

## **Supplementary Information for**

# **Tuning phase structures of *in-situ* polymerized elastomeric electrolyte *via* monomer structure engineering for achieving high stability in solid-state lithium metal batteries**

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## Experimental Section

### Preparation of electrolytes.

The X-SPEs (i.e., MA-SPE, EA-SPE, BA-SPE, HA-SPE) were fabricated in an argon-filled glove box, where the concentration of O<sub>2</sub> and H<sub>2</sub>O was maintained below 0.1 ppm. MA (99%; Sigma Aldrich), MA ( $\geq 99\%$ ; TCI), BA ( $\geq 99\%$ ; Sigma Aldrich), and HA (98%; Sigma Aldrich) were degassed by argon gas bubbling for 20 min before utilizing. The monomer-based solution was prepared by incorporating 1 mol% of PEGDA (average  $M_n$  575 g/mol; Sigma Aldrich), 0.5 mol% of AIBN (Sigma Aldrich), and 1 M LiTFSI ( $\geq 99\%$ ; Sigma Aldrich) powder in each monomer liquid. Unlike the degassing process of monomers, the SN needed the freeze-pump-thaw procedure: (1) Dissolve solid SN in a 70 °C oven to form a liquid state, (2) rest under a vacuum environment at room temperature for 10 min, and (3) repeat steps (1) and (2) more than three times. The SN-LiTFSI solutions were prepared by mixing SN ( $\geq 99\%$ ; TCI) with 1 M LiTFSI with 5 v/v% of fluoroethylene carbonate (FEC) ( $\geq 98.0\%$ ; TCI) additive, which could protect from undesired electrochemical reactions of SN with Li metal. Each monomer-based solution and SN-LiTFSI solution were mixed homogeneously in a 1:1 volume ratio at 30 °C to generate the X-SPE precursor solutions, which were subsequently in-situ polymerized at 70 °C for 2 hr to fabricate the X-SPEs. In addition, BA-SPE (Dual) was synthesized using the same method as X-SPEs, with the only difference being the salt conditions. In this case, the molar ratio of LiTFSI and LiDFOB was fixed at 8:2, while maintaining an overall salt concentration of 1 M.

### Material Characterization.

The bulk structures of X-SPEs were observed by field-emission SEM (Hitachi SU-8320). To

analyze the internal structure of X-SPEs, the fabricated X-SPEs were promptly frozen in the liquid nitrogen container for Cryo-EM measurement, followed by sectioning it into ultra-thin sections of  $\sim 100$  nm thickness at a temperature of  $-80$  °C using an EM UC7 ultramicrotome (Leica 3 Microsystems GmbH, Vienna, Austria) with a cryo chamber (EM FC7, Leica Microsystems GmbH, Vienna, Austria) equipped with a glass knife by cutting rate of  $0.2$  mm  $s^{-1}$ . The contact angles between polymer phase and the water droplet were measured by a contact angle analyzer (Phoenix 150, SEO, Inc., Korea). Thermogravimetric analysis (TGA) (TA Instruments Q500) was utilized from  $25$  to  $600$  °C at  $10$  °C  $min^{-1}$  of heating rate under a nitrogen atmosphere.  $^7Li$  solid-state NMR (Bruker Avance III HD, 500MHz) was analyzed at room temperature. A mechanical tensile test was conducted utilizing a universal testing machine (UTM; Lloyd Instruments LR5K) equipped with a  $100$  N force transducer. The tensile stress (y-axis) of elastomeric X-SPEs was expressed as a true stress value. To prepare the bulk samples, the X-SPEs precursor solutions were in-situ polymerized in dogbone-shaped specimens (ASTM D412 Type C).

### **3D Construction of EA-SPE and BA-SPE Films by TEM Tomography.**

A series of 2D TEM image projections of the EA-SPE and BA-SPE films for TEM tomography were acquired using a JEM-1400 TEM (JEOL Ltd., Tokyo, Japan) operating at  $120$  kV. The electron beam maintained a constant current density of  $10.2$  pA  $cm^{-2}$ . The tilt series of TEM images were captured at a magnification of  $15,000$  x and recorded with a  $1$  sec exposure time using a  $2048 \times 2048$  pixels Tengra CCD camera (EMSIS GmbH, Münster, Germany). The pixel size of the measured TEM images was estimated to be  $5.72$  nm. The sequence of projection images was obtained at angles from  $-70^\circ$  to  $70^\circ$ , with a tilt increment given by  $2^\circ$  using a high tilt holder (JEOL Ltd., Tokyo, Japan). After every individual tilt increase, tilting, refocusing, and repositioning were performed. The alignment and reconstruction of the tilt series were

