

## Supporting Information

### Ionic-electronic Dual-conductive Polymer Modified LiCoO<sub>2</sub> Cathodes for Solid Lithium Batteries

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#### Experimental Section:

In this study, the PEG doped PANI was synthesized via the emulsion polymerization, where dodecyl-benzene sulfonic acid (DBSA) was used as the emulsifier and PEG was used as the dopant. First, aniline, PEG (molecular weight: 1000), and DBSA were mixed in 60 ml of deionized water and stirred for 10 min to form a uniform mixture. The dosage of the above materials are listed in **Table S1**, the PANI-PEG prepared according to the different ratio of aniline, PEG, and DBSA were respectively denoted as PANI-PEG-1, PANI-PEG-2 and PANI-PEG-3. Subsequently, the oxidant solution composed of 5 g ammonium persulfate (APS) and 40 mL deionized water was added into the preparing mixture dropwise. The whole polymerization was performed at 0~5 °C for 6 h. The precipitate was sequentially washed and centrifuged several times with anhydrous ethanol, and then dried at 80 °C overnight.

**Table S1.** The dosage of aniline, PEG, and DBSA in the polymerization of PANI-PEG

	PANI-PEG-1	PANI-PEG-2	PANI-PEG-3
Aniline	2 mL	2 mL	2 mL
PEG	10 g	10 g	15 g
DBSA	1 g	2.5 g	2.5 g

2 g LCO powders were mixed with prepared PANI-PEG of 0.2 g in 30 ml anhydrous ethanol under constant stirring at 400 rpm at 60 °C for about 2 h until all the ethanol was removed. The resulting powders were subsequently moved to a drying oven of 80 °C for 12 h, the PANI-PEG modified LCO materials were obtained thereby, which was denoted as LCO/PANI-PEG.

The LCO composite cathodes were prepared by casting the cathode mixture composed of 80 wt% LCO, 10 wt% Super-P, and 10 wt% PVDF on Al foils. The mass loading of LCO cathodes was 2.5~3.0 mg cm<sup>-2</sup> for the regular test. Li metals which have a thickness of 1 mm and a diameter of 15.6 mm were applied as the anodes. The composite solid electrolytes consisted of poly(vinylidene fluoride) (PVDF), LiTFSI, and Li<sub>6.4</sub>La<sub>3</sub>Zr<sub>1.4</sub>Ta<sub>0.6</sub>O<sub>12</sub> (LLZTO) were acquired by casting the mixed slurry with the m<sub>(PVDF)</sub>:

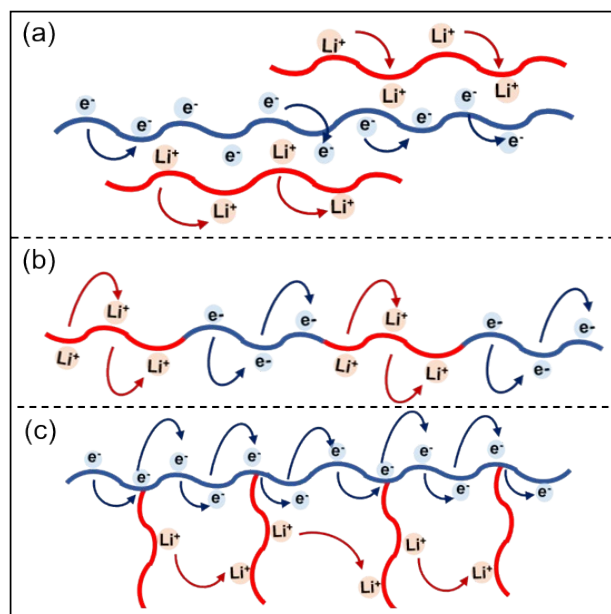
$m_{(\text{LiTFSI})}:m_{(\text{LLZTO})}$  ratio of 20:10:3 on polytetrafluoroethylene plates and drying at 80 °C overnight. The prepared composite solid electrolytes were denoted as PVDF:LLZTO, having a thickness of 40  $\mu\text{m}$  and a diameter of 19 mm. 1  $\mu\text{L cm}^{-2}$  N-Methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide (PP13-TFSI) ionic liquid with the LiTFSI concentration of 0.1 mol/L was used to wet the electrolyte/electrode interfaces before assembling. The LCO/PVDF:LLZTO/Li and LCO-PANI/PEG/PVDF:LLZTO/Li batteries were assembled using coin cells of 2032 in an Ar-filled glove box with  $\text{O}_2$  and  $\text{H}_2\text{O}$  contents below 0.1 ppm.

