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Supplementary Information

Composite Solid Electrolytes Based on Nickel-Doped Lithium Aluminum Silicate Ceramics Enable Lithium Metal Batteries with Enhanced Interfacial Stability and High-Rate Capability

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Experimental

Preparation of $LiAlSiO_4$ (LASO)

$(CH_3CH_2O)_4Si$ (TEOS, Macklin, 98%), $LiNO_3$ (Macklin, 99.99%), and $AlNO_3 \cdot 9H_2O$ (Macklin, 99.99%) are dissolved in 30 mL of ethanol in a molar ratio of 1/1/1 to form a turbid solution. Then excess citric acid (Macklin, 99.5%) was added to the mixed solution as dispersing agent. The mixed solution was magnetically stirred at 60 °C for 6h to form a uniform sol, and dried at 120 °C for 24 h to obtain a yellowish dry gel. Subsequently, it was placed in a muffle furnace and heated at a rate of 2 °C min-1 in air at 500 °C for 6 h. Then, it was heated at 900 °C for 6 h to decompose the precursor into white LASO powder.

Synthesis of $Li_{(1+0.05X)}Al_{(1-0.05X)}Ni_{0.05X}SiO_4$ (X=1~3) (Ni-doped LASO) Ceramic Powders ($Li_{1.1}Al_{0.9}Ni_{0.1}SiO_4$ (X=1), LANSO as the example)

$(CH_3CH_2O)_4Si$ (TEOS, Macklin, 98%), $LiNO_3$ (Macklin, 99.99%), $Ni(NO_3)_2 \cdot 6H_2O$ (Macklin, 99.99%), and $Al(NO_3)_3 \cdot 9H_2O$ (Macklin, 99.99%) are dissolved in 30 mL of ethanol in a molar ratio of 1/1.1/0.1/0.9 to form a turbid solution. Then excess citric acid (Macklin, 99.5%) was added to the mixed solution as dispersing agent. The mixed solution was magnetically stirred at 60 °C for 6h to form a uniform sol, and dried at 120 °C for 24h to obtain a yellowish dry gel. Subsequently, it was placed in a muffle furnace and heated at a rate of 2 °C min^{-1} in air at 500 °C for 6 hours. Then, it was heated at 900 °C for 6 hours. Subsequently, the sample was heat-treated under the Ar/H_2 atmosphere at 900 ^oC for 2 hours.

Other Ni-doped LASO can be prepared with the same procedure.

Fabrication of PMPV-LANSO-LiTFSI composite solid electrolytes (CSEs)

PVDF (Arkema, molecular weight ~100,000) and PMMA(Arkema, molecular weight ~800,000) were first dried in a vacuum oven at 80 °C for 12 hours to remove any moisture. Subsequently, 0.6 g of PVDF and 0.4 g of PMMA were weighed and placed in a flask, maintaining a mass ratio of 6:4 to obtain PMPV. 4 mL of N,N-dimethylacetamide (DMAc, MACKLIN, analytical reagent grade) was added in to the flask with stirring, and then the contents were heated and stirred at 60 °C for 3 hours to create a clear transparent polymer solution. Next, the LANSO (LASO) powder and Lithium bis(trifluoromethanesulfonyl)imide(LiTFSI, DoDoChem, 99.99% purity) were weighted and added to the polymer solution with the desired mass ratios of polymer to ceramic to salt. The solution was then stirred again under the same conditions for an additional 5 hours to ensure homogeneity and to obtain the cast film solution. The cast film solution was then spread onto a glass plate using a squeegee to form thin films with the thickness of about 30 μm, resulting in the composite solid electrolyte films. The solvent was evaporated from these films by placing them on a heating plate at 60 °C overnight. Eventually, the films were placed in a vacuum oven at 80 °C for additional 2 hours to ensure complete drying and punched into 19 mm diameter discs and stored in anAr-filled glovebox ($H_2O/O_2 < 0.1$ ppm). The obtained films are wetted with 10 ul of propyl carbamate (PC) solution on each side before used to relieve interface.