performed in IMOD software. 3D visualization of the final volumes was carried out using Amira 6.0 visualization software (Thermo Fisher, Waltham, MA, USA). To improve the quality of the reconstruction of the EA-SPE and BA-SPE films, a nonlinear anisotropic diffusion filter was applied to reduce noise and enhance segmentation. The specific slicing plane from the reconstructed volume was selected to illustrate the 3D morphology of EA-SPE and BA-SPE films, as shown in **Fig. 2**. The thickness of EA-SPE and BA-SPE films were to be 132 nm and 158 nm, respectively. The middle phase of EA-SPE and BA-SPE films shown in **Fig. 2f** and **g** at the height of 65 nm and 80 nm from the bottom was extracted from the reconstructed volume.

### **Electrode preparation.**

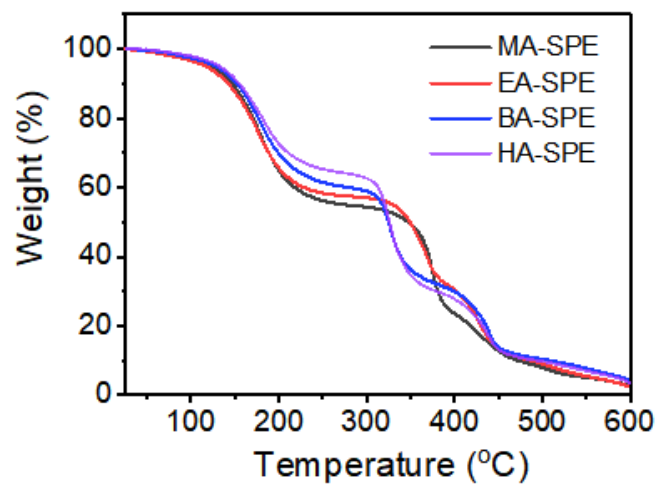
LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> (NCM811) cathode was prepared by a slurry casting process. NCM811, Super P carbon, and polyvinylidene fluoride were dissolved in N-methyl-2-pyrrolidone with a weight ratio of 8:1:1 to make a slurry by overnight stirring and then coated onto a current collector of aluminum foil. The fabricated cathodes were dried in a vacuum oven at 60 °C for more than 24 hr. The active loading densities of the cathode were 4.5 mg cm<sup>-2</sup> and over 10 mg cm<sup>-2</sup>.

### **Electrochemical measurements.**

The electrochemical performance of each cell was evaluated using 2032-type coin cells constructed with Li metal anode in a glovebox filled with argon gas (concentration of O<sub>2</sub> and H<sub>2</sub>O below 0.1 ppm). Each X-SPE solution was mixed uniformly at 30 °C and injected into the coin cells with a separator (i.e., Celgard 2500 for Li/NCM811 full cell tests, glass fiber (GF/A) for ionic conductivity measurements). The assembled cell was then heated for 2 hr at 70 °C for in-situ polymerization. Electrochemical impedance spectroscopy (EIS) (BioLogic SP-200) of X-SPEs was recorded from 10<sup>7</sup> to 10<sup>-3</sup> Hz for full cells with a peak voltage of 10 mV at an

open-circuit voltage. The ionic conductivity of electrolytes was measured by EIS with stainless steel (SS)/X-SPEs/SS symmetric cells at 20 °C. The 40  $\mu\text{m}$ -Li/25  $\mu\text{m}$  X-SPE/NCM811 (4.5 mg  $\text{cm}^{-2}$ ) cells with various X-SPEs including BA-SPE (Dual) were investigated by galvanostatic charge/discharge tests in the voltage range of 2.7-4.3 V (Neware battery tester) at 25 °C. After three formation cycles at a rate of 0.2C, the cycling stability tests of the cells were conducted at the rate of 0.5C in the same voltage range. The rate capability tests were performed in the voltage range of 2.7-4.3 V, while varying the C-rate from 0.2C to 3C. In the case of BA-SPE (Dual), high-loading full cells with 40  $\mu\text{m}$ -Li/NCM811 (>10 mg  $\text{cm}^{-2}$ ) were examined by galvanostatic charge/discharge tests in the voltage range of 2.7-4.3 V at different current densities of 0.5 mA  $\text{cm}^{-2}$  after three pre-cycles with 0.2 mA  $\text{cm}^{-2}$ .

