

Supplementary Information

Phase regulation enabling dense polymer-based composite electrolytes for solid-state lithium metal batteries

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Supplementary Note 1

The nonuniform distribution of the DMF solvent and the porous structure of the PVDF electrolyte could always induce uneven Li deposition and rapid Li dendrite growth, as evidenced by previous reports^{1, 2}. To further confirm this, we directly observed the Li deposition morphology in Li||Cu cells and tested the maximum Li deposition capacity in Li||Li cells. First, the plating morphologies of Li (1 mAh cm⁻²) on Cu substrates were examined. As shown in Supplementary Fig. 10, the Li|PVDF|Cu cell presents a highly loose and irregular deposition structure with many small Li particles, demonstrating the uneven Li deposition with the PVDF electrolyte. Second, to further quantitatively evaluate the effect of dense electrolyte structure on the uniform Li deposition, we assembled Li|PVDF|Li cell to test the critical deposition capacity (CDC), which is defined as the maximum endurable capacity of Li metal anode during cycling before Li dendrite growth and battery circuit short. The Li|PVDF|Li cell was cycled 5 times under current density of 0.1 mA cm⁻² to form the SEI, which was then operated by continuous charge (one side Li metal stripping and the other side Li metal plating), until the battery presents a short circuit. As shown in Supplementary Fig. 11, the CDC in the PVDF electrolyte is approximately 1 mAh cm⁻². Given this, we can conclude that the uneven Li deposition and limited capacity always induce rapid Li dendrite growth and restrict the performance of the solid-state batteries under high loadings.

Supplementary Note 2

To evaluate the electronic conductivities of the formed SEI, we directly measured them following our previous reported method³. Since the SEI has similar properties with the solid-state electrolyte (SSE), the SEI could be considered as a thin SSE layer⁴. Therefore, the assembly of the device for investigating the electronic conductivity of the SEI can follow the Hebb-Wagner method for measuring the electronic conductivity of the SSE. Given this, we cycled the Li||NCM811 full cells for 20 times at 0.5C and 25°C and then disassembled them to obtain the SEI-coated Li metal anode (denoted as SEI-Li). The SEI-Li was clamped by two steel plates, and then the (-) Li/SEI/blocking electrode (+) cells were assembled. A dc voltage was applied in a chronoamperometric mode to the cells using an AMETEK. In the stationary state, the remaining current only stems from electrons diffusing through the SEI^{5, 6}. The resistance of the SEI (R_e) could be calculated by equation (1):

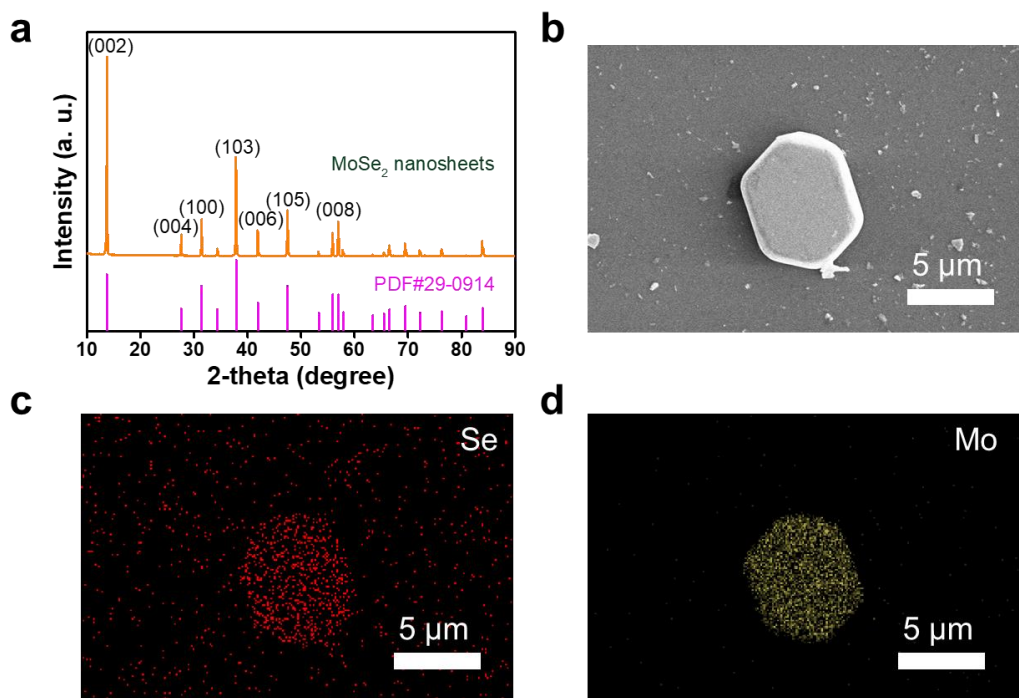
$$R_e = \frac{\Delta V}{\Delta I_l} \quad (1)$$

where ΔV is the step voltage of 10 mV, and ΔI_l is the steady state response current. Thus, the electronic resistivity (ρ) of the SEI could be calculated by equation (2):

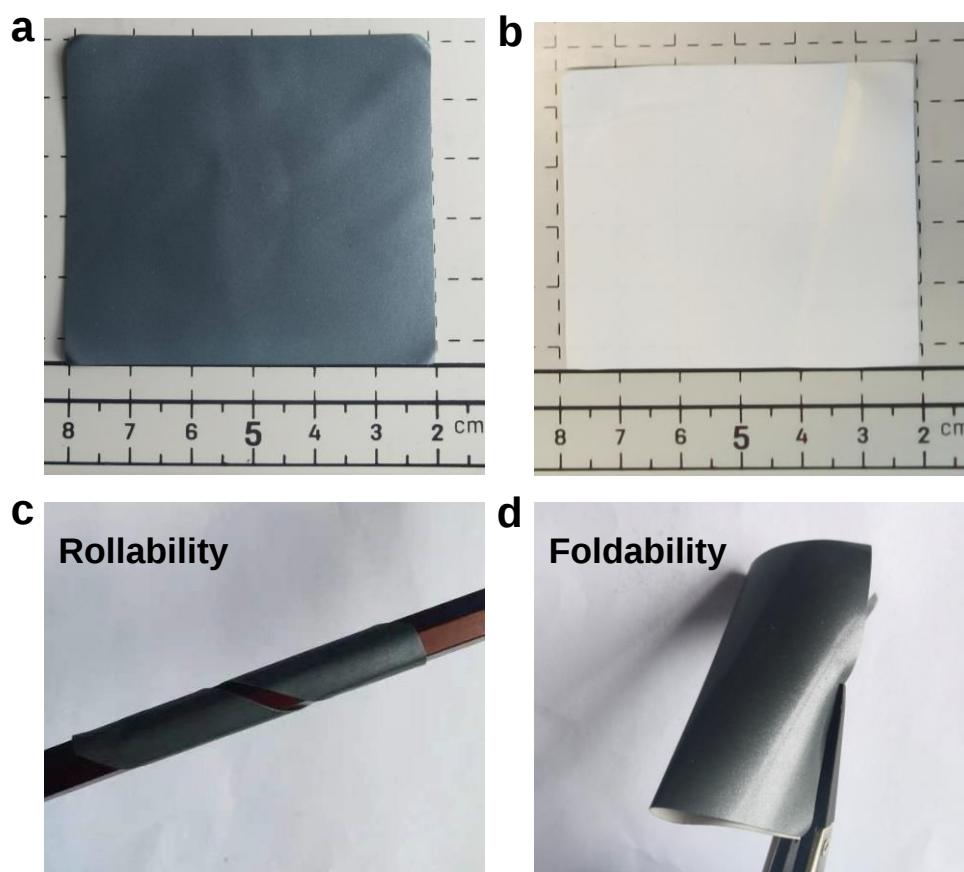
$$\rho = \frac{R_e \times A}{L} \quad (2)$$

where A is the area of SEI (2 cm²), L is the thickness of SEI which has been obtained by cryogenic scanning transmission electron microscopy (cryo-STEM). Although the resistivity value calculated by this method may be a little lower than the actual value due to the underestimated A and the complicated structure of Li deposition, this does not hinder us from judging the electroconductivity of the SEI. As shown in Supplementary Fig. 49, the electronic resistivity of the SEI in PVMS-15 electrolyte is $4.23 \times 10^5 \Omega \text{ cm}$, almost equal to that in the PVDF electrolyte ($4.21 \times 10^5 \Omega \text{ cm}$). The electronic conductivity is calculated to be $2.36 \times 10^{-6} \text{ S cm}^{-1}$ and $2.38 \times 10^{-6} \text{ S cm}^{-1}$, respectively. This result demonstrates that the formation of metallic Mo and Mo-containing species show negligible influence on the electroconductivity of the SEI. In addition, the value of the electronic conductivities is acceptable for practical lithium metal batteries⁷.