Material Characterization

The morphologies and elemental distributions of LANSO (LASO) ceramics and composite electrolytes were analyzed using field-emission scanning electron microscopy (SEM, Phenom ProX) with energy-dispersive X-ray spectroscopy (EDS). For cross-sectional imaging, samples were cryo-fractured after immersion in liquid nitrogen. Crystal structures were characterized by X-ray diffraction (XRD, Rigaku SmartLab 3KW) with Cu-Kα radiation ($\lambda = 1.5406$ Å) over 10-80° 2θ at 5° min^{-1}.

Electrochemical Characterization

Ionic conductivity σ was measured using electrochemical impedance spectroscopy (EIS) in symmetric stainless-steel (SS)/CSE/SS cells (Ø = 19 mm) from 25-105 °C. Spectra were recorded at open-circuit potential (1 MHz to 1 Hz, 10 mV amplitude). Conductivity was calculated as:

$$\sigma = \frac{l}{R_b A} \tag{1}$$

where, l is the membrane thickness, R_b is the bulk resistance, A is the electrode contact area. Activation energy (E_a) was derived from Arrhenius plots (ln σ vs. 1000/T).

The Li$^+$ transference number (t_{Li^+}) was determined in Li/CSE/Li cells using the Evans-Vincent-Bruce method:

$$t_{Li^+} = \frac{I_{ss}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{ss} R_{ss})} \tag{2}$$

where, I_0 and I_s are the initial and steady-state current, respectively. R_0 and R_s are the initial/steady-state interfacial resistance, respectively. $\Delta V = 10$ mV is the polarization potential.

Linear sweep voltammetry (LSV) was performed in Li/CSE/SS cells at 25 °C (0 to 6 V vs. Li$^+$/Li, 2 mV s^{-1}) to determine the oxidative stability limit.

Li^+ plating/stripping kinetics were evaluated in Li/CSE/Li cells. Critical current density (CCD) was determined by stepwise current increases (0.2 to 4 mA cm^{-2}, 10 h per step). Long-term cycling stability was assessed at 0.5 mA cm^{-2} (0.5 mAh cm^{-2} capacity limit).

Lithium iron phosphate ($LiFePO_4$, LFP, STL, China) cathodes were fabricated by coating slurries (LFP:carbon black:PVDF = 80:10:10 wt% in 1-methyl-2-pyrrolidinone (NMP, AR grade, Sinopharm)) onto aluminum foil. Electrodes were dried at 80 °C under vacuum (12 h), yielding mass loadings of 1-1.5mg cm^{-2}. Li/CSE/LFP full cells were assembled with 150-μm Li foil anodes. Cycling was performed at 25 °C (2.5-4.2 V cutoff) using a Land CT3001A (Land, Wuhan) tester. Rate capability was evaluated from 0.2-10 C (1 C = 170 mA g^{-1}). Celgard 2400 separators with 1M $LiPF_6$ in EC:DMC:EMC (1:1:1 v/v/v) served as liquid-electrolyte controls.

$LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811, Ronbay, China) cathodes were fabricated by coating slurries (NCM811:carbon black:PVDF = 80:10:10 wt% in 1-methyl-2-pyrrolidinone (NMP, AR grade, Sinopharm)) onto aluminum foil. Electrodes were dried at 80 °C under vacuum (12 h), yielding mass loadings of 0.7-1.5mg cm^{-2}. Li/CSE/NCM811 full cells were assembled with 150-μm Li foil anodes. Cycling was performed at 25 °C (3-4.35 V cutoff) using a Land CT3001A tester. Rate capability was evaluated from 0.2-10 C (1 C = 200 mA g^{-1}). Celgard 2400 separators with 1M $LiPF_6$ in EC:DMC:EMC (1:1:1 v/v/v) served as liquid-electrolyte controls.

