup>+</sup>/Li were applied, maintaining 1C as 120 mA g<sup>-1</sup>. The GITT curves of ASSLBs were obtained with a 20-minute discharge at 0.1 C followed by a 2-hour relaxation period. Electrochemical impedance spectroscopy (EIS) of ASSLBs was performed using an Autolab workstation (Wantong, Switzerland) with a frequency range from 3500 Hz to 0.01 Hz and an AC perturbation signal of 5 mV.

### ***Materials characterization***

Powder X-ray diffraction (XRD) was performed using a Rigaku Ultima IV with a Cu K $\alpha$  radiation source. Samples were scanned over a 2 $\theta$  range of 5° to 90° at a scan speed of 1° min<sup>-1</sup>. A scanning electron microscope (SEM, TESCAN MIRA4) was used to observe the morphology of the cathodes before and after reduction. A high-resolution transmission electron microscope (HRTEM) was employed to study the CoO/Li<sub>2</sub>CO<sub>3</sub>/LiF layer on the surface of LCO at an accelerating voltage of approximately 200 kV. Prior to TEM observation, thin sections of the PVDF-LCO particles were prepared using the Focused Ion Beam (FIB) technique. Surface components of the samples were analyzed using a PHI5000 Versaprobe III electron spectrometer (X-ray photoelectron spectroscopy, XPS). Al K $\alpha$  monochromatized radiation (h $\nu$  = 1486.6 eV) was used as the X-ray source. The surface of the specimen was sputtered by inert gas ion bombardment at a sputter rate of 15 nm (using SiO<sub>2</sub> as the standard reference) each time, and spectra were subsequently collected from the center of the etched area.