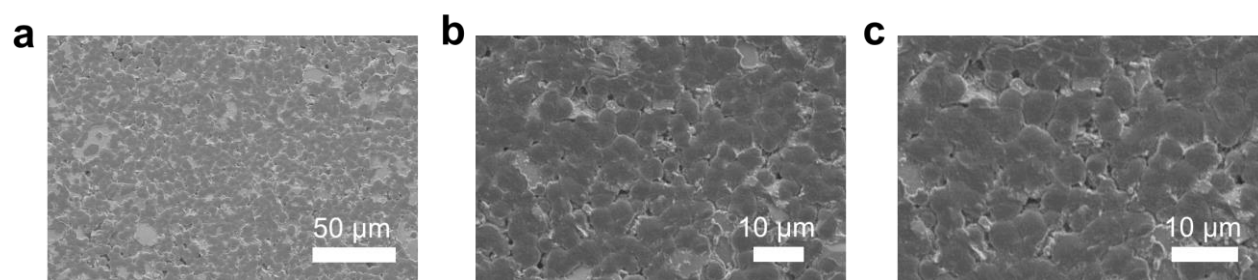
Supplementary Figures



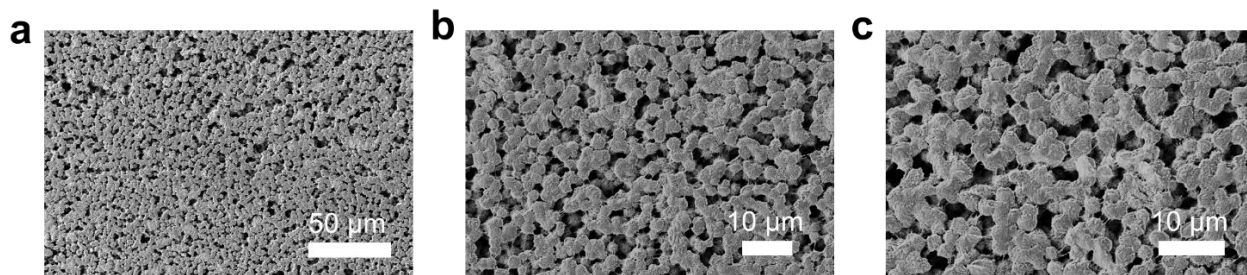
Supplementary Figure 1. Morphology and structure characterizations of MSs. **a** XRD pattern of MoSe₂ nanosheet. **b** SEM image of MoSe₂ nanosheet and its EDS mapping of Se (**c**) and Mo (**d**) element.



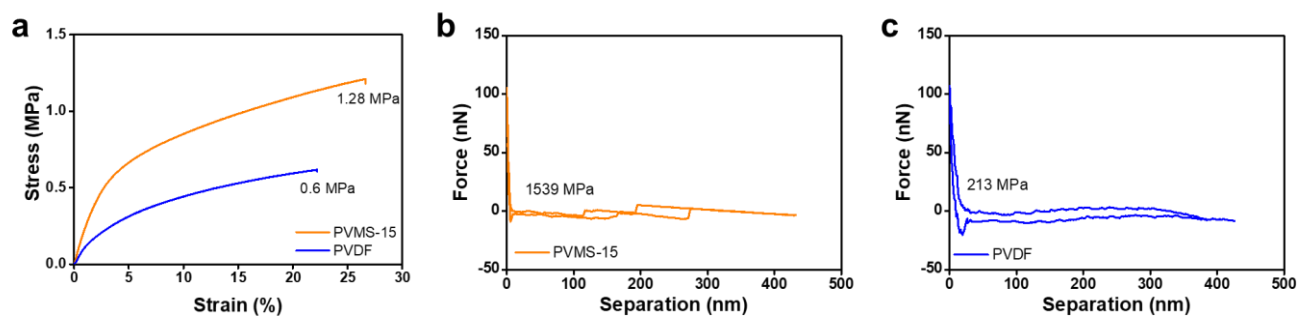
Supplementary Figure 2. Optical photographs of PVDF and PVMS-15 electrolytes. a PVDF electrolyte. **b** PVMS-15 electrolyte and rollability (**c**) and foldability (**d**) tests.



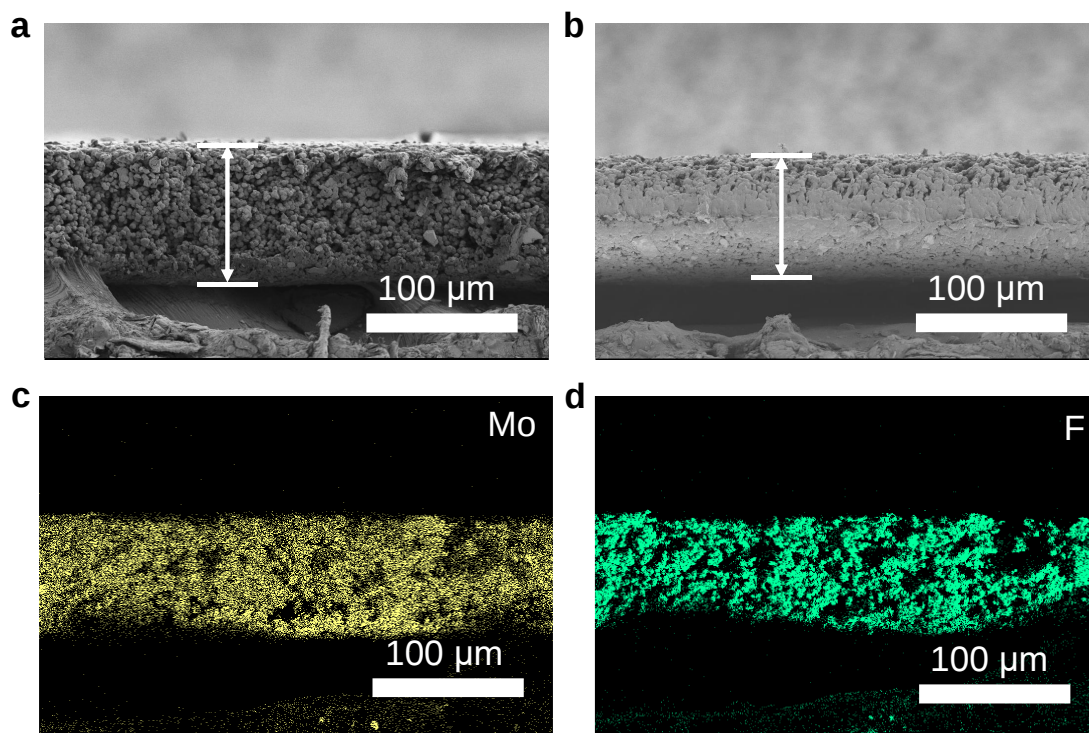
Supplementary Figure 3. SEM images of the PVMS-15 electrolyte. a 500 $\times$. b 1500 $\times$. c 2000 $\times$.



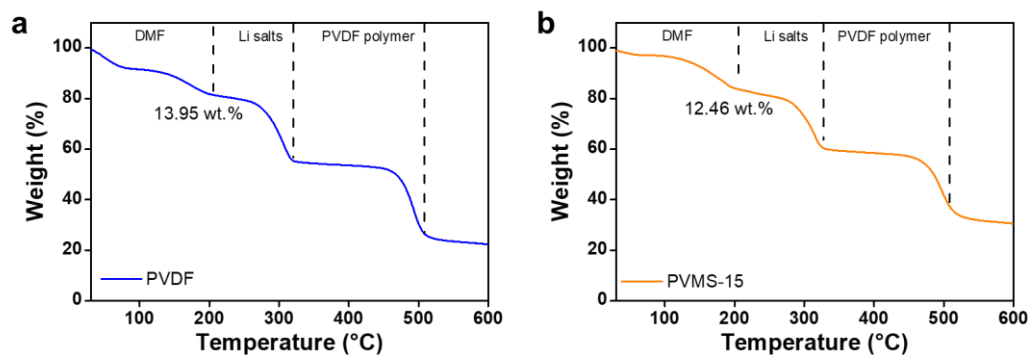
Supplementary Figure 4. SEM images of the PVDF electrolyte. a 500×. b 1500×. c 2000×.



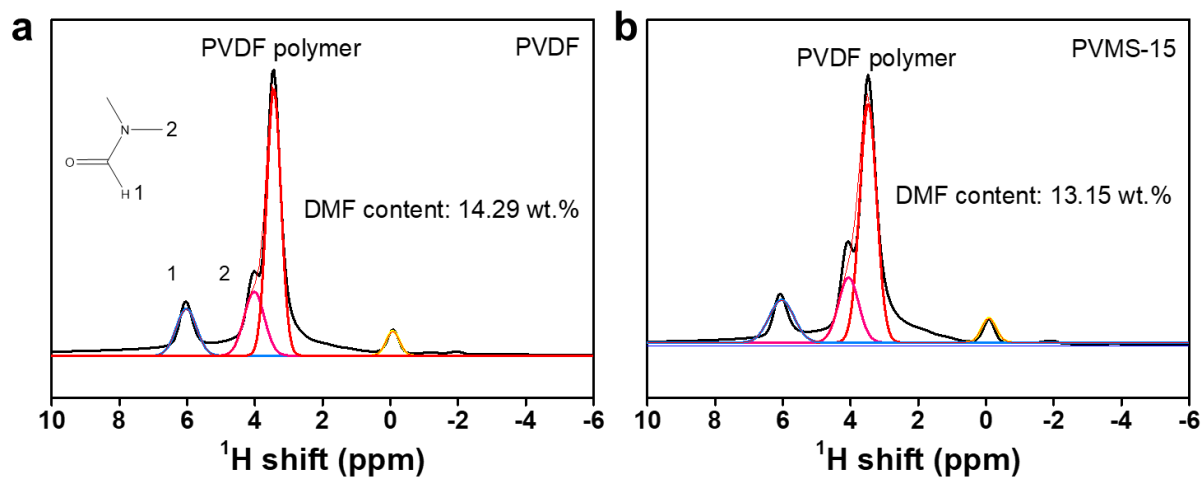
Supplementary Figure 5. Mechanical properties of electrolytes. **a** Tensile strength tested by stress-strain curves of PVDF and PVMS-15 electrolytes. Young's modules tested by force-separation curves of PVMS-15 (**b**) and PVDF (**c**) electrolytes.