Sample	a（=b）（Å）	c（Å）	a（=β）	γ	V(Å^3)
LANSO	10.5254	11.0971	90	120	1064.6758
LASO	10.5020	11.920	90	120	1069.0115

Table S1 Lattice parameters of LANSO and LASO.

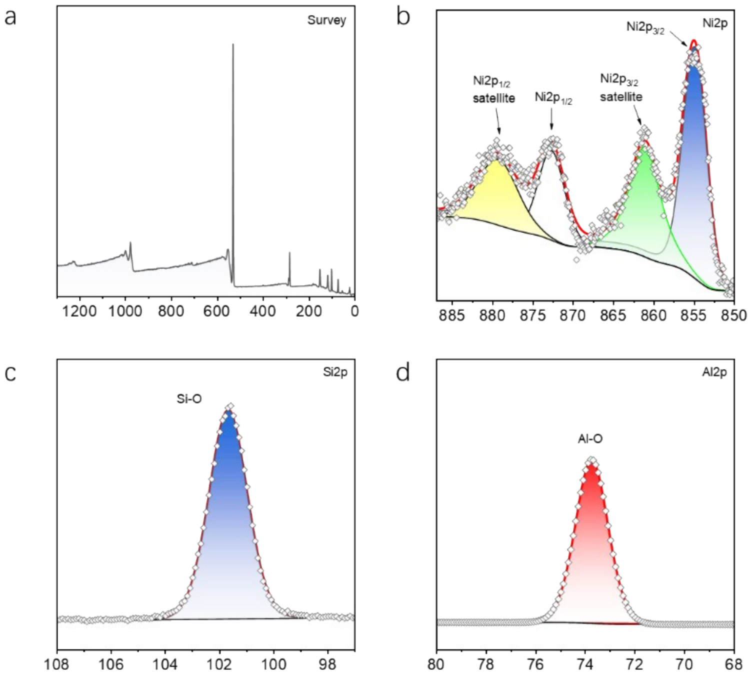

Figure S1 XPS Survey and the detail XPS spectra on (b) Ni 2p, (c) Si 2p, and (d) Al 2p of the LANSO.

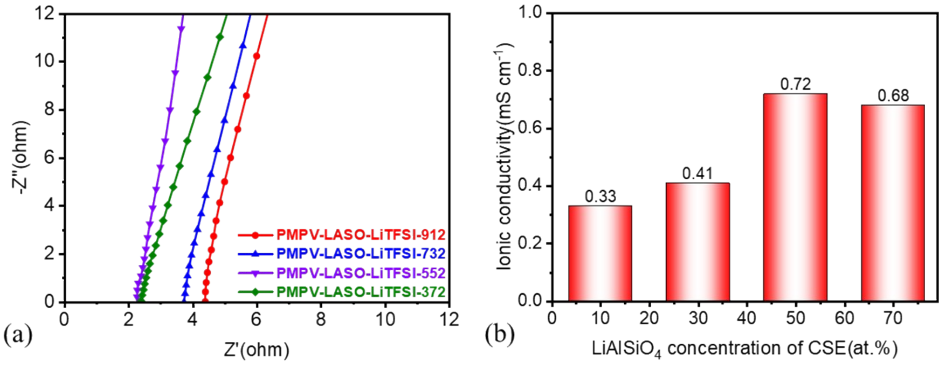

Figure S2 (a) EIS of LASO-based CSEs with the mass contents of LASO ranging from 8.3~58.3 wt%. (b) The calculated r.t. ionic conductivity of PVPM-LASO-LiTFSI-CSEs with varying $LiAlSiO_4$ contents