## Supplementary figures

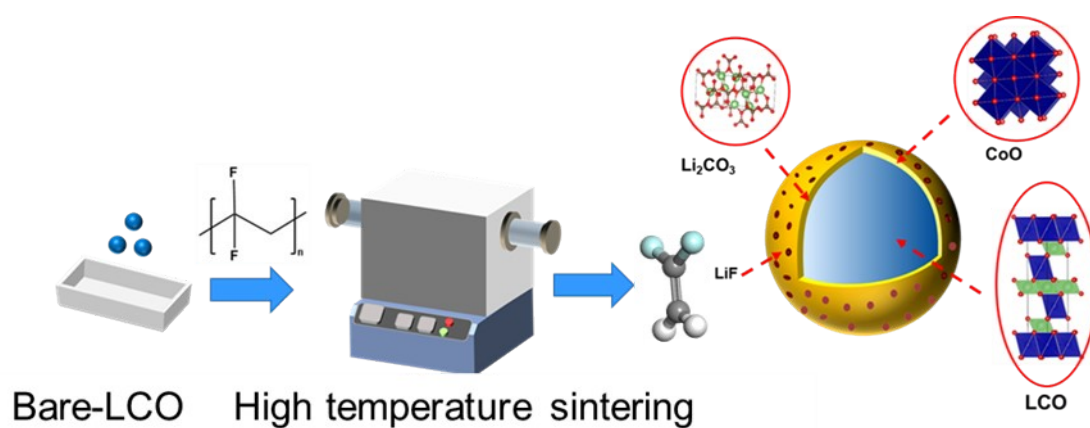
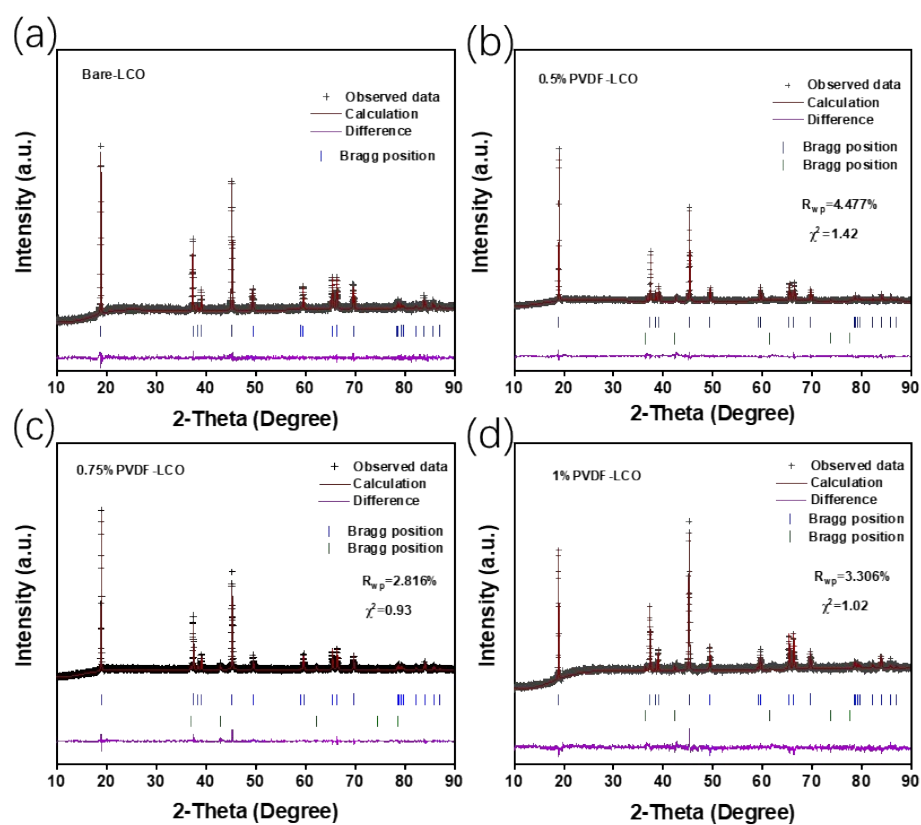
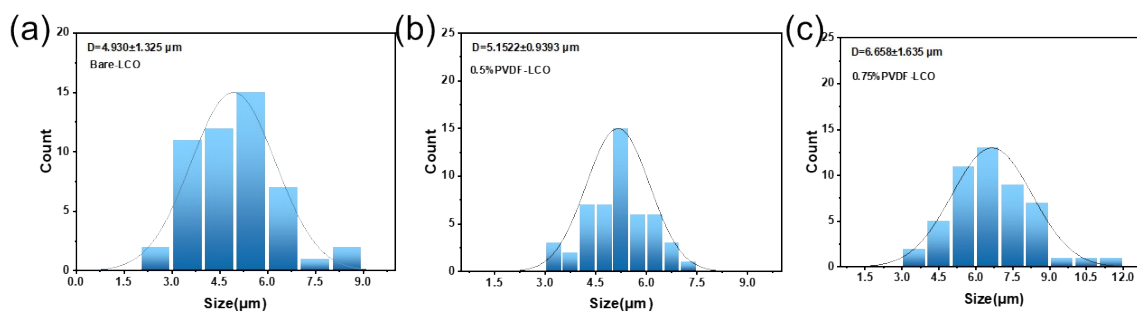


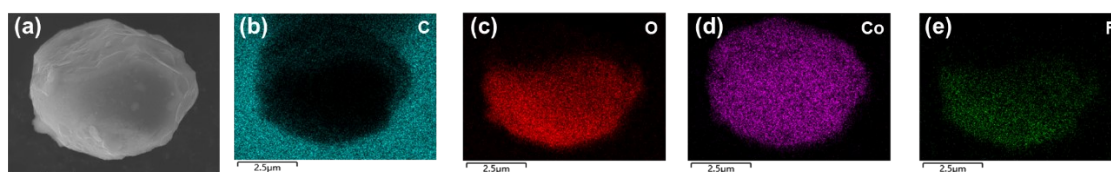
Figure S1. The preparation process of PVDF-LCO.