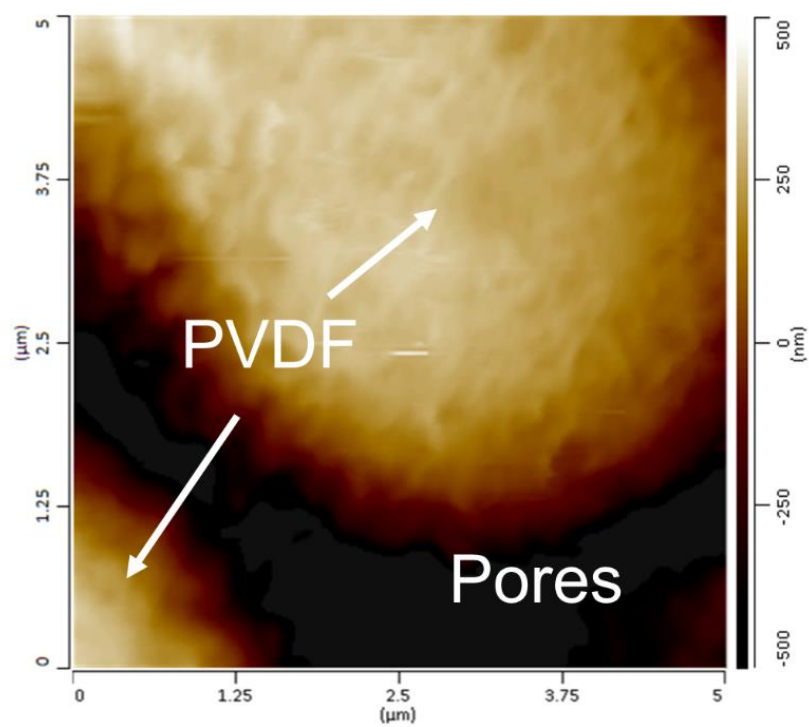
Supplementary Figure 6. Cross sectional SEM images of the electrolytes. a PVDF electrolyte. **b** PVMS-15 electrolyte and its EDS mappings of Mo (**c**) and F (**d**) elements.



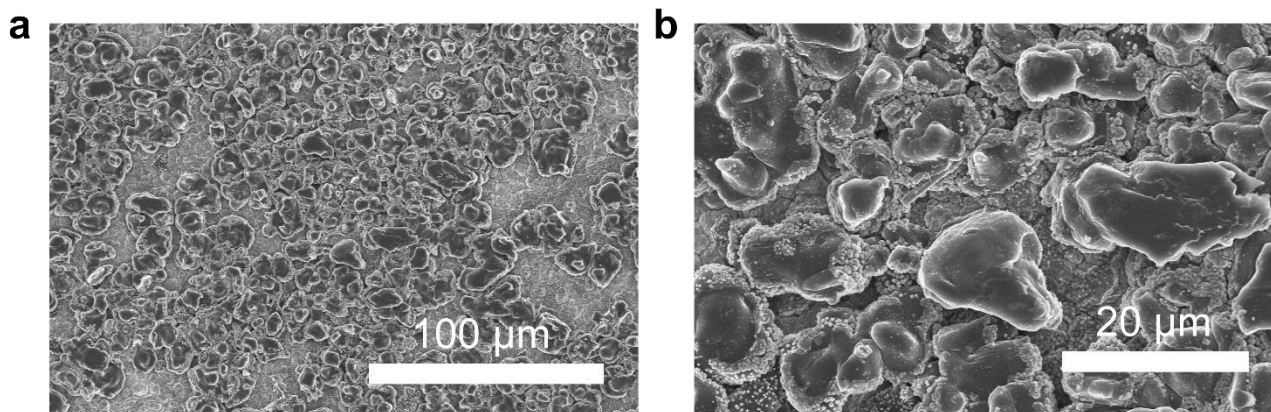
Supplementary Figure 7. Solvent content tested by TGA. TGA curves of PVDF (a) and PVMS-15 (b) electrolytes.



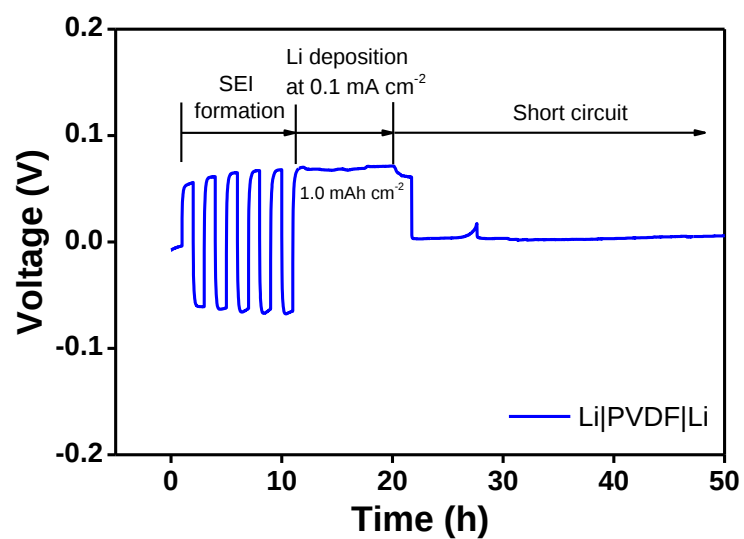
Supplementary Figure 8. Solvent content tested by ss-NMR. ^1H spectra of PVDF (a) and PVMS-15 (b) electrolytes.



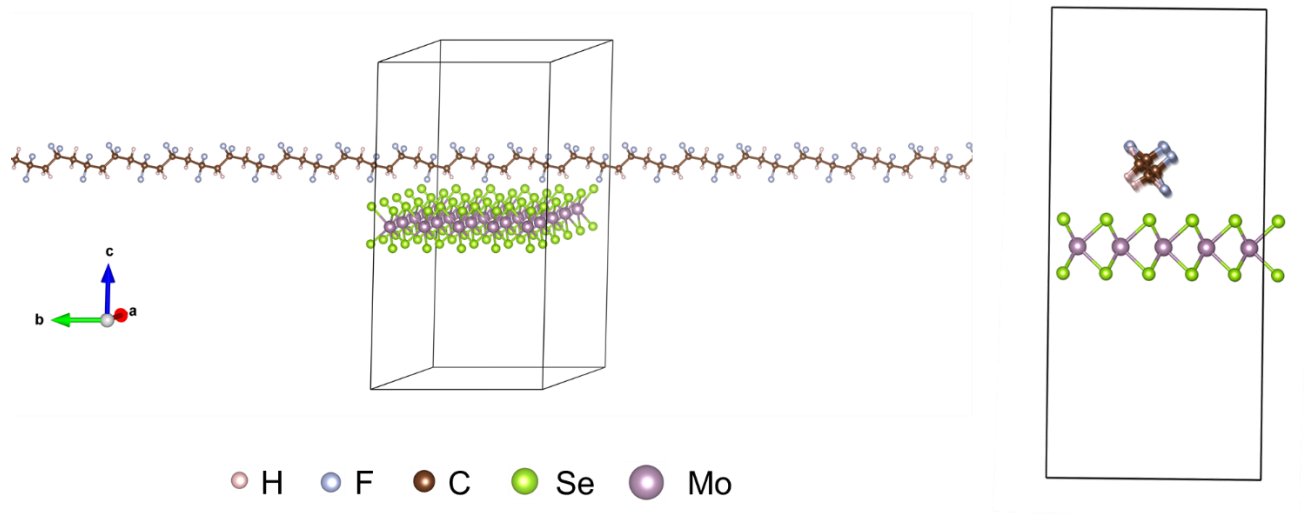
Supplementary Figure 9. AFM height map of the PVDF electrolyte.