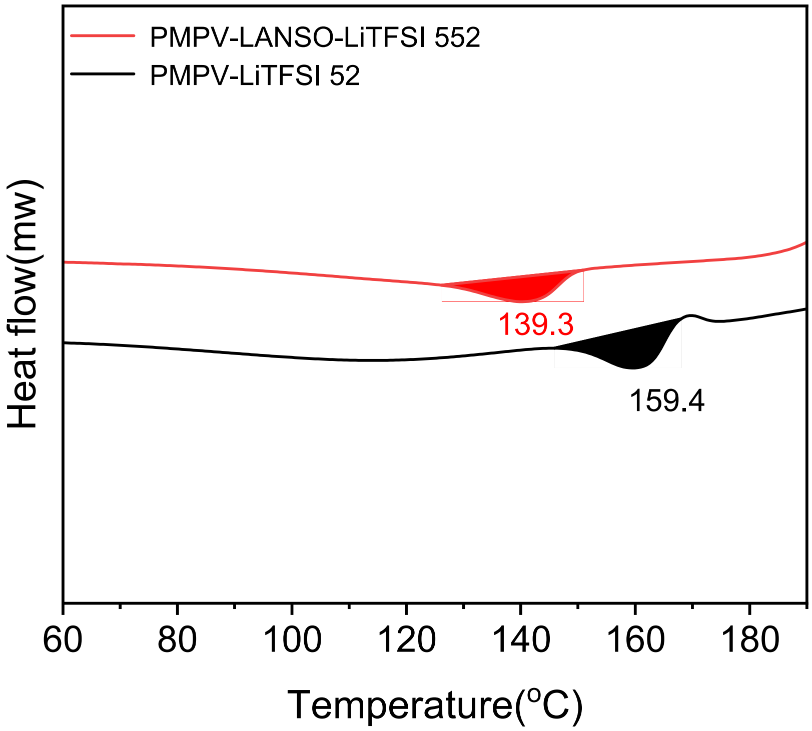

Figure S3 DSC date of PMPV-LANSO-LiTFSI-552 CSE and PMPV-LiTFSI-52 CSE between 30 and 200 degrees.

To evaluate the effect of LANSO filler, DSC was performed to investigate the thermal behavior and crystallinity of the polymer matrix. Based on the melting enthalpy by the DSC measurement, crystallinity can be calculated using the equation:

$$Crystallinity(\%) = \frac{\Delta H_m}{\Delta H_m^o} \times 100\%$$

Where △Hm is the actual melting enthalpy measured by DSC, and △Hmo is the equilibrium melting enthalpy corresponding to the melting enthalpy of 100% crystalline polymer. (Application Brief, TA No. 96, Evaluation of Crystallinity for Crystalline polymers, Hitachi High-Tech Science Corporation (2021))

As shown in Figure R7, the melting enthalpy (△Hm) of the PMPV-LANSO-

LiTFSI552 (7.28 J/g) is significantly lower than that of the PMPV-LiTFSI52 (8.38 J/g). ΔHmo is the constant value, we could compare the crystallinity (Xc) via comparing ΔHm. The PMPV-LANSO-LiTFSI552 exhibits a lower crystallinity than the PMPV-LiTFSI5. This represents the reduction in crystallinity upon addition of the LANSO filler, which demonstrate that the LANSO filler effectively disrupts the ordered packing of PMPV chains, reducing the crystalline phase and increasing the amorphous regions. The enlarged amorphous domains provide more pathways for Li^+ hopping and segmental motion.