## Supplementary Figures and Tables



**Fig. S1** Thermogravimetric analysis (TGA) measurements of MA-SPE, EA-SPE, BA-SPE and HA-SPE.

**Table S1** Functional group contribution values used for deriving Hansen solubility parameters (HSPs) of MA-SPE.<sup>1,2</sup>

Functional Group	Occurrences	$V$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$F_{di}$ ( $\text{J}^{1/2} \text{cm}^{3/2} \text{mol}^{-1}$ )	$F_{pi}$ ( $\text{J}^{1/2} \text{cm}^{3/2} \text{mol}^{-1}$ )	$U_{hi}$ ( $\text{J mol}^{-1}$ )
-CH <sub>3</sub>		33.5	420	0	0
-CH <sub>2</sub> -		16.1	270	0	0
>CH-		-1	80	0	0
-COO-		18.0	390	490	7000
Functional Group	Occurrences	$\Sigma V$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$\Sigma F_{di}$ ( $\text{J}^{1/2} \text{cm}^{3/2} \text{mol}^{-1}$ )	$\Sigma F_{pi}^2$ ( $\text{J}^{1/2} \text{cm}^{3/2} \text{mol}^{-1}$ )	$\Sigma U_{hi}$ ( $\text{J mol}^{-1}$ )
-CH <sub>3</sub>	1	33.5	420	0	0
-CH <sub>2</sub> -	1	16.1	270	0	0
>CH-	1	-1	80	0	0
-COO-	1	18.0	390	240100	7000
Total		66.7	1160	240100	7000

From the calculation above,  $\delta_D$ ,  $\delta_P$ , and  $\delta_H$  parameters were estimated to be 17.42 MPa<sup>1/2</sup>, 7.36 MPa<sup>1/2</sup>, and 10.25 MPa<sup>1/2</sup>, respectively.

**Table S2** Functional group contribution values used for deriving HSPs of EA-SPE.

Functional Group	Occurrences	$V$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$F_{di}$ ( $\text{J}^{1/2} \text{cm}^{3/2} \text{mol}^{-1}$ )	$F_{pi}$ ( $\text{J}^{1/2} \text{cm}^{3/2} \text{mol}^{-1}$ )	$U_{hi}$ ( $\text{J mol}^{-1}$ )
-CH <sub>3</sub>		33.5	420	0	0
-CH <sub>2</sub> -		16.1	270	0	0
>CH-		-1	80	0	0
-COO-		18.0	390	490	7000
Functional Group	Occurrences	$\Sigma V$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$\Sigma F_{di}$ ( $\text{J}^{1/2} \text{cm}^{3/2} \text{mol}^{-1}$ )	$\Sigma F_{pi}^2$ ( $\text{J}^{1/2} \text{cm}^{3/2} \text{mol}^{-1}$ )	$\Sigma U_{hi}$ ( $\text{J mol}^{-1}$ )
-CH <sub>3</sub>	1	33.5	420	0	0
-CH <sub>2</sub> -	2	32.2	540	0	0
>CH-	1	-1	80	0	0
-COO-	1	18.0	390	240100	7000
Total		82.7	1430	240100	7000

From the calculation above,  $\delta_D$ ,  $\delta_P$ , and  $\delta_H$  parameters were estimated to be 17.29 MPa<sup>1/2</sup>, 5.92 MPa<sup>1/2</sup>, and 9.20 MPa<sup>1/2</sup>, respectively.