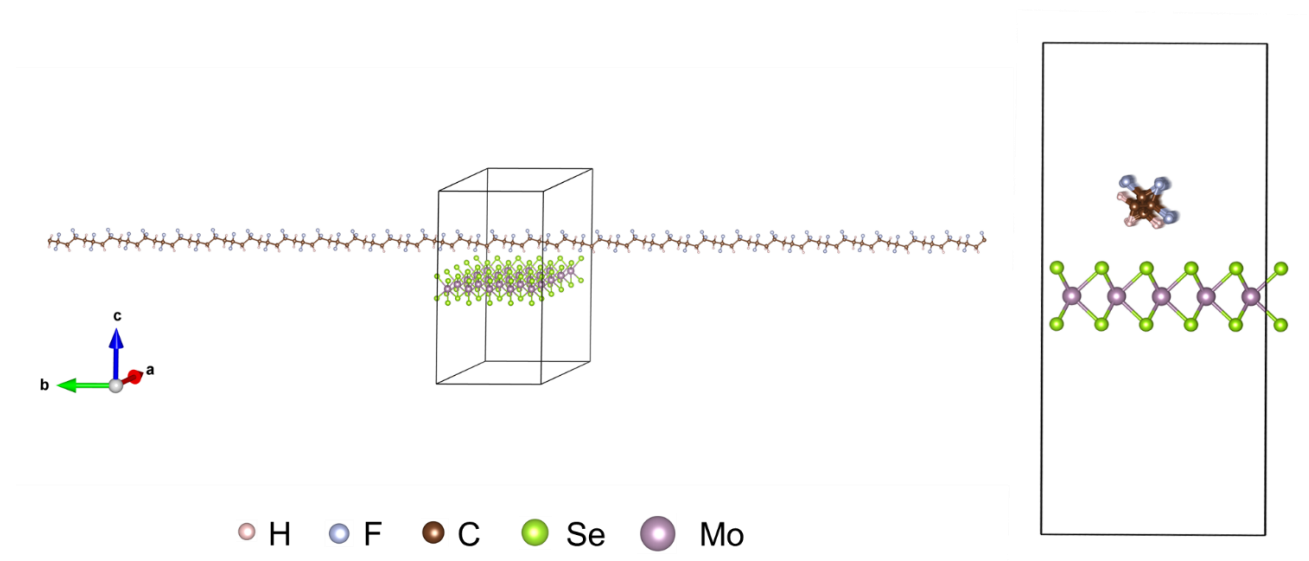
Supplementary Figure 10. SEM images of the Li deposition obtained by plating 1 mAh cm^{-2} Li on Cu substrate at 0.1 mA cm^{-2} in Li||Cu cells using PVDF electrolyte. a 500 $\times$. b 2000 $\times$.



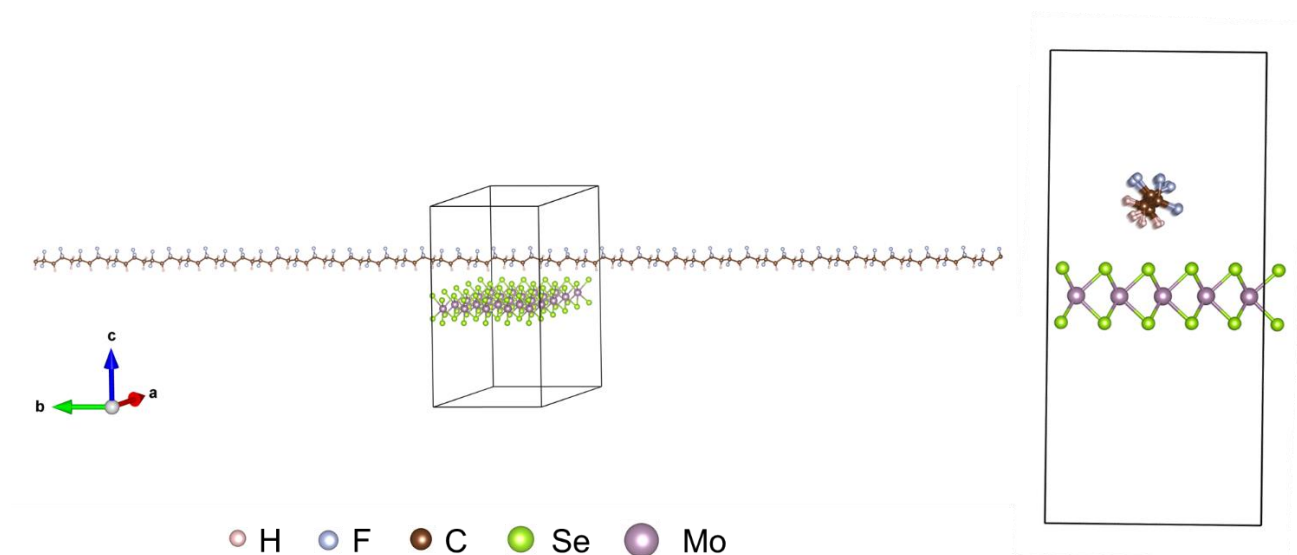
Supplementary Figure 11. CDC test curves in Li||Li cells at 0.1 mA cm^{-2} using PVDF electrolyte.



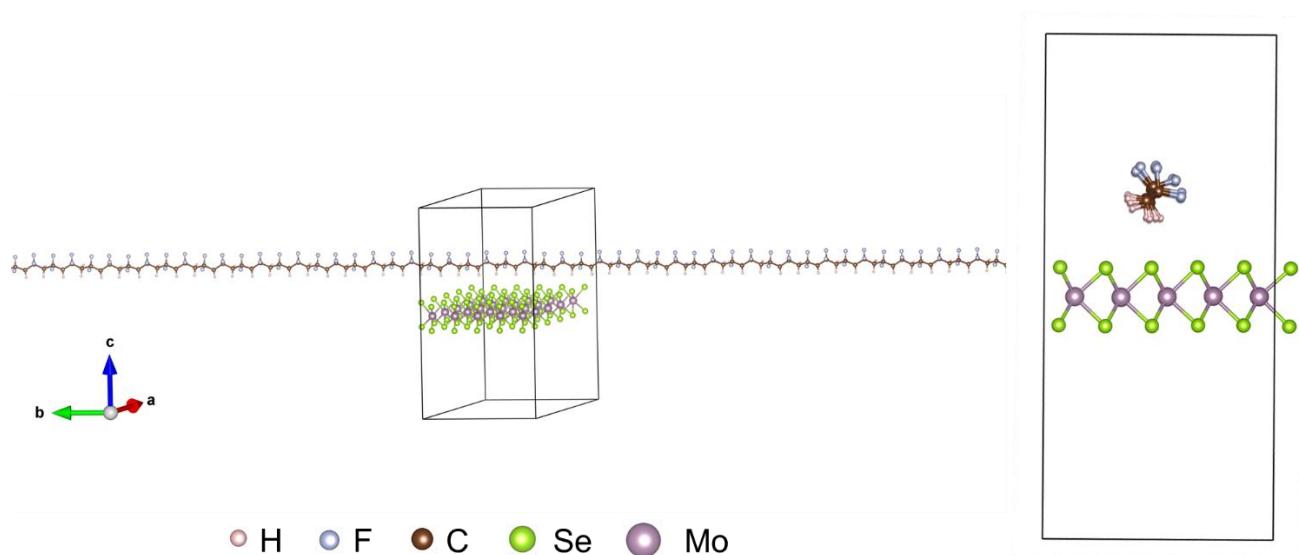
Supplementary Figure 12. DFT Geometry optimization of the interactions between MSs and PVDF at step 1.



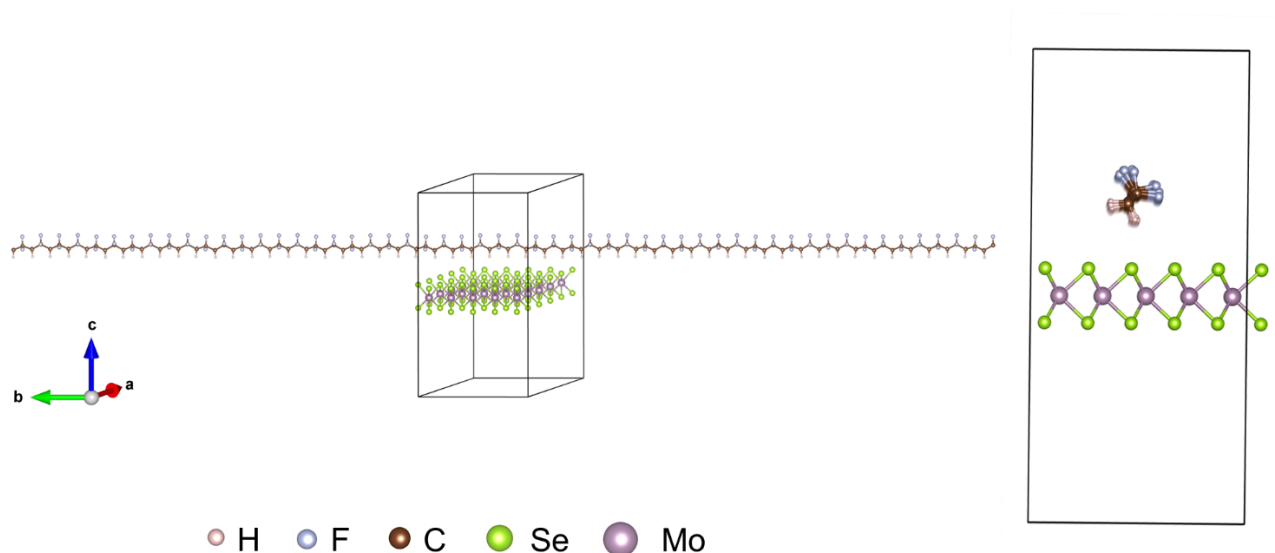
Supplementary Figure 13. DFT Geometry optimization of the interactions between MSs and PVDF at step 60.



