

## I. Supporting Text

### 1. Experimental Section

#### 1.1. Preparation of current collectors

The carbon papers (CP) (HCP005, Shanghai Hesens Electric Co., Ltd.) were dried in vacuum oven at 333 K for 12 h and then put into Ar-filled glove box with the content of O<sub>2</sub> and H<sub>2</sub>O below 0.1 ppm. Then the CP were cut into discs with the diameter of 10 mm for mold cells, or into small square pieces with sides of 20 to 50 mm for pouch cell. The CP sheets for pouch cells were further sputtered with Pt metal seeds for 120 s under vacuum at 10 mA. The apparent density of CP is 2.76 g cm<sup>-2</sup>. The porosity of structured framework is 80%. The thickness of the pristine CP is 50 μm.

As for the bare Cu, a 9 μm thick copper foils were cut into discs with the diameter of 10 mm for mold cells. As for the SP composite layer, SuperP (Timcal) and polyvinylidene fluoride (PVDF, Solvay) were mixed in a weight ratio of 93:7 in N-methylpyrrolidone (NMP, Sigma-Aldrich) to prepare a slurry. The slurry was then coated on a 10 μm thick stainless-steel foil using a blade and dried in air at 333 K for 30 min. The obtained foil was further dried under vacuum at 373 K for 12 h. The thickness of the SP composite layer was ~20 μm.

#### 1.2. Preparation of SE and electrodes

Sulfide Li<sub>6</sub>PS<sub>5</sub>Cl (Zhejiang Ningbo Linengxin New Materials Co., Ltd.) was used as SE. For the cathode active materials, LiNbO<sub>3</sub>-coated single-crystal NCM was prepared by the sol-gel method<sup>[1]</sup> with a coating thickness of ~4 nm. The composite cathode was fabricated by mixing LiNbO<sub>3</sub>-coated NCM and Li<sub>3</sub>InCl<sub>6</sub> (Hefei Kejing Material Technology Co., Ltd.) in a weight ratio of 70:30. The SE and cathode sheets for pouch cells were prepared by the dry film process as previously reported.<sup>[2]</sup>

#### 1.3. Material Characterization

The morphologies of the CP were observed by SEM (JSM 7401F, JEOL, Japan) operated at

3.0 kV, and TEM (JEOL, 2100Plus) operated at 180 kV. The materials structures were characterized by X-ray Diffraction (XRD, Bruker D8 diffractometer) with a Cu-K $\alpha$  radiation source. The internal structure of the CRIEC was characterized by X-ray CT (Xradia 620 Versa 3D X-ray microscope, Zeiss) operated at 80 kV. The sample was non-destructively imaged while achieving a high spatial resolution of 700 nm. The digital camera photos of CP and pouch cells were taken by Leica camera on Huawei Mate 40.