**Table S3** Functional group contribution values used for deriving HSPs of BA-SPE.

Functional Group	Occurrences	$V$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$F_{di}$ ( $\text{J}^{1/2} \text{cm}^{3/2} \text{mol}^{-1}$ )	$F_{pi}$ ( $\text{J}^{1/2} \text{cm}^{3/2} \text{mol}^{-1}$ )	$U_{hi}$ ( $\text{J mol}^{-1}$ )
-CH <sub>3</sub>		33.5	420	0	0
-CH <sub>2</sub> -		16.1	270	0	0
>CH-		-1	80	0	0
-COO-		18.0	390	490	7000
Functional Group	Occurrences	$\Sigma V$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$\Sigma F_{di}$ ( $\text{J}^{1/2} \text{cm}^{3/2} \text{mol}^{-1}$ )	$\Sigma F_{pi}^2$ ( $\text{J}^{1/2} \text{cm}^{3/2} \text{mol}^{-1}$ )	$\Sigma U_{hi}$ ( $\text{J mol}^{-1}$ )
-CH <sub>3</sub>	1	33.5	420	0	0
-CH <sub>2</sub> -	4	64.4	1080	0	0
>CH-	1	-1	80	0	0
-COO-	1	18.0	390	240100	7000
Total		114.9	1970	240100	7000

From the calculation above,  $\delta_D$ ,  $\delta_P$ , and  $\delta_H$  parameters were estimated to be 17.15 MPa<sup>1/2</sup>, 4.26 MPa<sup>1/2</sup>, and 7.81 MPa<sup>1/2</sup>, respectively.

**Table S4** Functional group contribution values used for deriving HSPs of HA-SPE.

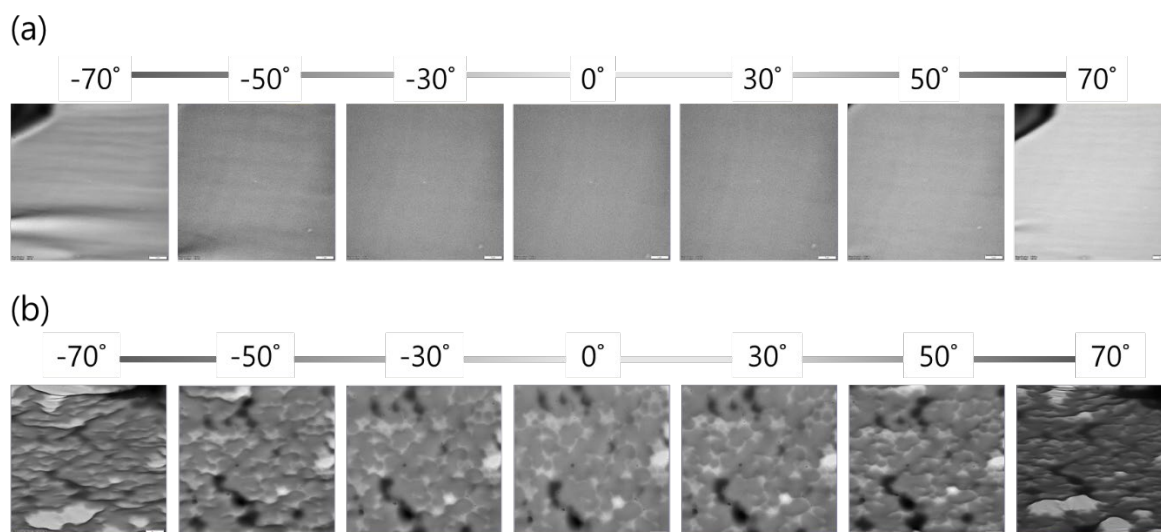
Functional Group	Occurrences	$V$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$F_{di}$ ( $\text{J}^{1/2} \text{cm}^{3/2} \text{mol}^{-1}$ )	$F_{pi}$ ( $\text{J}^{1/2} \text{cm}^{3/2} \text{mol}^{-1}$ )	$U_{hi}$ ( $\text{J mol}^{-1}$ )
-CH <sub>3</sub>		33.5	420	0	0
-CH <sub>2</sub> -		16.1	270	0	0
>CH-		-1	80	0	0
-COO-		18.0	390	490	7000
Functional Group	Occurrences	$\Sigma V$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$\Sigma F_{di}$ ( $\text{J}^{1/2} \text{cm}^{3/2} \text{mol}^{-1}$ )	$\Sigma F_{pi}^2$ ( $\text{J}^{1/2} \text{cm}^{3/2} \text{mol}^{-1}$ )	$\Sigma U_{hi}$ ( $\text{J mol}^{-1}$ )
-CH <sub>3</sub>	1	33.5	420	0	0
-CH <sub>2</sub> -	6	96.6	1620	0	0
>CH-	1	-1	80	0	0
-COO-	1	18.0	390	240100	7000
Total		147.1	2510	240100	7000

From the calculation above,  $\delta_D$ ,  $\delta_P$ , and  $\delta_H$  parameters were estimated to be 17.06 MPa<sup>1/2</sup>, 3.33 MPa<sup>1/2</sup>, and 6.90 MPa<sup>1/2</sup>, respectively.