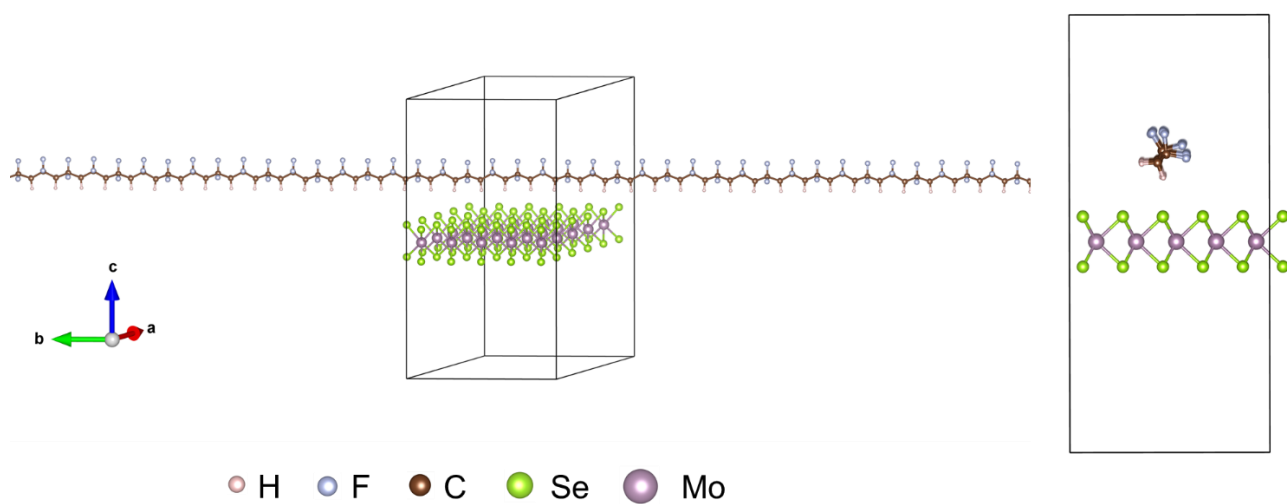
Supplementary Figure 14. DFT Geometry optimization of the interactions between MSs and PVDF at step 80.



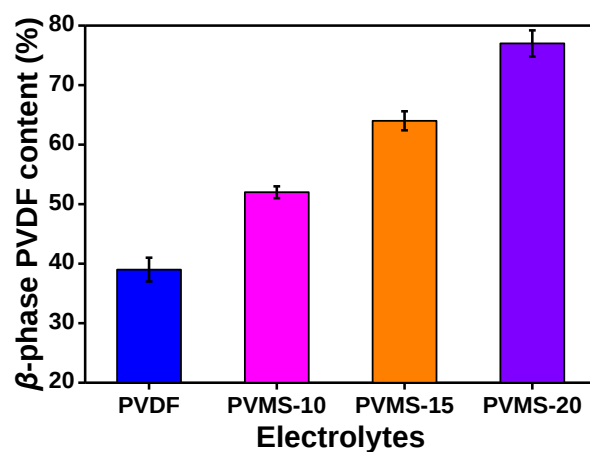
Supplementary Figure 15. DFT Geometry optimization of the interactions between MSs and PVDF at step 90.



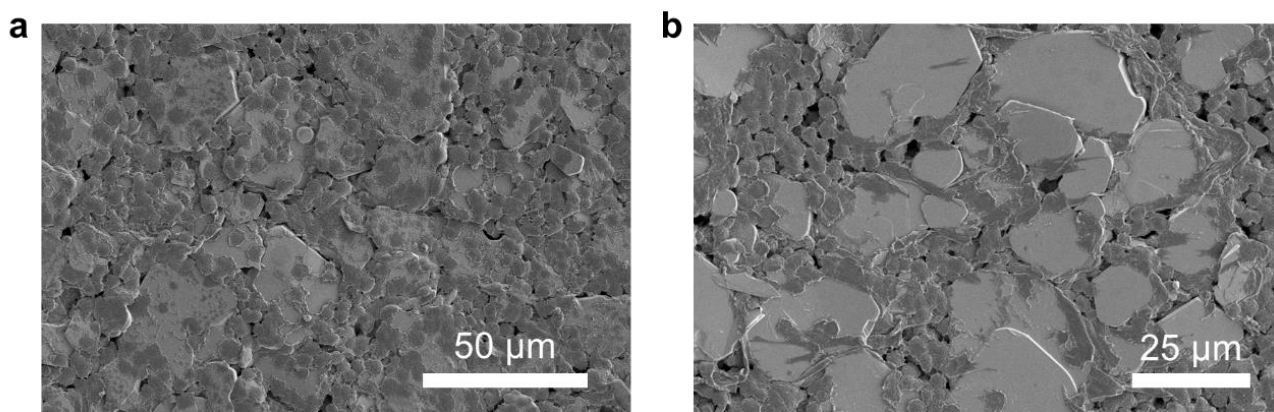
Supplementary Figure 16. DFT Geometry optimization of the interactions between MSs and PVDF at step 110.



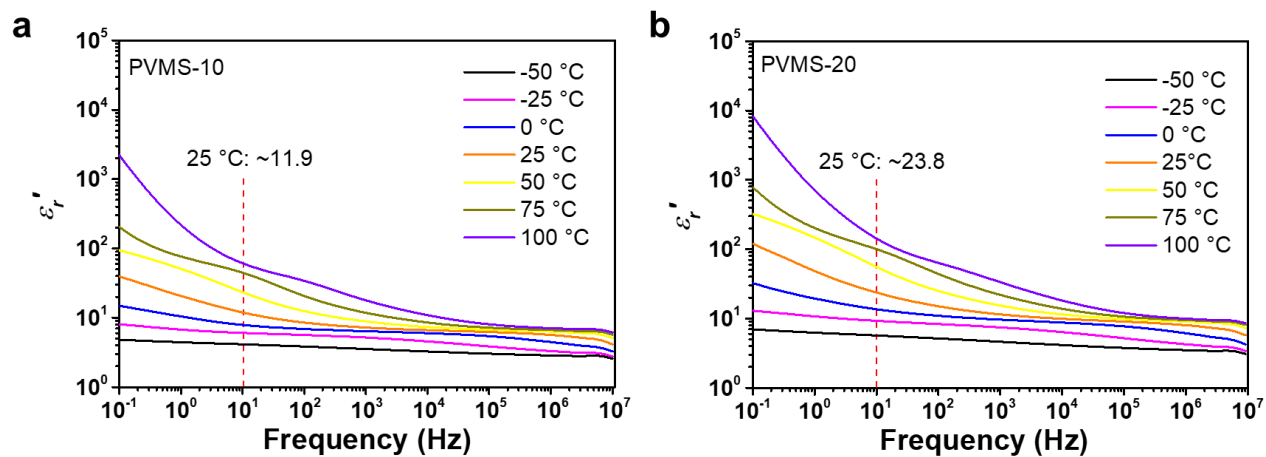
Supplementary Figure 17. DFT Geometry optimization of the interactions between MSs and PVDF at step 189.



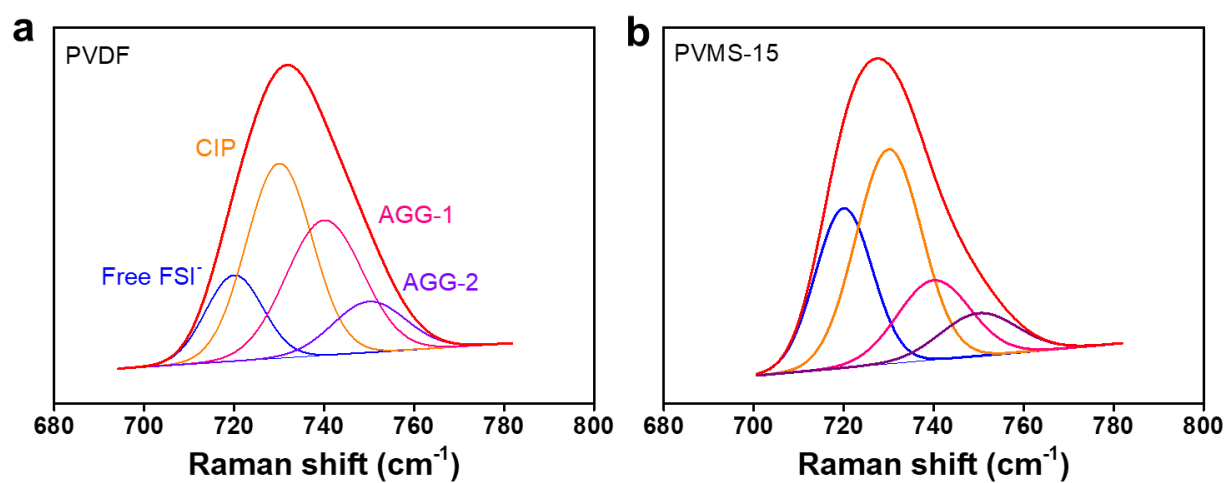
Supplementary Figure 18. Calculated β -phase PVDF content of the electrolytes from FTIR spectra. Values are means, and error bars were calculated by taking the standard errors from the measurements with three identical samples.