#### *1.4. Fabrication of ASSBs*

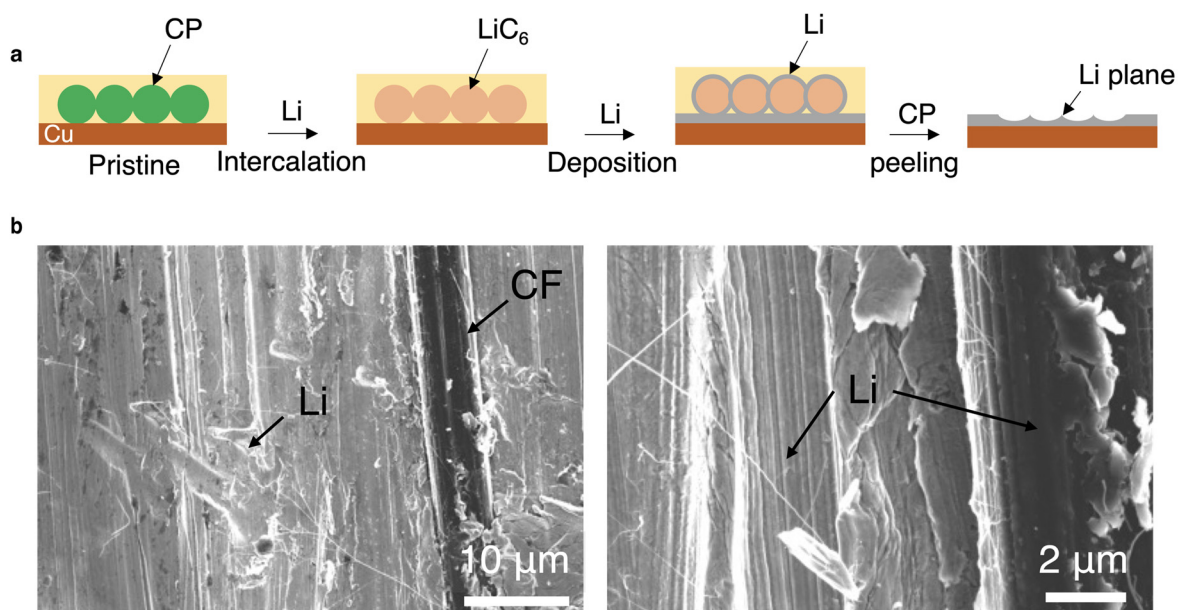
The all-solid-state mold cells were assembled in an Ar-filled glovebox with the content of O<sub>2</sub> and H<sub>2</sub>O below 0.1 ppm. For the asymmetric Li|SE|CP (SP, Cu) cells, CP (SP, Cu) and 100 mg of SE were transferred into a polyaryletheretherketone (PEEK) cylinder (with a diameter of 10 mm) and pressed together at 360 MPa for 2 min. Then a Li foil (with a diameter of 8 mm and a thickness of 100  $\mu$ m) was attached on the other side. For the asymmetric Li-In|SE|CP (Cu) cells, an indium foil (with a diameter of 10 mm and a thickness of 100  $\mu$ m) was pressed on the other side before the attachment of Li foil. For the NCM|SE|CP (Cu) full cells, the composite cathode of 10 mg was pressed at 360 MPa for 2 min on the other side of SE. Finally, the cells were fixed into a stainless-steel mold at  $\sim$ 20 MPa.

The anode-free all-solid-state pouch cells were assembled in a dry room (dew point below 223 K). The composite cathode, SE and CP sheets were stacked and packed into a laminate bag. After applying vacuum to the laminate bag, it was sealed and the cell was pressurized at 300 MPa by the cold isostatic. After the press, the cell was removed from the laminate bag and the Al and Ni terminals of the cathode and anode, respectively, were welded using an ultrasonic welder (MRX-DH1000, Shenzhen Mingruixiang Automation Equipment Co., Ltd.). The cell was then packed into a laminate bag and vacuum sealed again. Finally, the cell was fixed into a stainless-steel mold at  $\sim$ 2 MPa.

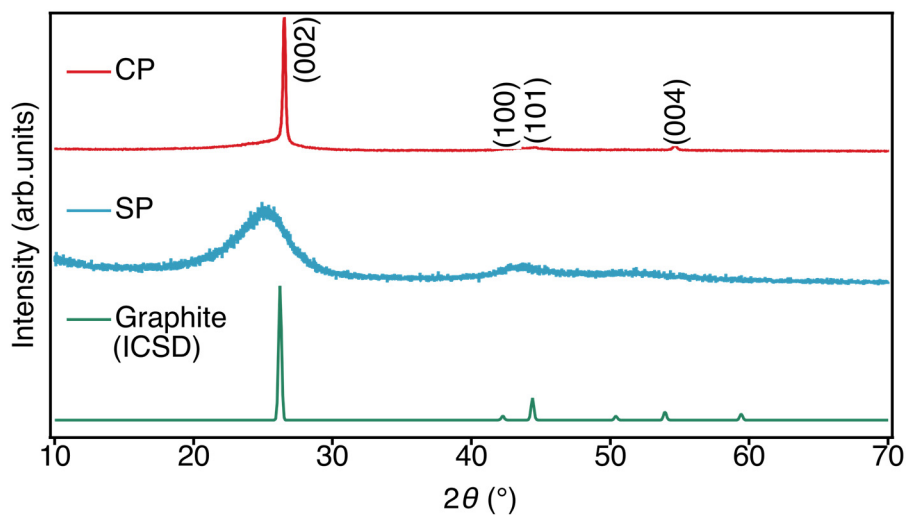
#### *1.5. Electrochemical Measurements*