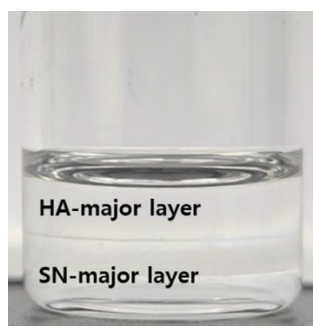
**Table S5** Functional group contribution values used for deriving HSPs of SN.

Functional Group	Occurrences	$V$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$F_{di}$ ( $\text{J}^{1/2} \text{cm}^{3/2} \text{mol}^{-1}$ )	$F_{pi}$ ( $\text{J}^{1/2} \text{cm}^{3/2} \text{mol}^{-1}$ )	$U_{hi}$ ( $\text{J mol}^{-1}$ )
-CH <sub>2</sub> -		16.1	270	0	0
-CN		24.0	430	1100	2500
Functional Group	Occurrences	$\Sigma V$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$\Sigma F_{di}$ ( $\text{J}^{1/2} \text{cm}^{3/2} \text{mol}^{-1}$ )	$\Sigma F_{pi}^2$ ( $\text{J}^{1/2} \text{cm}^{3/2} \text{mol}^{-1}$ )	$\Sigma U_{hi}$ ( $\text{J mol}^{-1}$ )
-CH <sub>3</sub>	2	32.2	540	0	0
-CN	2	48.0	860	2420000	5000
Total		179.3	3050	2420000	5000

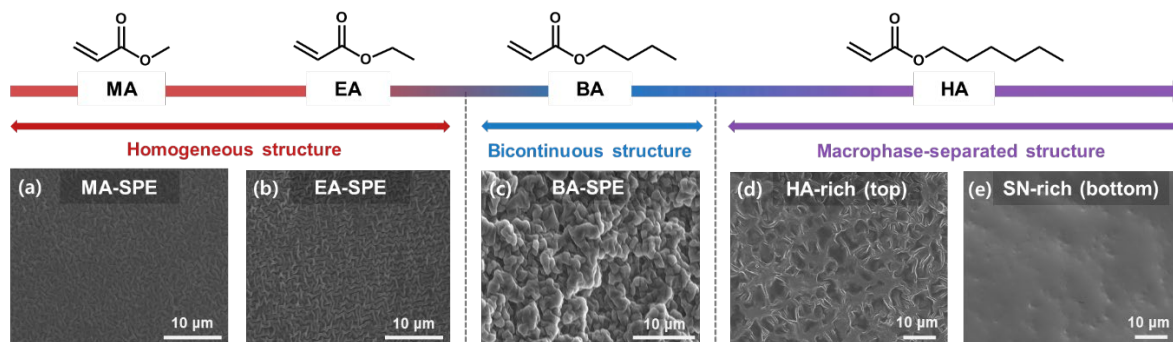
From the calculation above,  $\delta_D$ ,  $\delta_P$ , and  $\delta_H$  parameters were estimated to be 17.46 MPa<sup>1/2</sup>, 19.4 MPa<sup>1/2</sup>, and 7.90 MPa<sup>1/2</sup>, respectively.



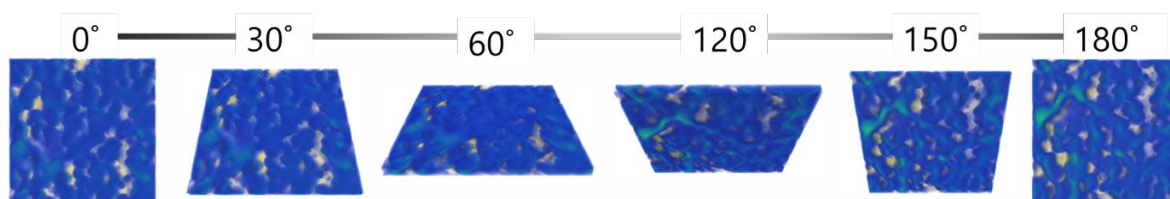
**Fig. S2** Cryo-EM images of (a) EA-SPE and (b) BA-SPE at different tilt angles.