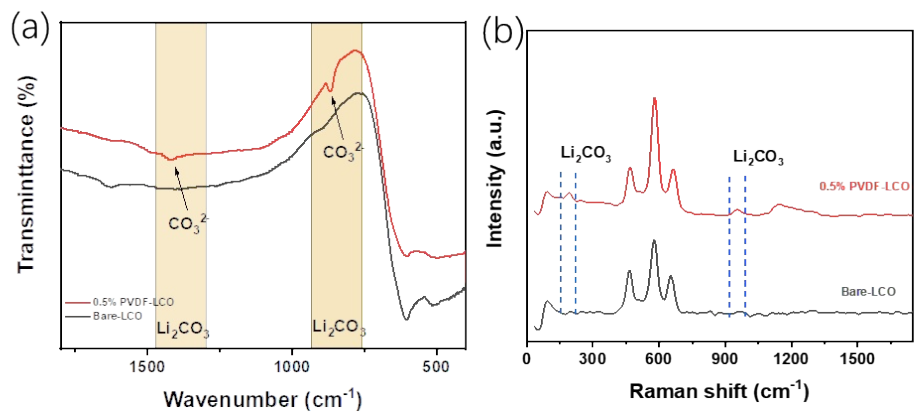
**Figure S2.** Rietveld refinement on the XRD data of LCO.



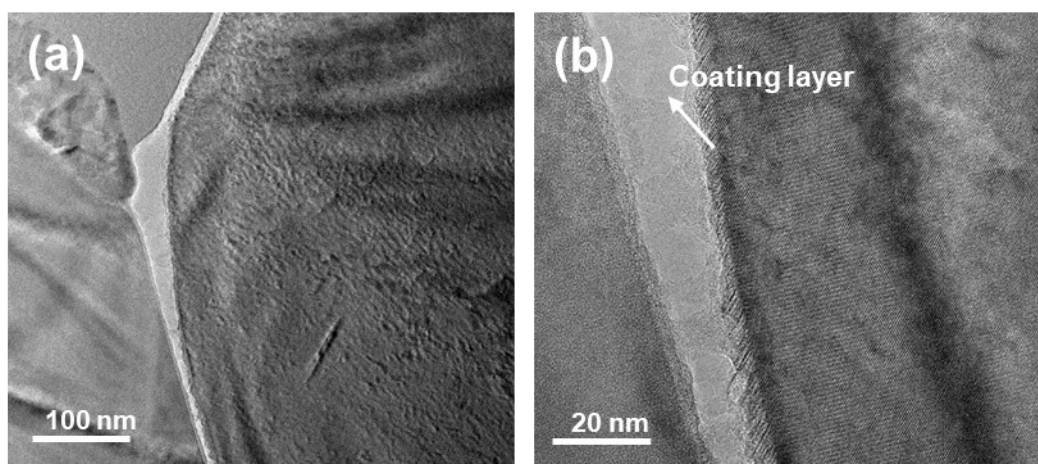
**Figure S3.** Bare-LCO and PVDF-LCO particle size analysis.



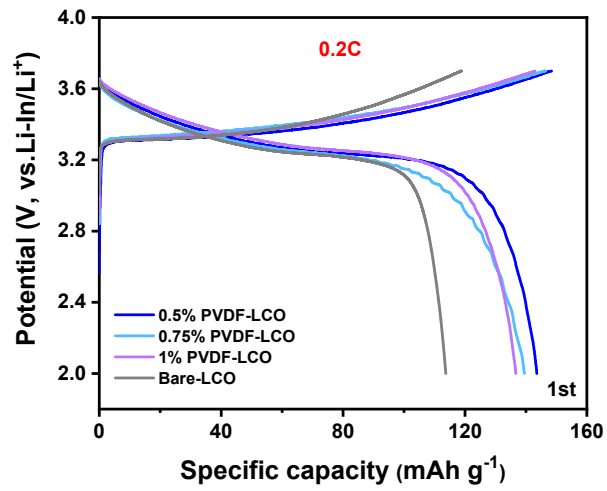
**Figure S4.** SEM-EDS images of 0.5%-PVDF-LCO. a is the total elemental distribution. b, c, d and e are the elemental distributions of C, O, Co and F, respectively.