Galvanostatic cycling of ASSBs was performed on LAND testing system (Wuhan LAND Electronic Co., Ltd.). The asymmetric Li|SE|CP (SP, Cu) cells were discharged at  $0.05 \text{ mA cm}^{-2}$  until short-circuit occurred. The asymmetric Li-In|SE|CP (Cu) cells were initial discharged at  $0.05 \text{ mA cm}^{-2}$  with an areal capacity of  $2.0 \text{ mAh cm}^{-2}$ . Then the cells were cycled once at a charge/discharge rate of 1 C, 2 C, and 5 C ( $1 \text{ C} = 0.05 \text{ mA cm}^{-2}$ ) in the first three cycles for the initial formation. Finally, the cells were cycles at a charge/discharge rate of 10 C. The NCM|SE|CP (Cu) full cells were cycled at  $0.05 \text{ mA cm}^{-2}$  in a voltage range of 2.8–4.2 V. Unless otherwise stated, the mold cells were operated at ambient temperature and the pouch cells were at 333 K.

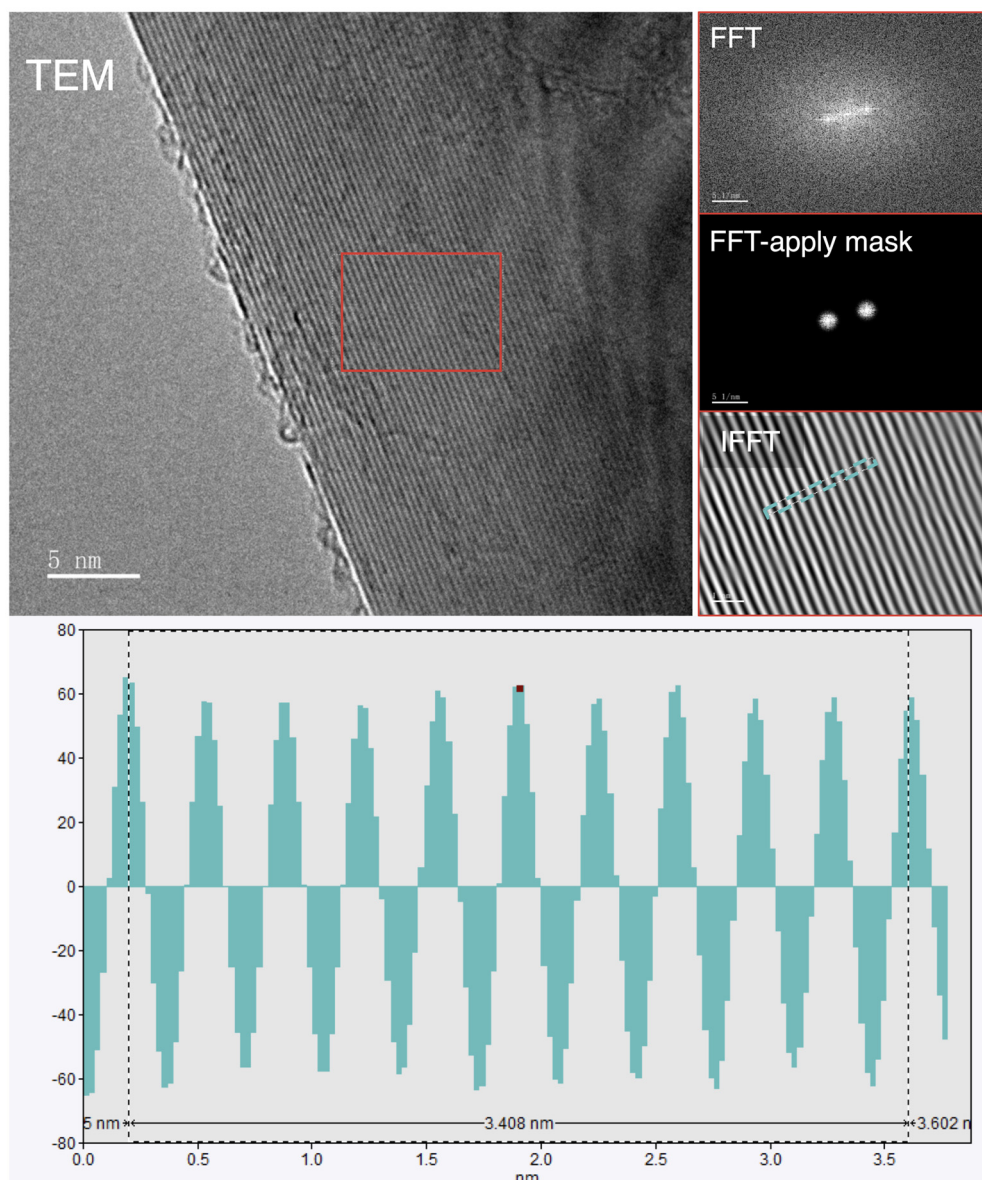
## II. Supporting Figures



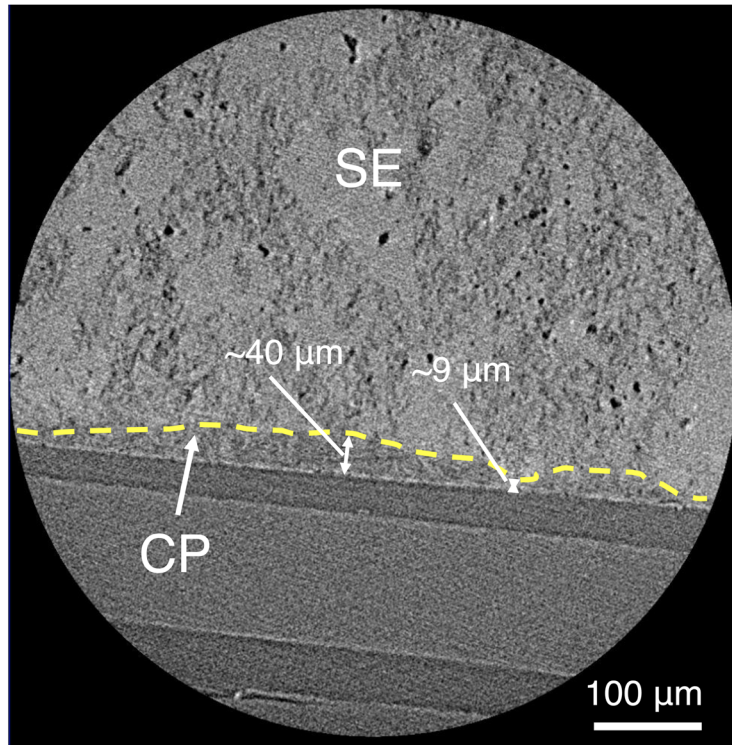
**Figure S1.** **a**, Schematic diagram of lithium deposition behavior in the CRIEC. **b**, SEM images of lithium metal deposition morphology in the CRIEC. After lithium intercalated in CP forming LiC<sub>6</sub>, lithium metal was subsequently deposited on the surface of LiC<sub>6</sub> and Cu substrate. After peeling of the CRIEC, lithium metal was not only observed on the surface of carbon fibers (CF) but also on the Cu substrate (with the trace generated by peeling with CRIEC).



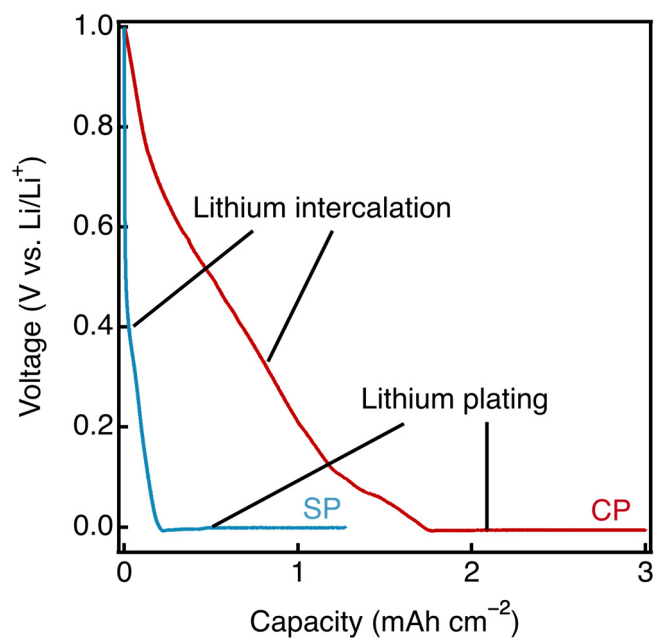
**Figure S2.** X-ray diffraction patterns of the carbon paper (CP) and SuperP (SP) with the reference spectra of graphite from ICSD database.



