

Electronic Supplementary Information

Stabilizing the oxide cathode/sulfide solid electrolyte interface via a novel polyaniline coating prepared by ball milling

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Material preparations

Polyaniline (PANI) coated commercially available lithium cobalt oxide (LCO) was prepared via a mechanical ball milling followed by annealing in the air. LCO (HF-Kejing materials technology) and PANI (Aladdin, average M_w 50 000–60 000, 98%) with different weight ratios were firstly ground in a mortar for 10 min. Then the mixture was ball milled in a zirconia-lined jar via a planetary ball mill (Changsha Miqi Instrument and Equipment) at a speed of 600 rpm for 2 h. The mixed powder was then recovered from the jar and remix in a mortar. Finally, the mixture was annealed in the air at different temperatures for 2 h to obtain PANI coated LCO (LCO@PANI) samples.

As the reference material, 3 wt.% LiNbO₃ coated LCO (LCO@LNO) was prepared by a sol-gel route. Typically, 127.3 mg niobium ethoxide (Aladdin, 99.95 %) and 3.1 mg lithium metal (plate) were dispersed in absolute ethanol (Sinopharm Chemical Reagent Co., Ltd, 99.9 %), then 2 g LCO was added to form a suspension.

After stirring for 1 h, the obtained suspension was spun and evaporated at 35 °C to get the precursor. The obtained precursor powders were finally calcined at 350 °C for 2 h under air to prepare LCO@LNO.

$\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ (LPSCl) sulfide electrolyte was prepared by a solid-state synthesis route. Lithium sulfide (Li_2S , Macklin, 99.99%), phosphorus pentasulfide (P_2S_5 , Macklin, 99%), and lithium chloride (LiCl , Macklin, 99.9%) powders were used as the raw materials. The stoichiometric amounts of raw materials (the total mass is 1.0 g) were planetary ball milled at 380 rpm for 17 h in a sealed zirconia-lined jar. Then the mixed raw materials were pelletized at 2 tons in a 10 mm die. The pellets were finally vacuum-sealed in a quartz tube and heat treated at 550 °C for 7 h to prepare LPSCl solid-state electrolyte.

Lithium-indium (LiIn) alloys were prepared by a solid-state diffusion method. Typically, a piece of lithium (30 μm in thickness) and a piece of indium (100 μm in thickness) with a weight ratio of 3:97 were pressed together at 10 MPa. After the mutual diffusion of lithium and indium, a LiIn alloy can be prepared. The LiIn alloy was cut into disks with a diameter of 8 mm for cell assembly.

Materials characterizations

The crystalline structures of prepared LCO@PANI and LPSCl were analyzed by an X-ray diffractometer (XRD, X'PRO Pert, PANalytical) with $\text{Cu K}\alpha$ radiation. A scanning electron microscope (SEM, S-4800, Hitachi) equipped with an energy dispersive X-ray spectroscopy (EDS) and a transmission electron microscope (TEM, Tecnai G2 F30, FEI) were used to investigate the morphology, crystalline phase, and surface element distribution of prepared LCO@PANI. The surface chemistry of LCO@PANI was studied by a Fourier transform infrared spectrometer (FT-IR) and an X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, ThermoFisher Scientific).

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed with a Mettler-Toledo TGA DSC 1 Stare system.

Electrochemical performance tests

The ionic conductivity of the prepared LPSCl electrolyte was determined by electrochemical impedance spectroscopy (EIS) tests of blocking cells with two stainless steel discs (SSDs) on an Autolab electrochemical workstation. The test frequencies were ranged from 1 Hz to 1 MHz with an amplitude of 5 mV. 100 mg of LPSCl was pressed into a disc pellet with a diameter of 10 mm and a thickness of 0.96 mm under a pressure of 300 MPa. Two stainless steel blocks were attached to each side of the electrolyte pellet to form a blocking cell. The ionic conductivity was calculated by equation (1):

$$\sigma_{Li^+} = \frac{L}{RS} \quad (1)$$

where L (cm) is the thickness, R (ohm) is the total resistance of the solid electrolyte, and S (cm²) is the area of the electrolyte pellet. The electronic conductivity was determined by a chronoamperometry test and calculated by equation (2):

$$\sigma_{e^-} = \frac{LI}{ES} \quad (2)$$

where L (cm) is the pellet thickness, I (A) is the steady current, E (V) is the polarization voltage, and S (cm²) is the area of the pellet.