The surface morphologies of samples were examined by SEM (Hitachi S-4800) with the accelerating voltage of 5 kV. The morphological images of cathode particles were observed by TEM (JEM 2100F) with EDS operated at 200 kV. The crystal structures of materials were identified by X-ray diffraction (XRD, Bruker D2 Phaser). The compositions of samples were investigated by Fourier transform infrared spectroscopy (FTIR, NETZSCH X70) with the wavenumber ranging from 600  $\text{cm}^{-1}$  to 4000  $\text{cm}^{-1}$  and X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI). The TGA analysis (TA, SDT-650) was conducted with a temperature range of 35 to 600 °C at a heating rate of 10 °C  $\text{min}^{-1}$ . Differential scanning calorimetry data (DSC) were also collected in nitrogen from 35 °C to 200 °C at a heating rate of 10 °C  $\text{min}^{-1}$ .

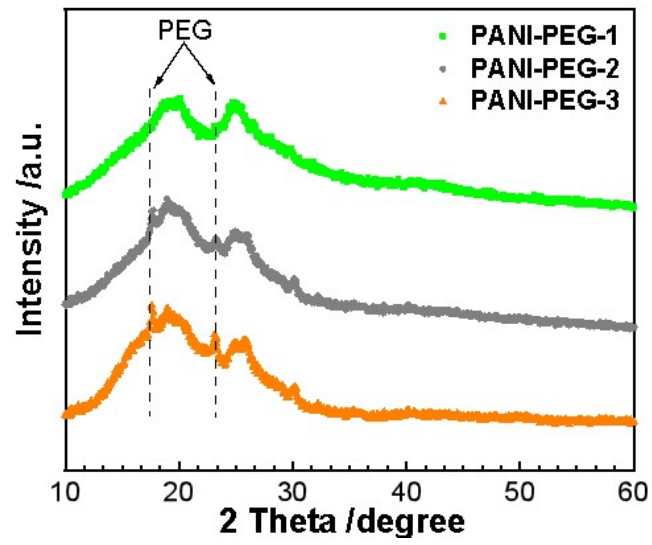
The ionic conductivities of PANI-PEG pellets were obtained via measuring the electrochemical impedance spectroscopies (EIS) data by the electrochemical working station (Princeton, USA) in the frequency ranging from 7 MHz to 1 Hz with a 10 mV AC amplitude. Herein, the PANI-PEG pellets were obtained by tableting PANI-PEG powders with 1 wt% LiTFSI under an axial pressure of 15 MPa and splayed by gold on both sides. The electronic conductivity of the PANI-PEG pellets was measured by a four-point probe d.c. techniques. All the electrochemical measurements of PANI-PEG were carried out at 30 °C.

The ionic conductivities of PVDF:LLZTO electrolytes were got via EIS measurements with the frequency range of 7 MHz~1 Hz and the AC amplitude of 10 mV, during which the temperature was increased from 90 °C and decreased to 30 °C with each step of 15 °C. The PVDF:LLZTO electrolytes were sandwiched by stainless steel (SS) plates to assemble the SS/PVDF:LLZTO/SS symmetric blocking electrodes. 1  $\mu\text{L cm}^{-2}$  PP13-TFSI ionic liquid with the LiTFSI concentration of 0.1 mol/L was used to wet the double sides of solid electrolyte membranes. Linear sweep voltammetry (LSV) was carried out by SS/PVDF:LLZTO/Li coin cells in the voltage range of 1.0~5.0 V with a scan rate of 1  $\text{mV s}^{-1}$ . Cyclic voltammetry (CV) at various sweep rates was measured by an electrochemistry workstation (Princeton). All the electrochemical measurements of PVDF:LLZTO solid electrolytes were performed at 30 °C.