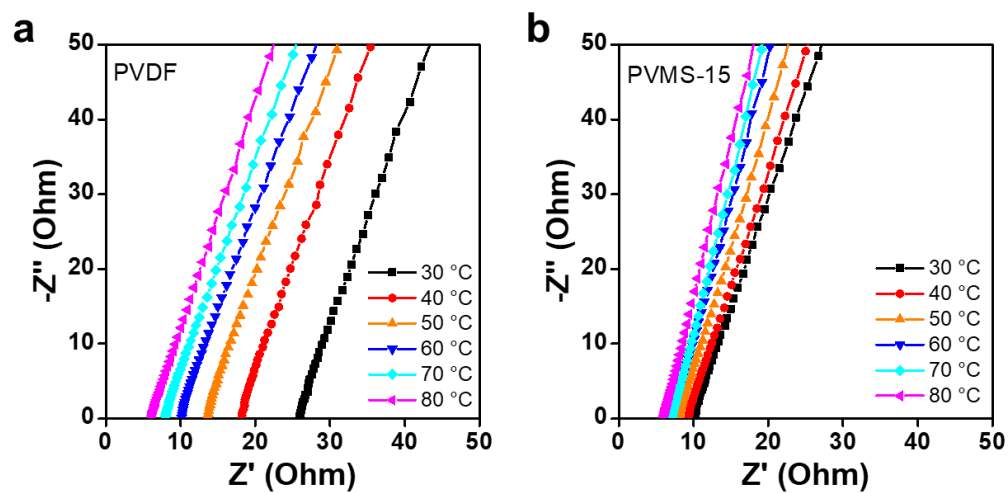
Supplementary Figure 19. SEM images of the PVMS-20 electrolyte at 700 $\times$ (a) and 1000 $\times$ (b).



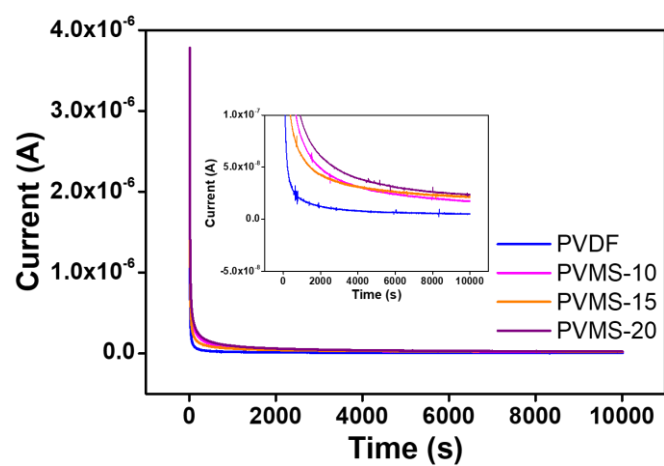
Supplementary Figure 20. Dielectric constant tests of the electrolytes. Real part (ϵ_r') of the relative permittivity as a function of frequency at different temperatures for the PVMS-10 (a) and PVMS-20 (b) electrolytes.



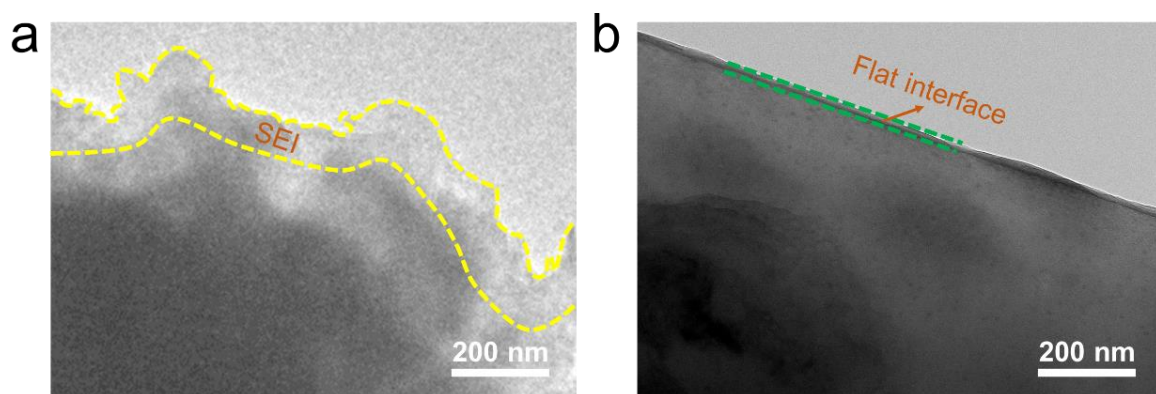
Supplementary Figure 21. Raman spectra of the electrolytes. a PVDF electrolyte. **b** PVMS-15 electrolyte.



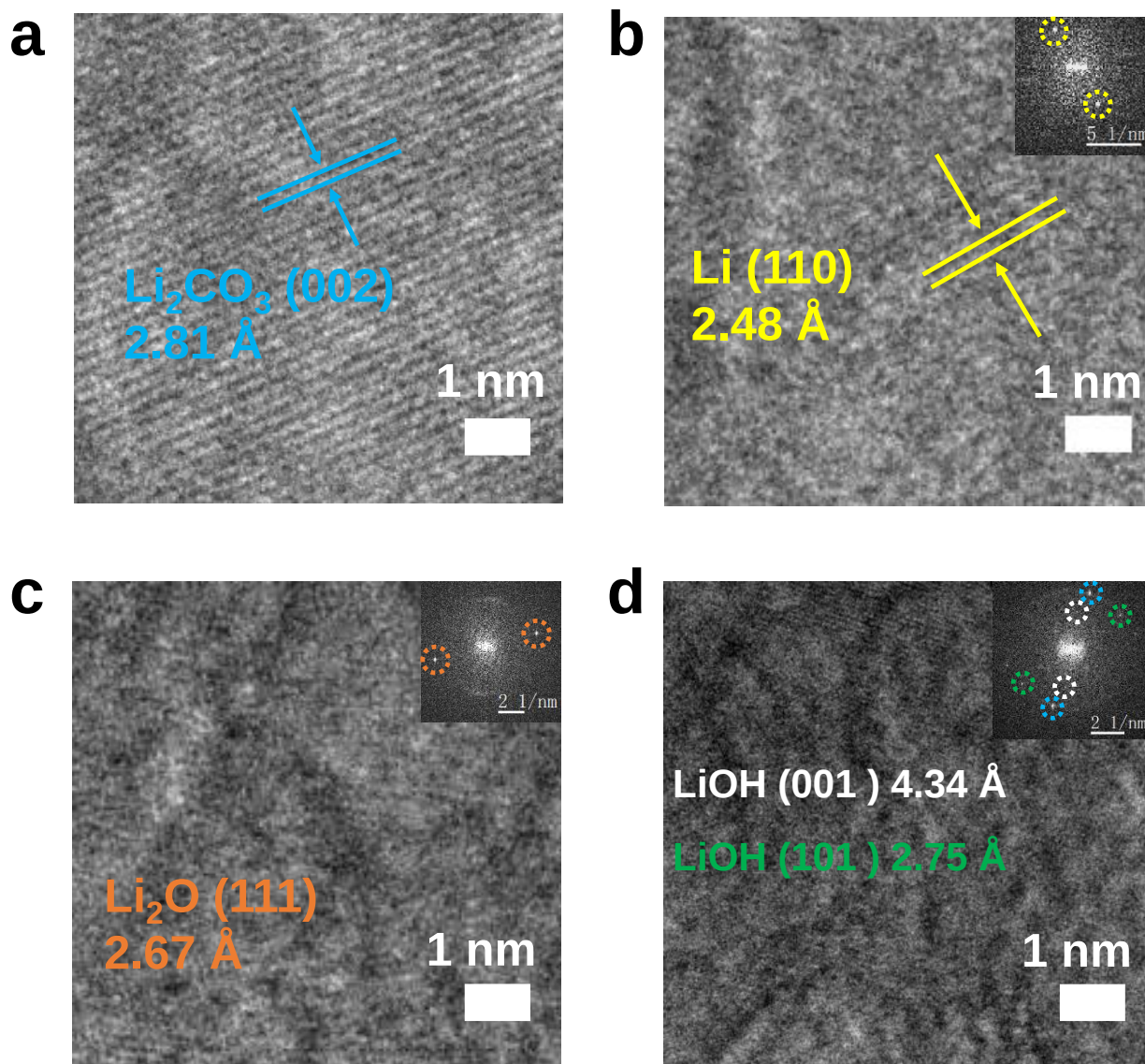
Supplementary Figure 22. Ionic conductivities tests of the electrolytes. EIS of SS||SS cells at different temperatures using the PVDF (**a**) and PVMS-15 (**b**) electrolytes.



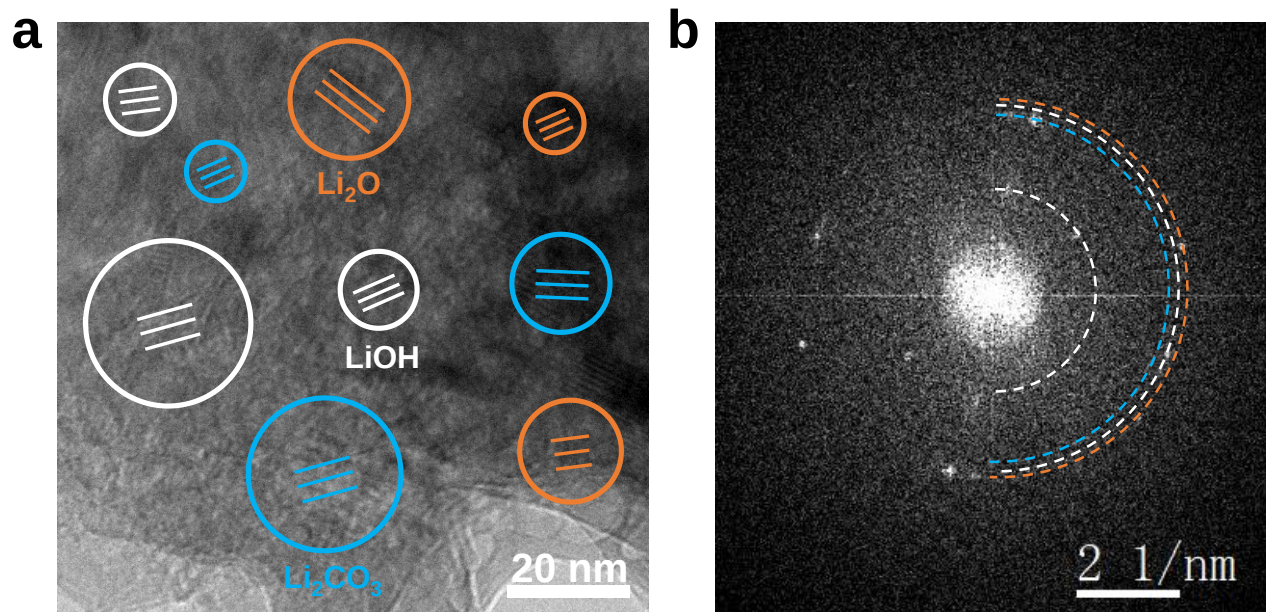
Supplementary Figure 23. Electronic conductivities tests of the electrolytes.