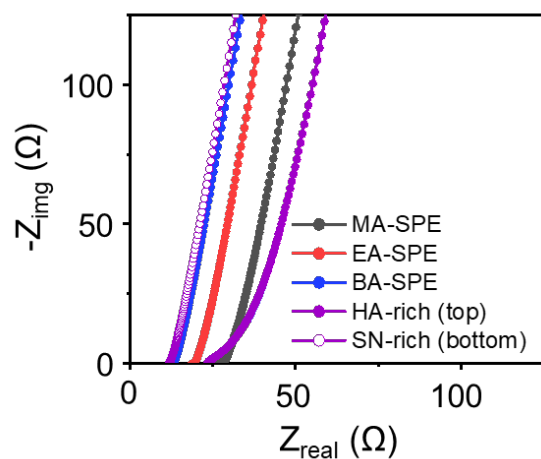
**Fig. S3** Photo image of the layered structure of HA-SPE precursor solution before polymerization. The HA-major solution forms the upper layer (i.e., HA-major layer), while the SN-major solution settles as the lower layer (i.e., SN-major layer).



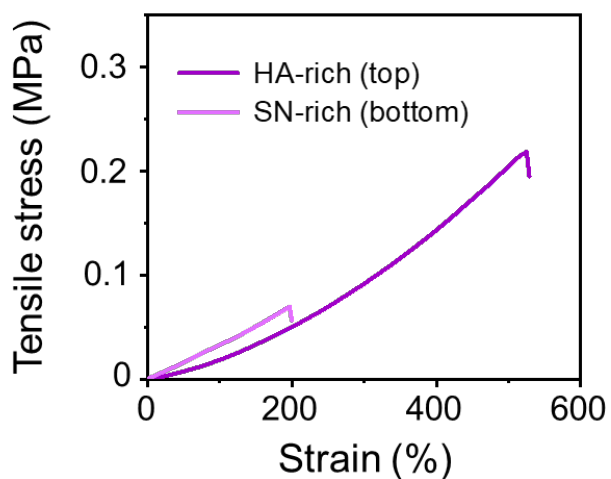
**Fig. S4** SEM images of XA-SPEs with different alkyl chain lengths of acrylate monomer: (a) MA, (b) EA, (c) BA, (d,e) HA.



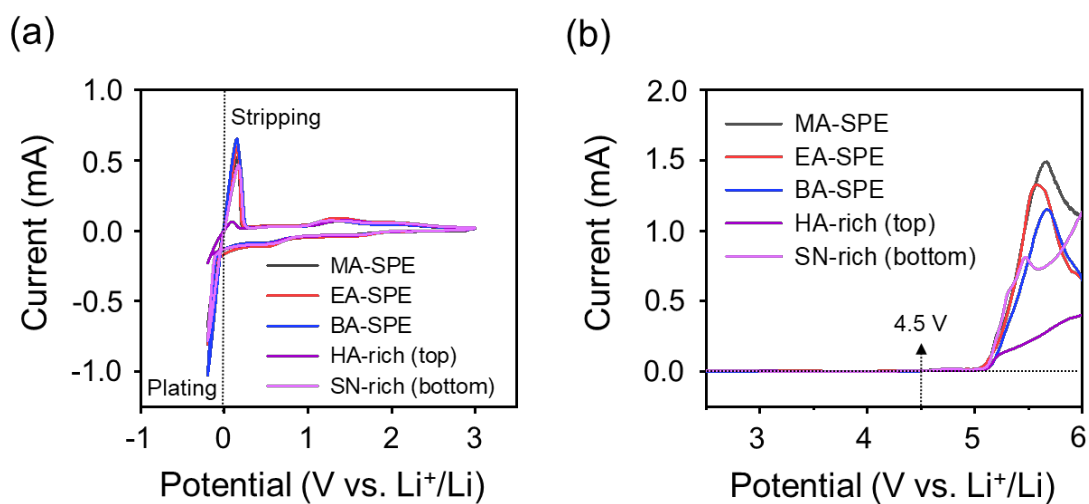
**Fig. S5** 3D TEMT images of BA-SPE under different rotation degrees along the vertical z-axis: 0°, 30°, 60°, 120°, 150°, and 180°.