The prepared LCO/PVDF:LLZTO/Li and LCO-PANI/PEG/PVDF:LLZTO/Li cells were cycled at 30 °C between 3.0 and 4.2 V with the charge/discharge rate of 0.1 C. The C-rate measurements of Li/LCO cells were carried out between 3.0 and 4.2 V at varied currents at 30 °C.



**Fig. S1** The schemes of dual-conductive materials prepared by: (a) physical mixing of electronic conductive and ionic conductive materials; (b) copolymerization of electronic conductive and ionic conductive materials; (c) doping the electronic conductive polymers with ionic conductive groups.



**Fig. S2** XRD scans of PANI-PEG powders.

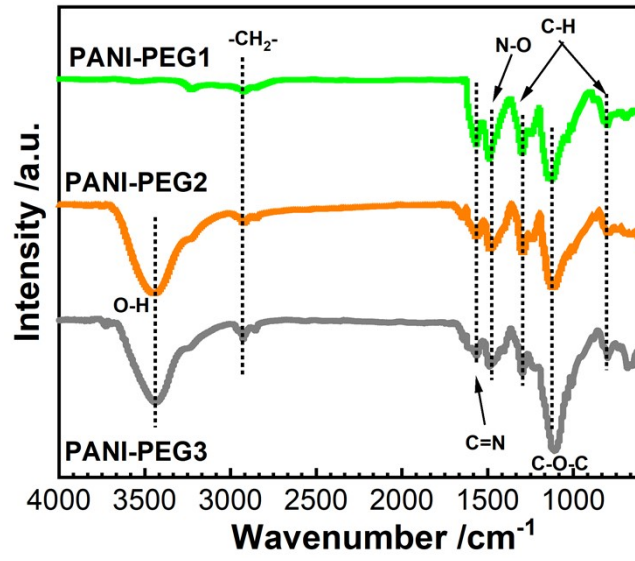
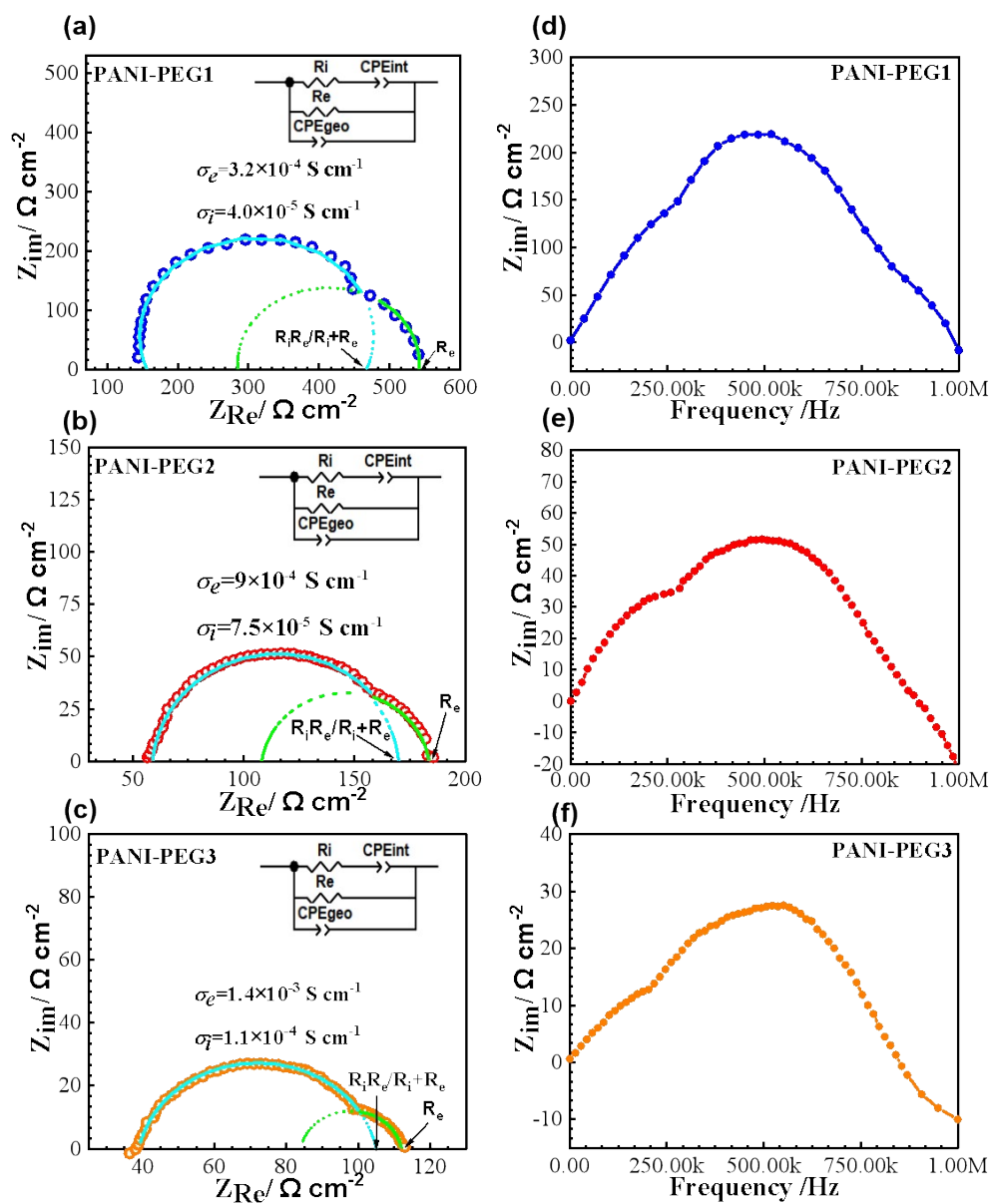
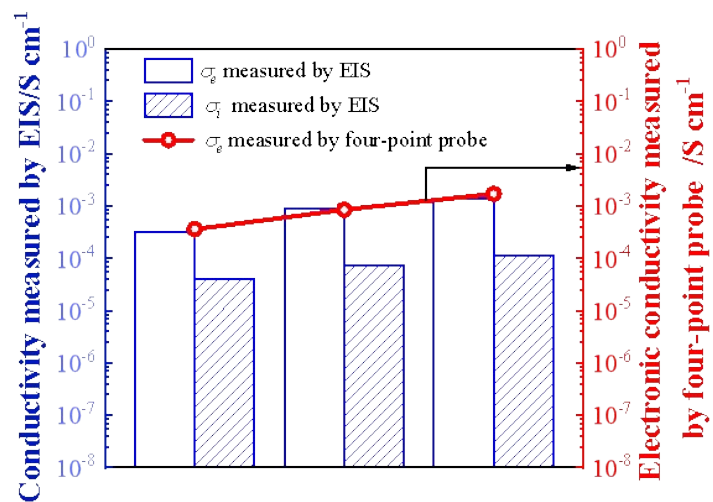