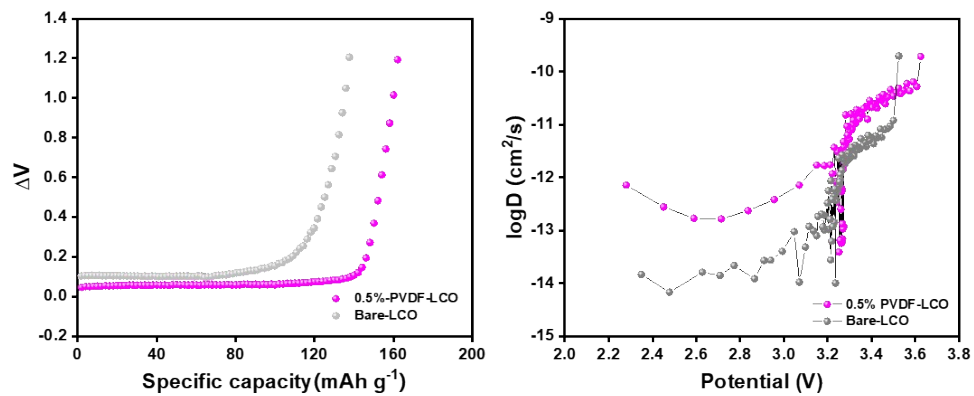
**Figure S5.** a, b are the FTIR spectra and Raman spectra of Bare-LCO and 0.5%-PVDF-LCO.



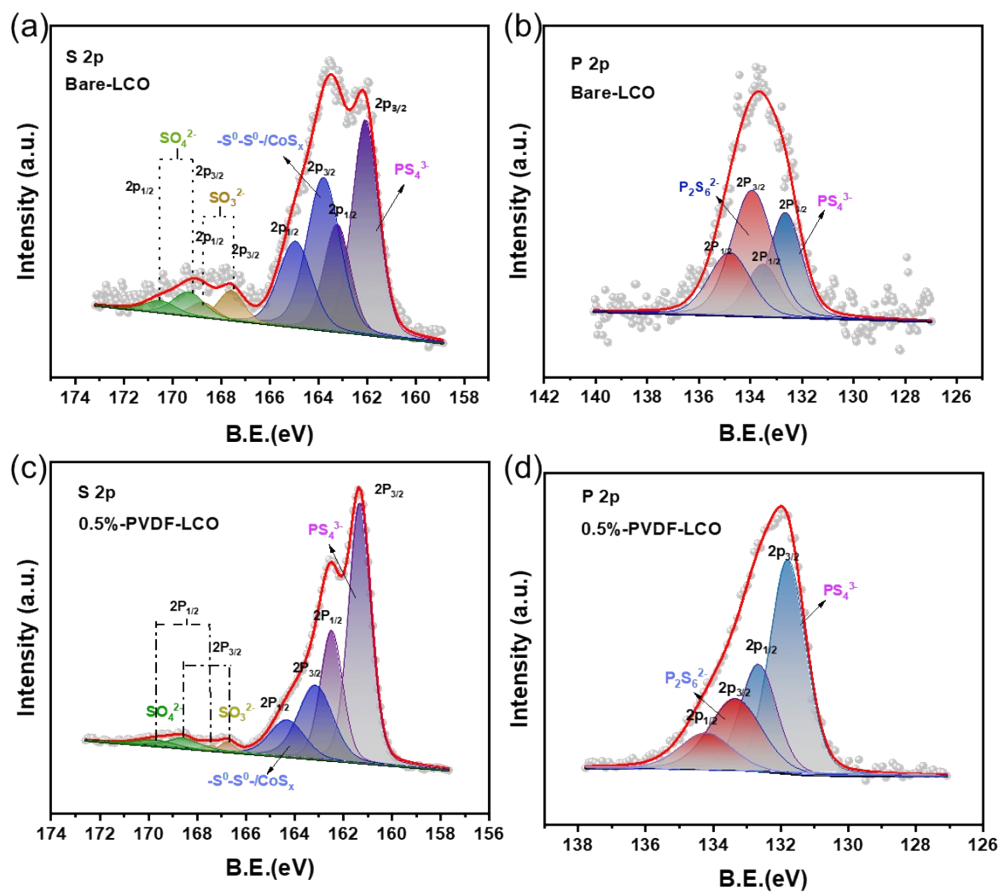
**Figure S6.** a is the TEM image of the FIB-cut PVDF-LCO, and b is the corresponding high-resolution TEM image.