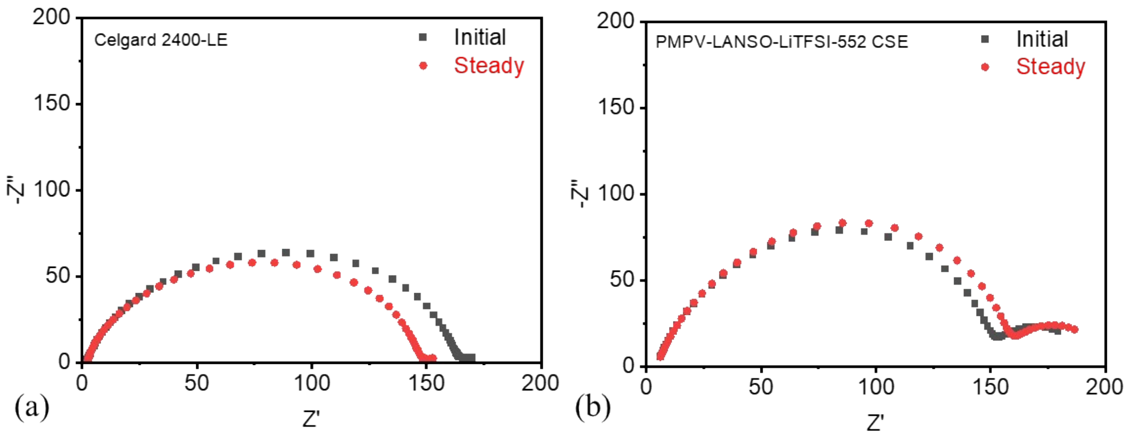

Figure S4 Impedance plots before and after polarization of the (a) Celgard2400-LE system and (b) PMPV-LANSO-LiTFSI-552 CSE.