The performances of LCO@PANI cathodes were investigated by an all-solid-state cell with an LCO@PANI cathode, a Li_{5.5}PS_{4.5}Cl_{1.5} (LPSCl) electrolyte, and a LiIn alloy anode. 70 mg of LPSCl was pressed into an electrolyte pellet under 300 MPa by a polyether ether ketone (PEEK) mold with a diameter of 10 mm. A composite cathode was prepared by grounding LCO, LPSCl, and vapor-grown carbon fibers (VGCF) (Guangdong Canrd New Energy Technology Co., Ltd.) in a weight ratio of 60:34:6. 10 mg of the composite cathode was pressed to a pellet under 300 MPa. As the anode, a

LiIn alloy film was pressed onto the other side of the LPSCl pellet. A constant pressure of 30 MPa was maintained during all the electrochemical tests. The galvanostatic charge/discharge behaviors of the LCO@PANI (or pristine LCO)/LPSCl/LiIn cells at different rates were tested from 2.0 to 3.7 V on a multichannel battery test system (CT2001A, LAND, China) at room temperature (1 C rate = 140 mA g⁻¹). The electrochemical impedance spectroscopy (EIS) tests of the fresh and cycled cells were carried out at room temperature in a frequency range of 0.01 Hz to 1 MHz with an AC voltage amplitude of 5 mV using an Autolab electrochemical workstation.

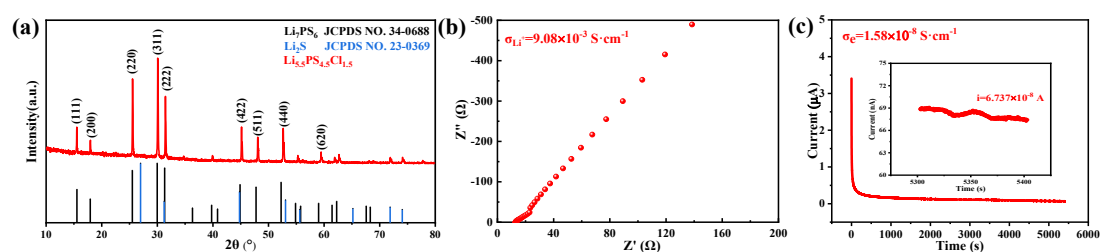


Fig. S1 (a) the XRD pattern of prepared Li_{5.5}PS_{4.5}Cl_{1.5}, (b) the EIS plot and (c) the current-time curve of the SSD/LPSCl/SSD blocking cell.

The discussion of LPSCl preparation and characterizations

The Li_{5.5}PS_{4.5}Cl_{1.5}(LPSCl) sulfide electrolyte was prepared by a solid-state synthesis route, which shows a typical argyrodite phase (F-43 m) (Fig. S1a), a high ion conductivity of 9.08 mS cm⁻¹ and a low electronic conductivity of 1.58 × 10⁻⁸ S cm⁻¹ at 25 °C (Fig. S1b and S1c).

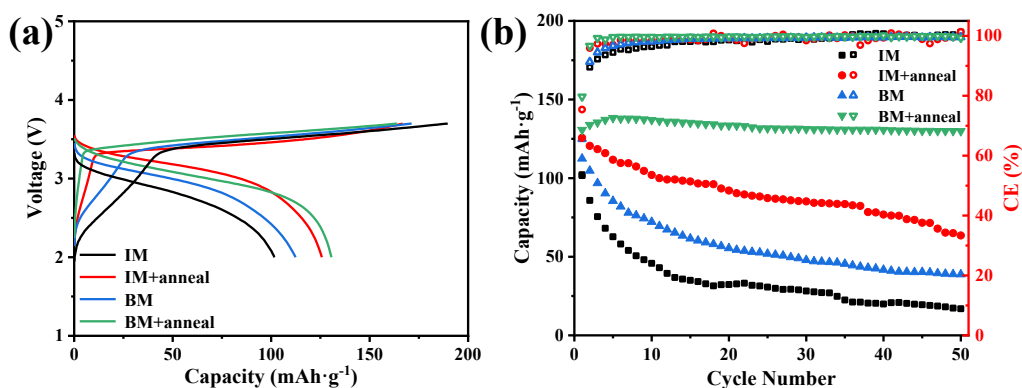


Fig. S2 (a) the voltage profiles and (b) cycling performance of LCO@PANI prepared by mechanical milling and impregnation route at 0.5 C. “BM+anneal” and “BM” denote the samples prepared by ball milling with and without annealing respectively. “IM+anneal” and “IM” denote the samples prepared by the impregnation method with and without annealing respectively.