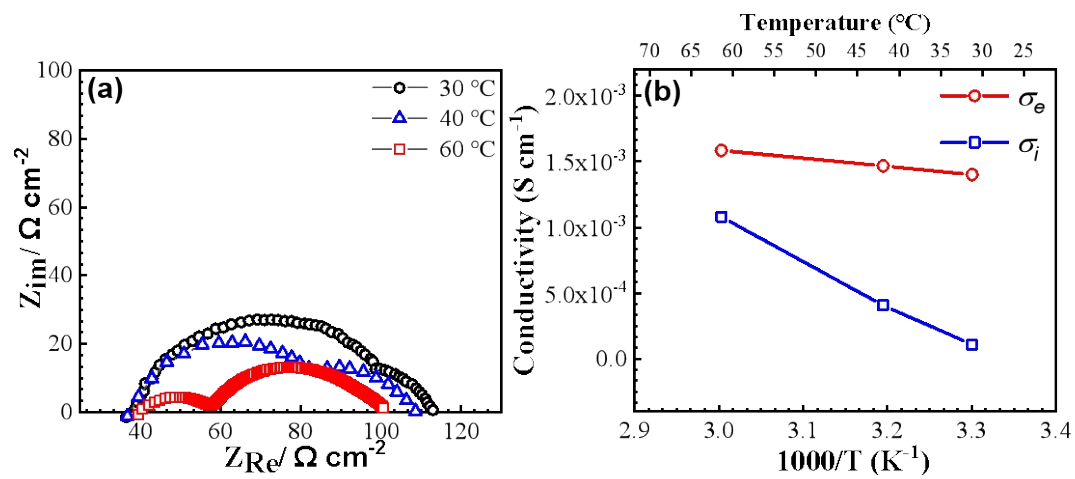
Fig. S3 FT-IR spectra of PANI-PEG powders.