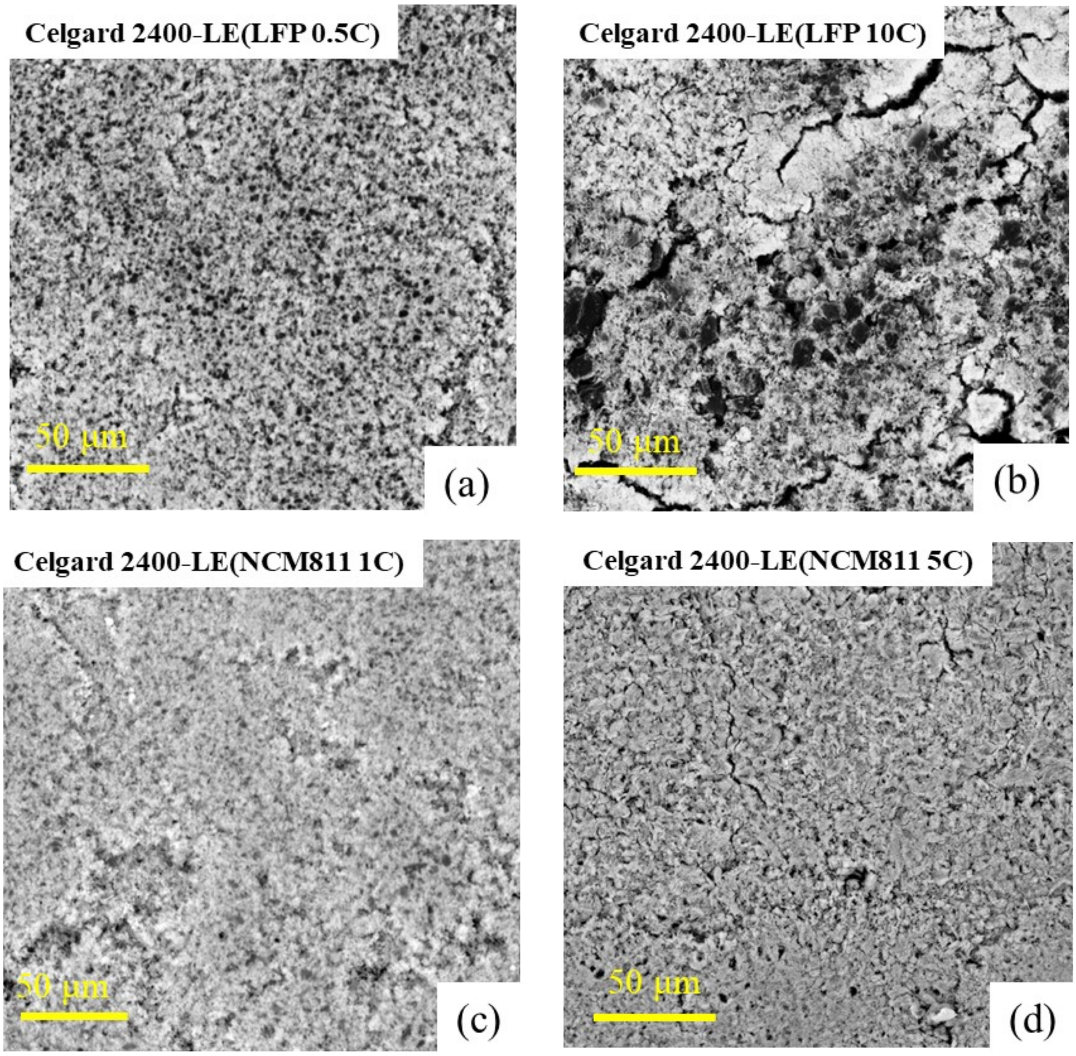

Figure S5 The corresponding surface morphology of the cycled Li metal anodes from (a) Celgard 2400-LE based Li||LFP cells after 200 cycles at 0.5 C and (b) Celgard 2400-LE based Li||LFP cells after 200 cycles at 10 C. The corresponding surface morphology of the cycled Li metal anodes from (a) Celgard 2400-LE based Li||NCM811 cells after 200 cycles at 1 C and (b) Celgard 2400-LE based Li|| NCM811 cells after 200 cycles at 5 C.

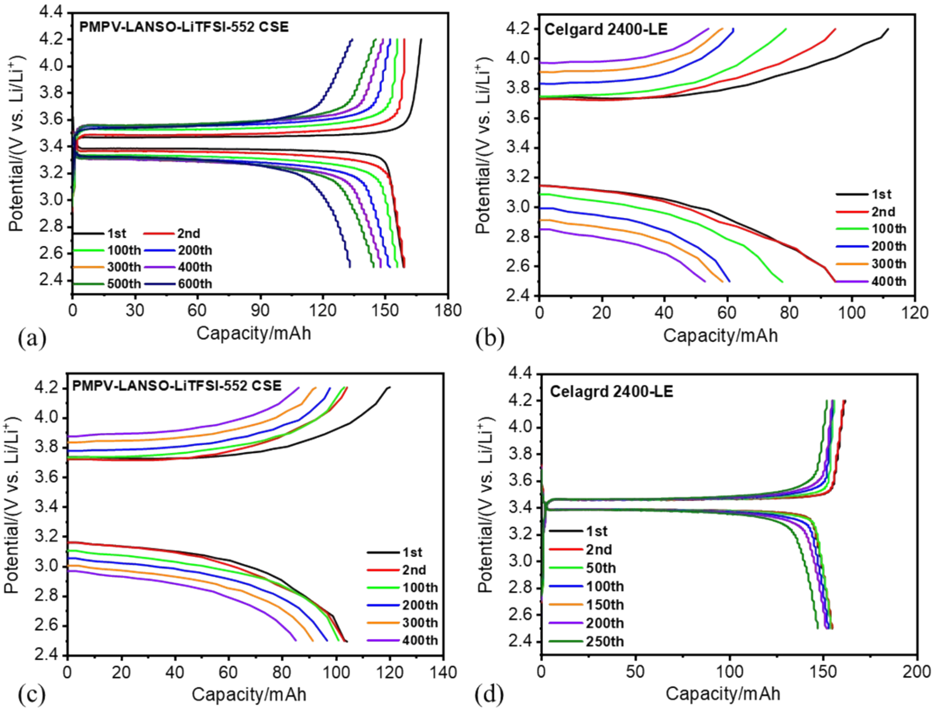

Figure S6. The charge-discharge curves of Li| PMPV-LANSO-LiTFSI-552 CSE |LFP cells at (a) 0.5 C and (c) 10C cycling at room temperature. The charge-discharge curves of Li|Celgard2400-LE|LFP cells at (b) 0.5 C and (d) 10 C cycling at room temperature.