**Figure S7.** The initial charge-discharge curves of LCO ASSLBs at 0.2 C in the voltage range of 2.6-4.3 V.



**Figure S8.** Polarization curves and Ion diffusion coefficient  $\log D$  of 0.5%-PVDF-LCO.



**Figure S9.** Energy spectra of S and P at the positive/electrolyte interface of Bare-LCO and 0.5%-PVDF-LCO after cycling.



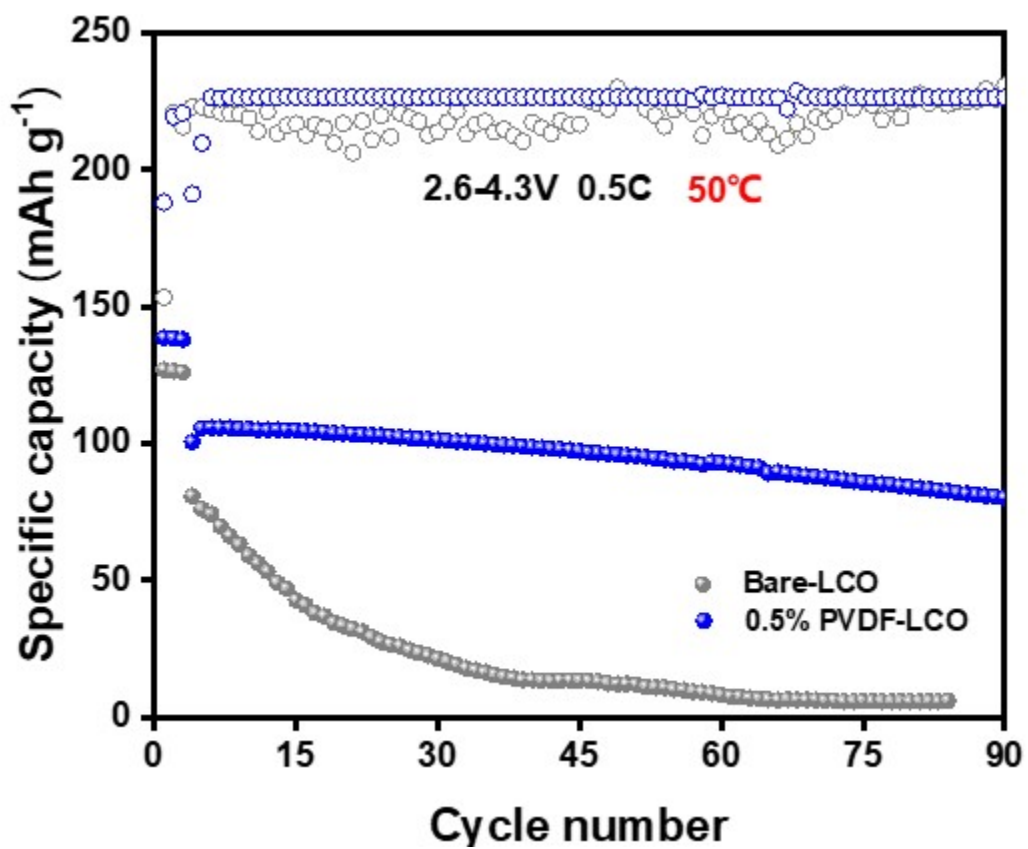


Figure S10. Cycling performance of Bare-LCO and 0.5% PVDF-LCO at 4.3 V at 50 °C.