**Fig. S4** Nyquist plots of (a) PANI-PEG1; (b) PANI-PEG2; and (c) PANI-PEG3 pellets; Bode plots of (d) PANI-PEG1; (e) PANI-PEG2; and (f) PANI-PEG3 pellets.

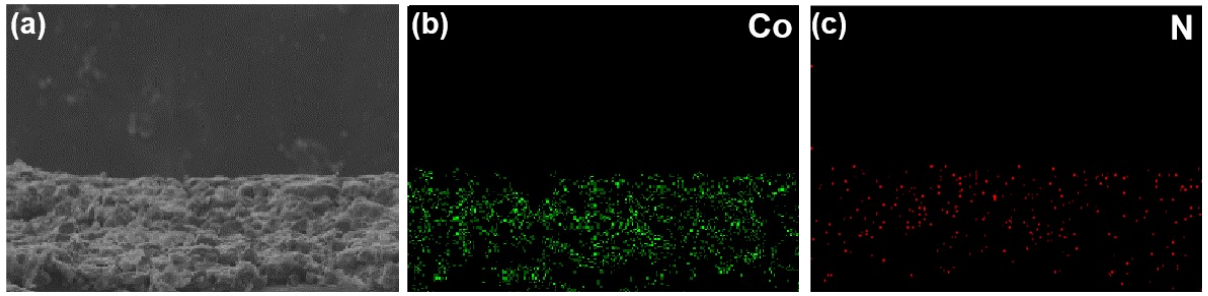


**Fig. S5** The electronic and ionic conductivities of PANI-PEG materials measured by EIS and four-point probe technique.

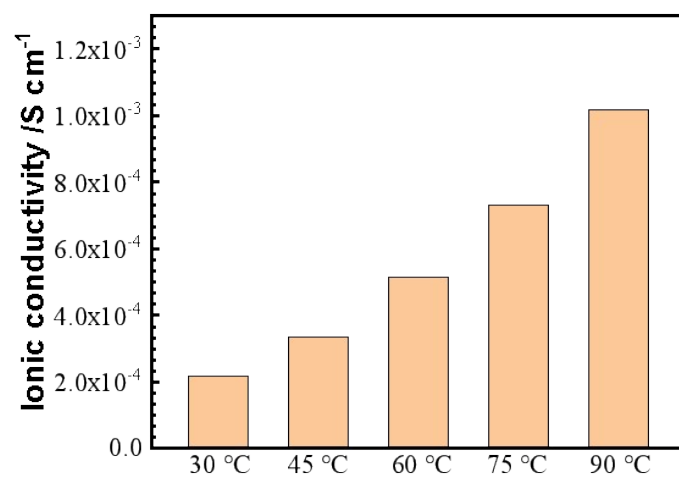


**Fig. S6** Nyquist plots of (a) PANI-PEG3 pellet at different temperatures; (b) The relationship between the conductivity of PANI-PEG and the temperature.