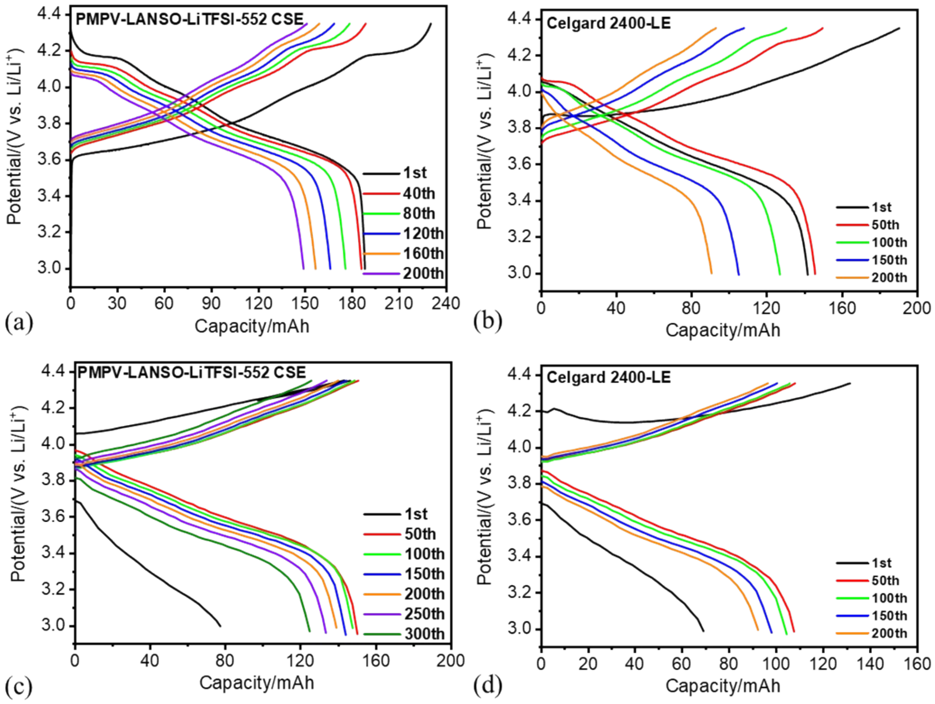

Figure S7 The charge-discharge curves of Li| PMPV-LANSO-LiTFSI-552 CSE |NCM811 cells at (a) 1 C and (c) 5C cycling at room temperature. The charge-discharge curves of Li|Celgard2400-LE|NCM811 cells at (b) 1 C and (d) 5C cycling at room temperature.

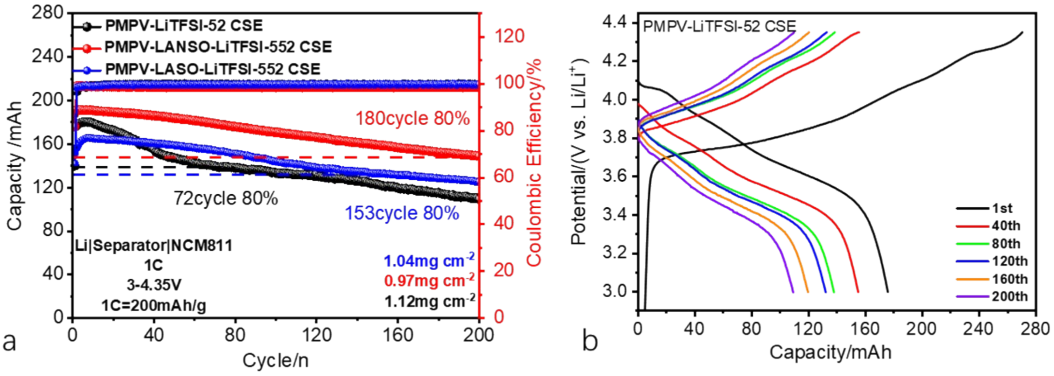

Figure S8 (a)Cycling performances of Li|PMPV-LANSO-LiTFSI-552 CSE|NCM ,Li| PMPV -LiTFSI-52 CSE |NCM and Li| PMPV-LASO-LiTFSI-552 CSE |NCM cells at 1 C,(b) The charge-discharge curves of Li| PMPV -LiTFSI-52 CSE |NCM.