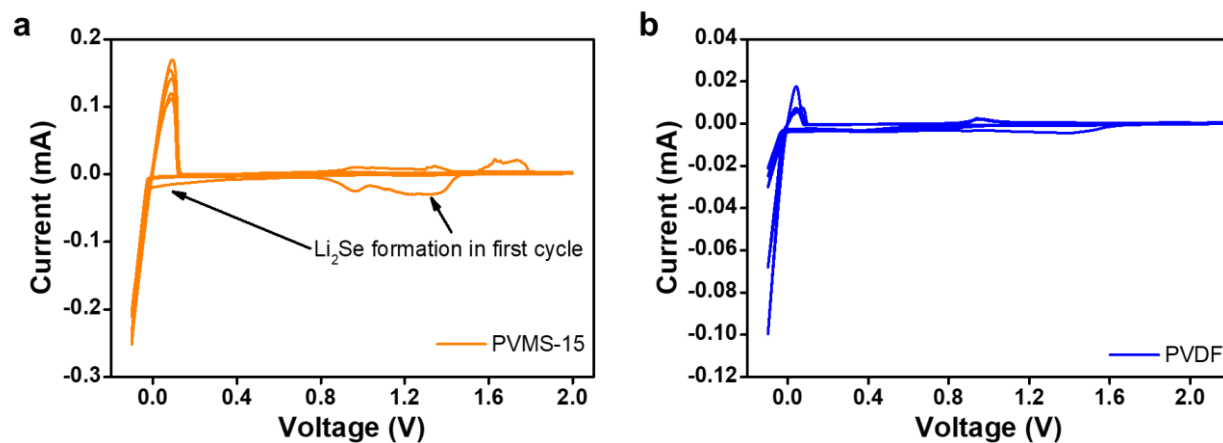
Supplementary Figure 24. SEI characterizations. Cryo-TEM images of formed SEI by PVDF (a) and PVMS-15 (b) electrolytes.



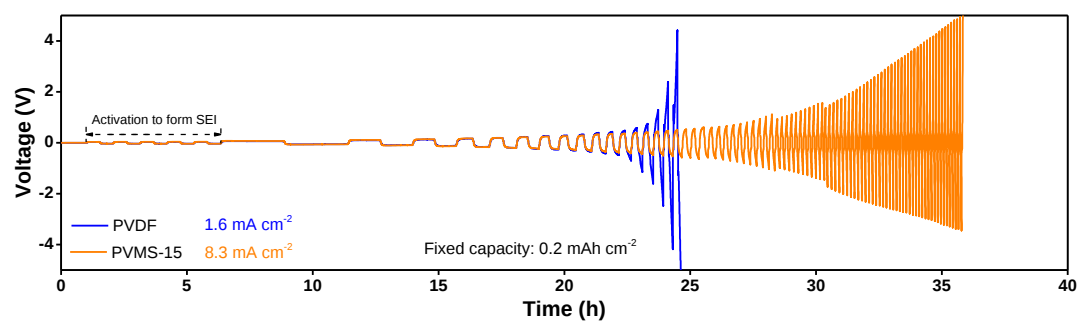
Supplementary Figure 25. Nanostructures of the SEI formed by PVMS-15 electrolyte. HRTEM images of Li_2CO_3 (a), Li (b), Li_2O (c) and LiOH (d) crystals.



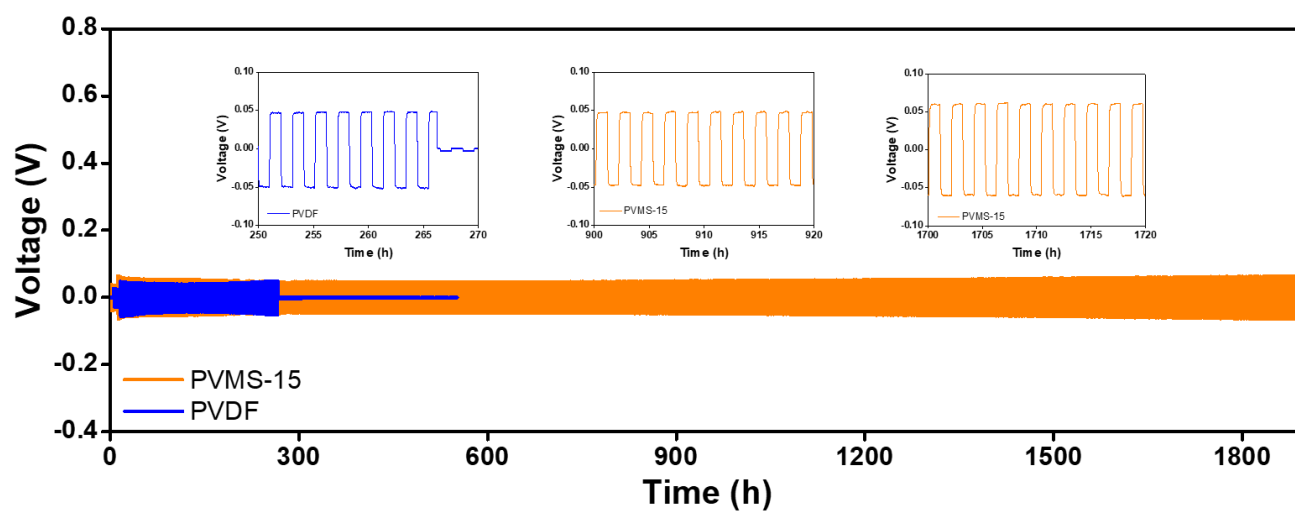
Supplementary Figure 26. SEI images formed by PVDF electrolyte. a Enlarged TEM image of SEI formed by PVDF electrolyte. **b** FFT pattern.



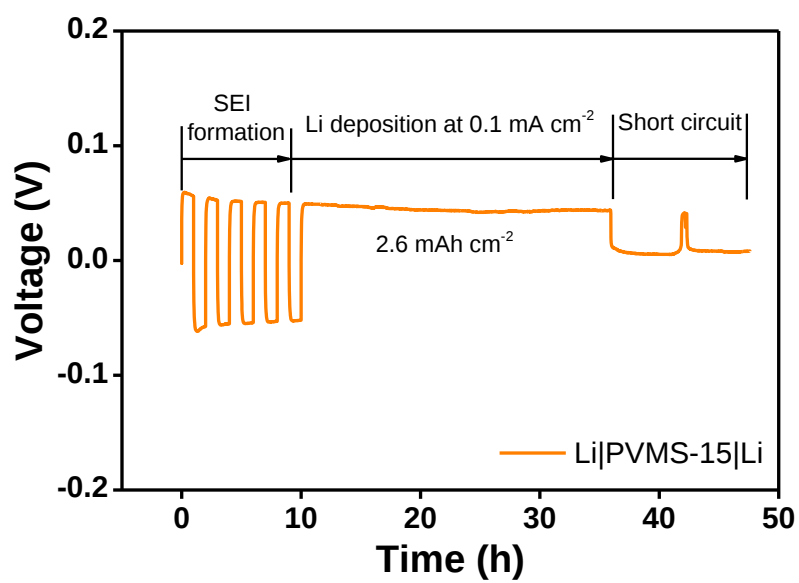
Supplementary Figure 27. Li metal compatibility tests of the electrolytes. CV curves of Li||Cu cells using PVMS-15 (a) and PVDF (b) electrolytes.