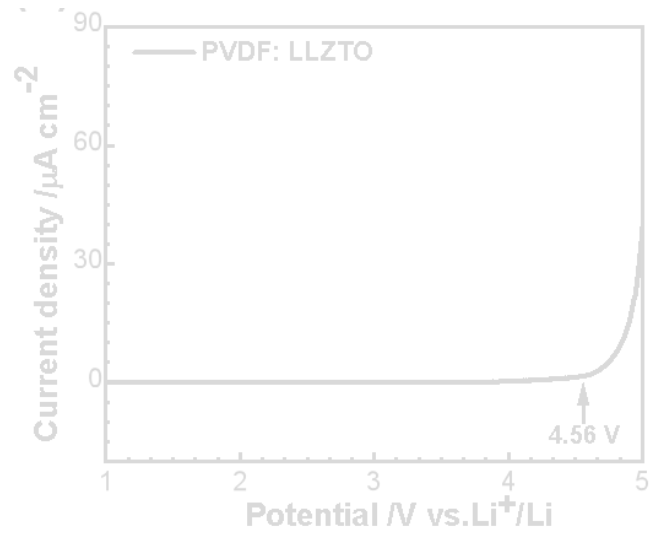




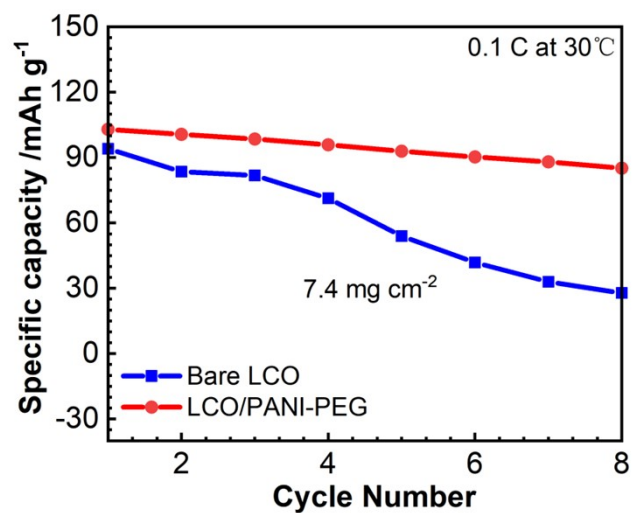
**Fig. S7** The cross-sectional EDS mappings of LCO/PANI-PEG composite cathode



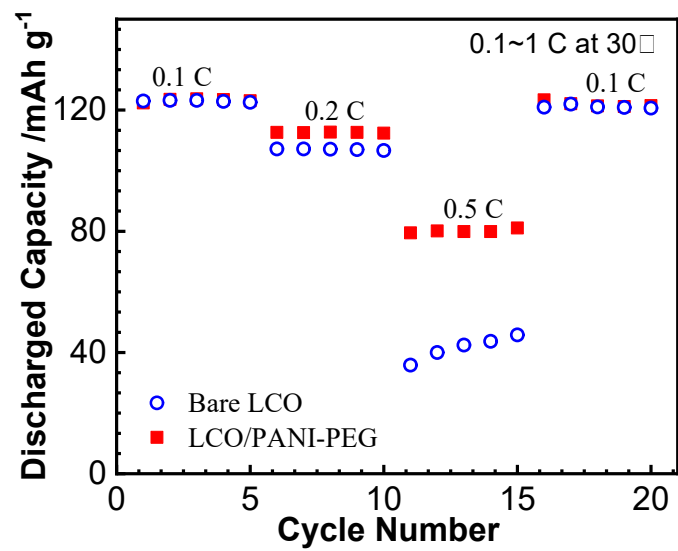
**Fig S8** Ionic conductivities of PVDF:LLZTO composite solid electrolytes as a function of LLZTO content at different temperatures.