**Figure S3.** Representative high resolution transmission electron microscopy (HR-TEM) image for the carbon paper, and the corresponding images of Fast Fourier transformation (FFT), Inversed Fast Fourier transformation (IFFT) and interplanar spacing.

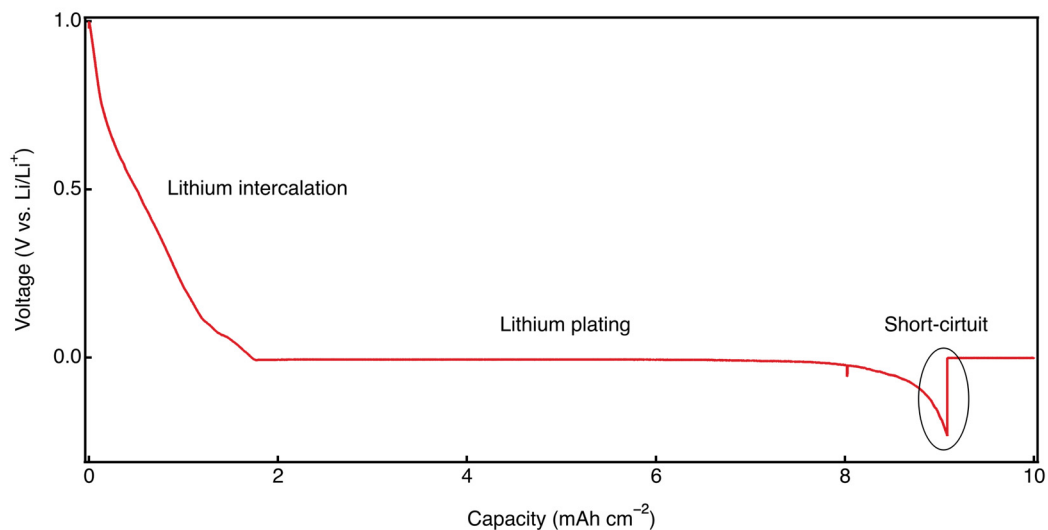


**Figure S4.** Phase-contrast XCT of a Li/SE/CP cell showing three-dimensional electron-ion conducting network of the carbon paper and solid-state electrolyte composite.

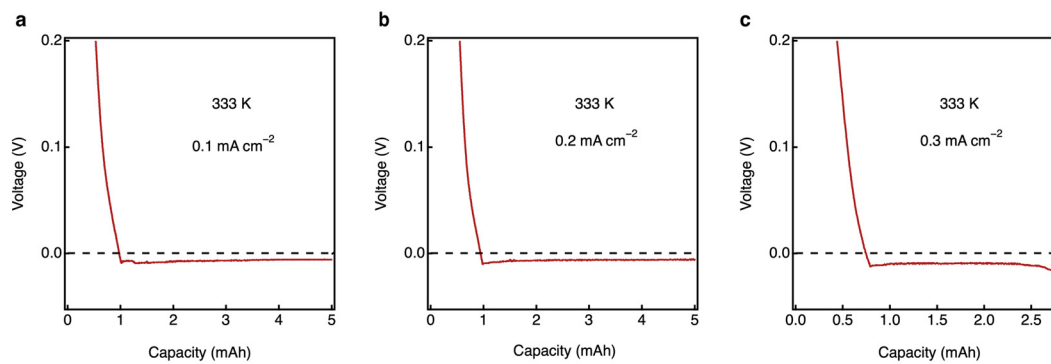


**Figure S5.** Voltage profiles of the lithium deposition processes of CP and SP with lithium metal as the reference electrode at 0.05 mA cm<sup>-2</sup>.