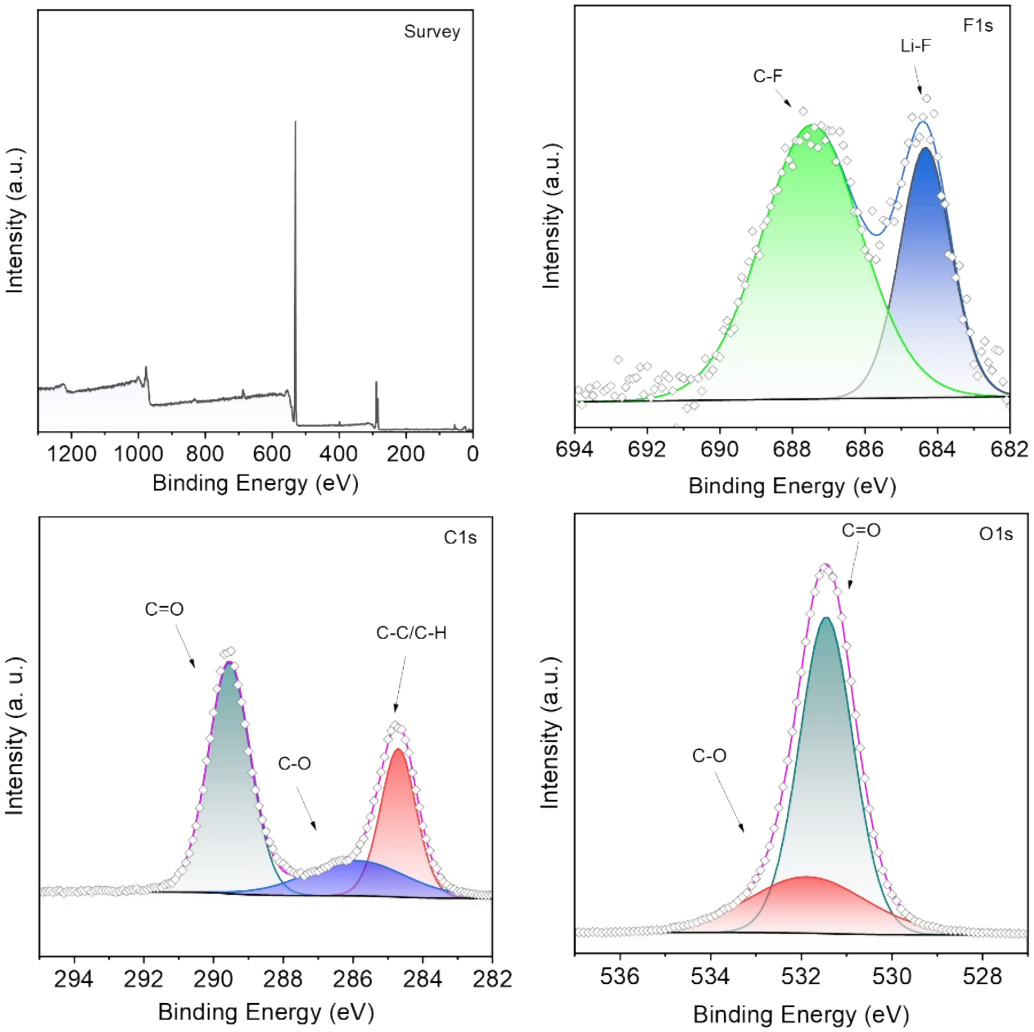

Figure S9 XPS Survey and the detail XPS spectra on (b) F 1s, (c) C 1s, and (d) O 1s of the Li which cycled 200 from Li|PMPV-LANSO-LiTFSI-552 CSE|NCM.