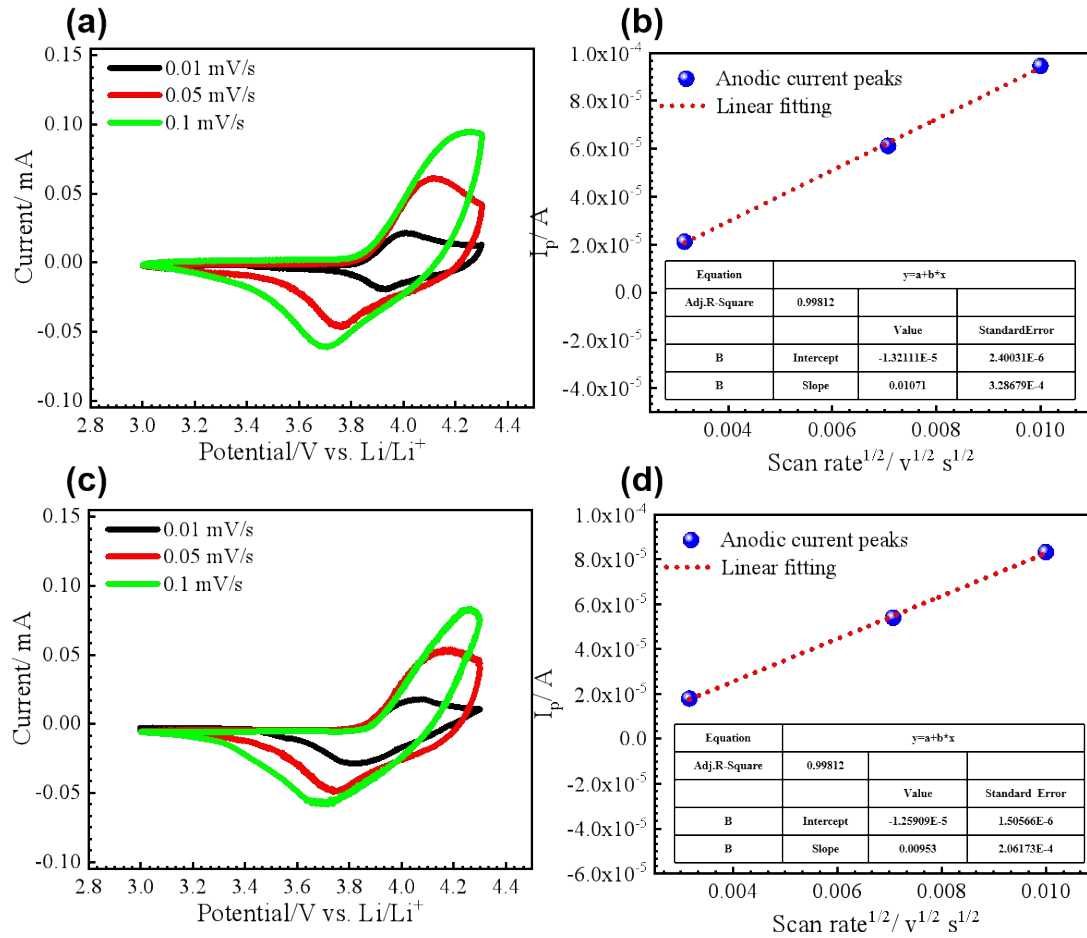
**Fig. S9** LSV scan at the scanning rate of  $1 \text{ mV s}^{-1}$  for the PVDF:LLZTO composite solid electrolyte.



**Fig. S10** Specific capacities of LCO-based/PVDF:LLZTO/Li batteries with the cathode mass loading of 7.4 mg cm<sup>-2</sup>.



**Fig. S11** Rate capabilities of LCO-based/PVDF:LLZTO/Li batteries with the cathode mass loading of 7.4 mg cm<sup>-2</sup>.