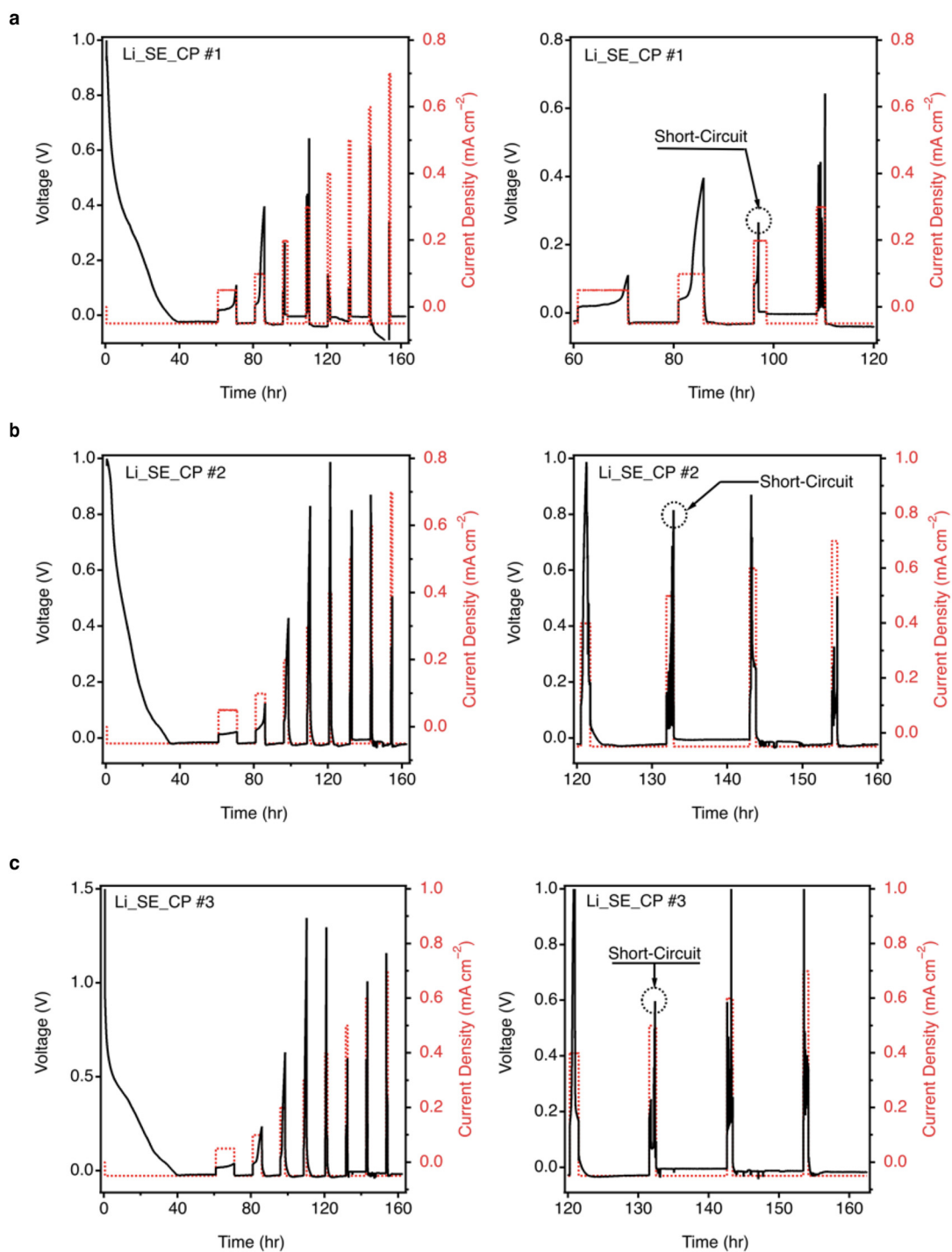




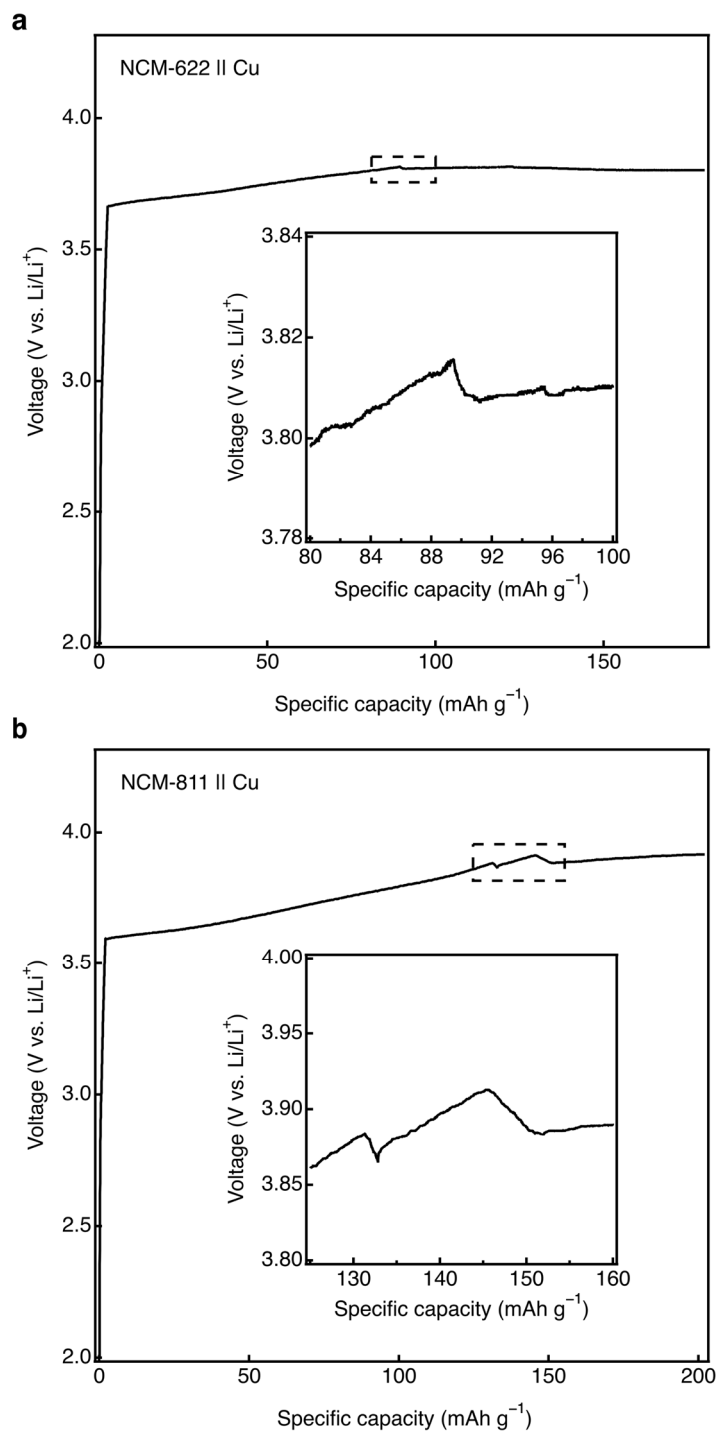
**Figure S6.** Voltage profiles of the lithium deposition process of CP with lithium metal as the reference electrode at  $10 \text{ mAh cm}^{-2}$ . The overpotential increases as the deposited capacity increases, eventually triggering a short-circuit at  $>9 \text{ mAh cm}^{-2}$ .



**Figure S7.** Lithium plating performances in the CRIEC at 333 K.



**Figure S8.** Critical current density (CCD) of lithium dissolution at room temperature when difference pressures are applied. They are (a)  $0.1 \text{ mA cm}^{-2}$  at 2 MPa, (b)  $0.4 \text{ mA cm}^{-2}$  at 3.5 MPa, and (c)  $0.4 \text{ mA cm}^{-2}$  at 5 MPa, respectively.



**Figure S9.** Charge curves of the AFSSLBs **(a)** NCM-622 || Cu and **(b)** NCM-811 ||

Cu at 0.05 mA cm<sup>-2</sup>.

### III. Supporting References

[1] N. Ohta, K. Takada, L. Zhang, R. Ma, M. Osada, T. Sasaki, *Adv. Mater.* 2006, **18**, 2226–2229.

[2] J.-K. Hu, H. Yuan, S.-J. Yang, Y. Lu, S. Sun, J. Liu, Y.-L. Liao, S. Li, C.-Z.

Zhao, J.-Q. Huang, *J. Energy Chem.* 2022, **71**, 612–618.