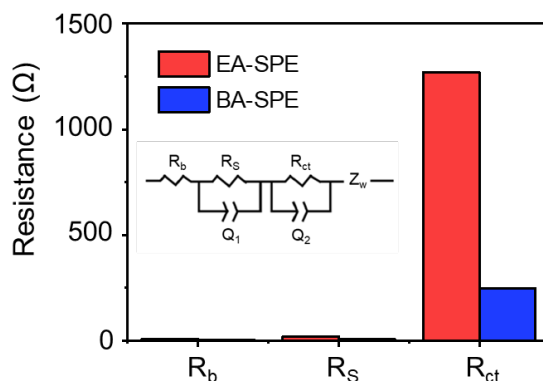
**Fig. S6** Nyquist plots of the X-SPEs measured by EIS.



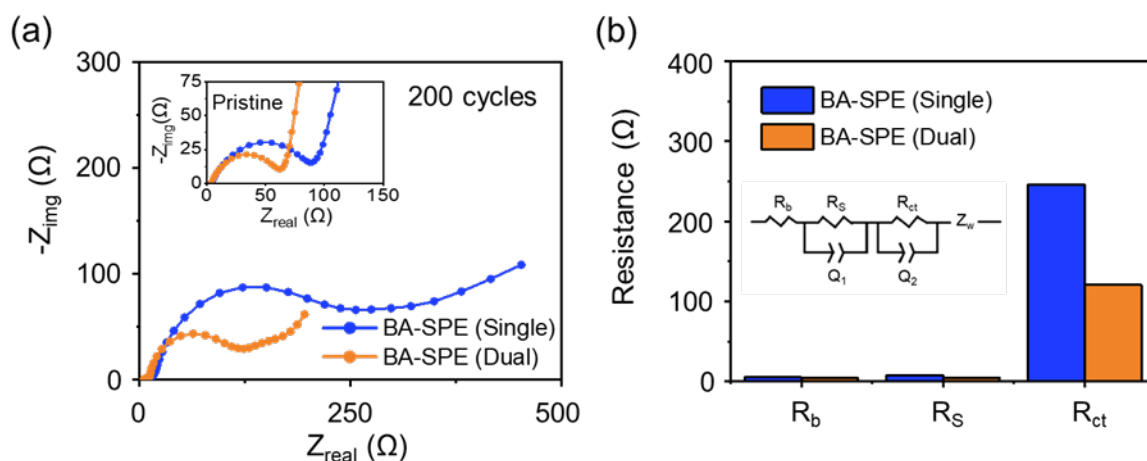
**Fig. S7** Stress-strain curves of HA-rich (top) and SN-rich (bottom) at an extension rate of 100 mm min<sup>-1</sup>. The HA-rich (top) and SN-rich (bottom) showed elongation at break point of 525% and 200%.



**Fig. S8** (a) Cyclic voltammetry (CV) and (b) linear sweep voltammetry (LSV) tests of X-SPEs. CV was conducted using Li||stainless steel (SS) asymmetric cells from -0.2 V to 3 V with a scan rate of  $2 \text{ mV s}^{-1}$ . LSV was carried out using Li||SS cells from 2.5 V to 6.0 V at a scan rate of  $1 \text{ mV s}^{-1}$ .



**Fig. S9** Different types of resistances derived at the 200 cycles for EA-SPE and BA-SPE from Fig. 4f. ( $R_b$ , bulk electrolyte resistance;  $R_s$ , surface film resistance;  $R_{ct}$ , charge transfer resistance). The inset in the plot represents an equivalent circuit for modeling Nyquist plots of full cells.



**Fig. S10** (a) Nyquist plot of the full cells of BA-SPE (Single) and BA-SPE (Dual); Pristine (inset) and after 200 cycles.  $Z_{real}$  and  $-Z_{img}$  are the real and imaginary values of the Nyquist plot. (b) Different types of resistances derived at the 200 cycles for BA-SPE (Single) and BA-SPE (Dual). ( $R_b$ , bulk electrolyte resistance;  $R_s$ , surface film resistance;  $R_{ct}$ , charge transfer resistance). The inset in the plot represents an equivalent circuit for modeling Nyquist plots of full cells.



## References

- 1 Barton, A. F. M. *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*, CRC Press, 1991.
- 2 Hansen, C. M. *Hansen solubility parameters: a user's handbook, Second Edition*, CRC Press, 2007.