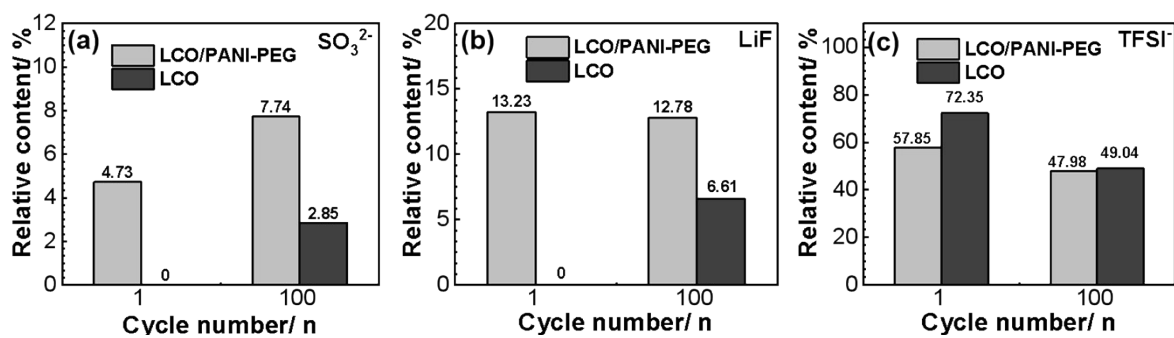


**Fig. S12** Cyclic voltammetric profiles of (a) LCO and (c) LCO/PANI-PEG at various scan rates (0.01–0.1 mV s<sup>-1</sup>); peak current density as a function of the square root of the scan rate of (b) LCO and (d) LCO/PANI-PEG.

The chemical diffusion coefficient of Li<sup>+</sup> ( $D_{Li^+}^C$ ) in LCO cathodes is measured by cyclic voltammetry (CV) and calculated according to the Randles–Sevcik equation:

$$I_M = 2.69 \times 10^5 \times n^{2/3} \times A \times D_{Li^+}^C{}^{1/2} \times v^{1/2} \times \Delta C \quad (1)$$

Herein,  $I_M$  is the anodic peak current intensity (A) obtained from the CV profile,  $A$  is the electrode area (0.5 cm<sup>2</sup>),  $\Delta C$  is the bulk concentration of Li<sup>+</sup> in electrode (0.051 mol cm<sup>-3</sup>), and  $v$  is the potential scan rate (V s<sup>-1</sup>). The slope  $I_M/v^{1/2}$  can be acquired from the linear fitting results as 0.00953 and 0.01071 for LCO and LCO/PANI-PEG as displayed in the inset tables of Fig. S12b and d. The values of  $D_{Li^+}^C$  for the delithiation process are  $2.43 \times 10^{-12}$  cm<sup>2</sup> S<sup>-1</sup> for LCO and  $1.93 \times 10^{-12}$  cm<sup>2</sup> S<sup>-1</sup> for LCO@PANI-PEG at RT.



**Fig. S13** Relative content histograms of the cathode interface for (a)  $\text{SO}_3^{2-}$ , (b) LiF, (c) TFSI<sup>-</sup> derived from the above XPS spectra.

**Table S2.** Comparison on cycling performances between our work and recent publications.

Electrolyte	Liquid addition	Cathode mass loading /mg cm <sup>-2</sup>	C rate /C	Voltage range /V	1 <sup>st</sup> capacity (discharge) / mAh g <sup>-1</sup>	Capacity retention /%	Cycle number	T /°C	Ref.
PVDF-based composite	5 μL cm <sup>-2</sup>	1.5	0.5	3~4.5	164.4	90.1	30	25	[1]
LLZTO-Cu <sub>3</sub> N	0.75 mg cm <sup>-2</sup>	2.0	0.2	3.2~4.2	130	81.1	300	25	[2]
PEO-based composite electrolyte	8.5 wt%	1.2	0.025	3.0~4.2	135.5	74.3	100	60	[3]
Poly(vinyl alcohol)-based hybrid electrolyte	80 wt%	6.4	0.2	2.5~4.2	139.7	97	100	25	[4]
LLZO pellet	10 μL	1.5	0.4	2.8~4.2	135.1	64.7	70	25	[5]
LLZO pellet	1 μL cm <sup>-2</sup>	2.0	0.2	3~4.05	106.1	80.2	400	60	[6]
LLZO/PVDF composite	1 μL cm <sup>-2</sup>	2.5~3.0	0.1	3~4.2	126.3	98.8	200	25	<b>This work</b>

**Table S3.** Impedance data for PANI-PEG samples at 30 °C

Samples	R <sub>i</sub> (Ω)	Fitting errors (%)	R <sub>e</sub> (Ω)	Fitting errors (%)
PANI-PEG-1	3232.91	2.3621	541.72	1.1724
PANI-PEG-2	2201.12	0.5987	183.45	0.5281
PANI-PEG-3	142.55	1.3372	111.96	0.9118

**References:**

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