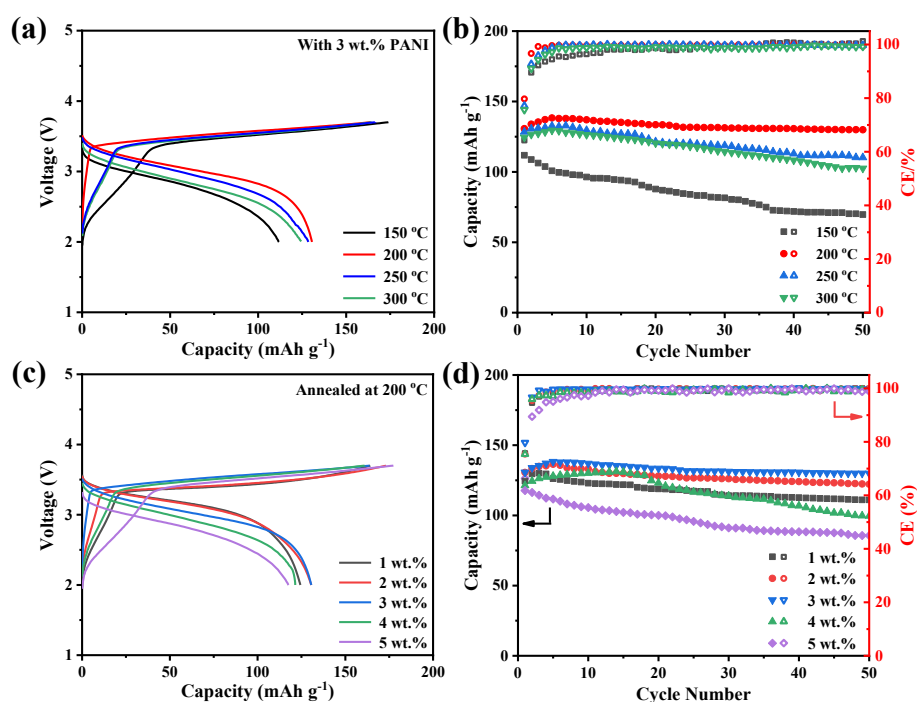


Fig. S3 The (a) voltage profiles and (b) cycling performances of LCO@PANI samples annealed at 150, 200, 250, and 300 °C, the (c) voltage profiles and (d) cycling performances of LCO@PANI samples with 1~5 wt.% PANI.

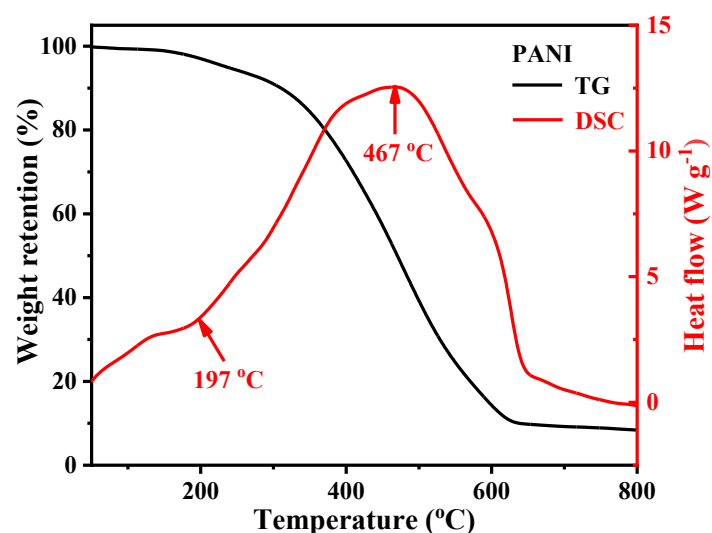


Fig. S4 TGA and DSC curves of PANI polymer in the air.

Table S1 The discharge capacities, Coulombic efficiencies, and capacity retentions of the LCO@PANI samples annealed at different temperatures.

Annealing temperatures (°C)	Discharge capacity (mA h g ⁻¹)	Coulombic efficiency	Capacity retention
150	111.7	64.25%	62.32%
200	130.7	79.75%	93.93%
250	128.4	77.13%	83.11%
300	124.5	75.64%	79.15%

Table S2 The discharge capacities, Coulombic efficiencies, and capacity retentions of the LCO@PANI (annealed at 200 °C) samples coated with different amounts of PANI.

PANI weight ratios	Discharge capacity (mA h g ⁻¹)	Coulombic efficiency	Capacity retention
1 wt.%	124.4	75.26%	85.37%
2 wt.%	130.6	75.31%	89.59%
3 wt.%	130.7	79.75%	93.93%
4 wt.%	121.3	75.45%	75.9%
5 wt.%	117.7	66.34%	72.79%

Table S3 The EIS fitting results of cycled cells.

Cathode	R_s / Ω		R_e / Ω		R_{ct} / Ω	
	1 st cycle	200 th cycle	1 st cycle	200 th cycle	1 st cycle	200 th cycle
LCO	17.81	20.79	216.2	1234	75.84	133.8
LCO@PANI	20.75	21.71	294.4	578.2	23.34	31.95
LCO@LNO	21.15	22.38	182.4	843.3	11.84	35.28