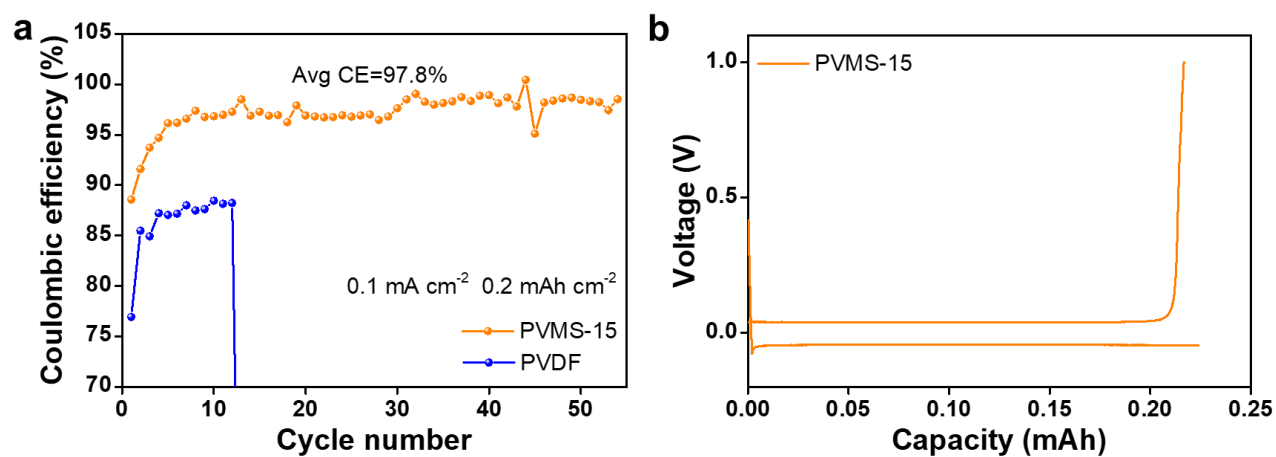
Supplementary Figure 28. CCD tests of the electrolytes using capacity control method.



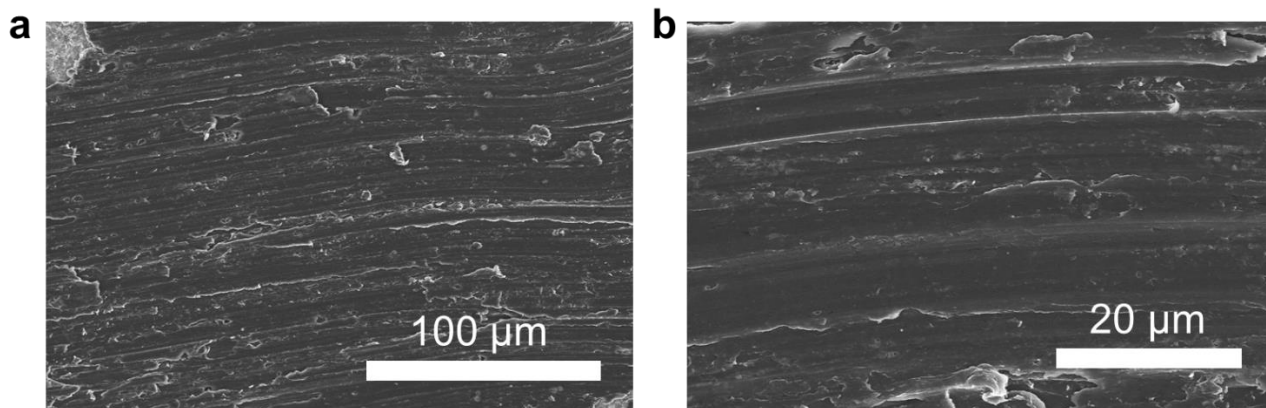
Supplementary Figure 29. Galvanostatic cycling curves of Li||Li cells with PVDF and PVMS-15 electrolytes at current density of 0.1 mA cm⁻².



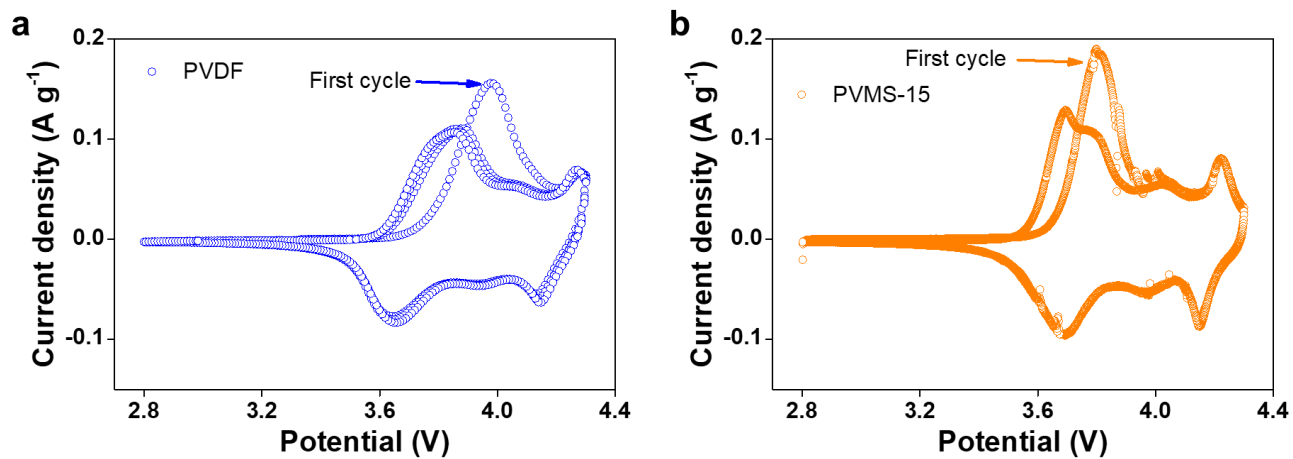
Supplementary Figure 30. CDC test curves in Li||Li cells at 0.1 mA cm⁻² using PVMS-15 electrolyte.



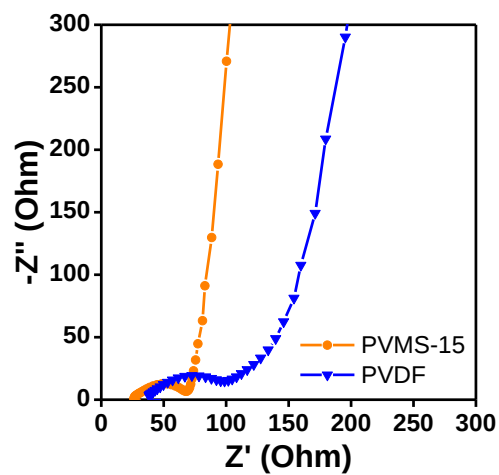
Supplementary Figure 31. CE tests in Li||Cu cells using PVDF and PVMS-15 electrolytes. a Long-term cycling stability. **b** Li deposition-stripping curve in the 30th cycle.



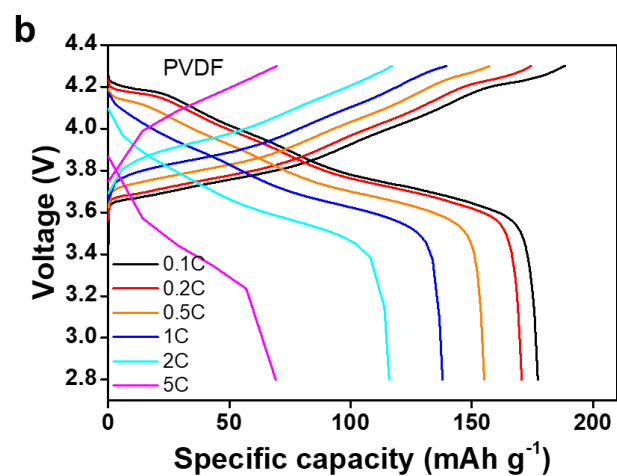
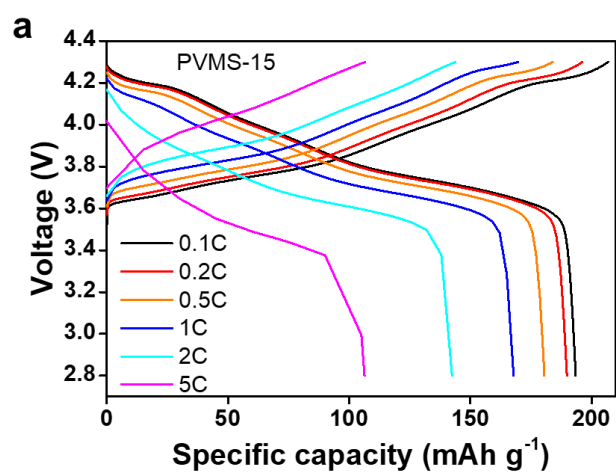
Supplementary Figure 32. SEM images of the Li deposition obtained by plating 1 mAh cm^{-2} Li on Cu substrate at 0.1 mA cm^{-2} in Li||Cu cells using PVMS-15 electrolyte. a 500 $\times$. b 2000 $\times$.



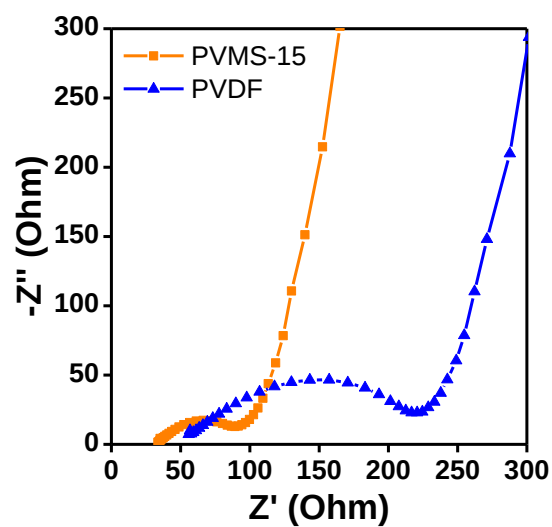
Supplementary Figure 33. CV tests of Li||NCM811 full cells. CV curves of Li|PVDF|NCM811 (a) and Li|PVMS-15|NCM811 (b) cells in voltage range of 2.8~4.3 V at scanning rate of 0.05 mV s⁻¹.



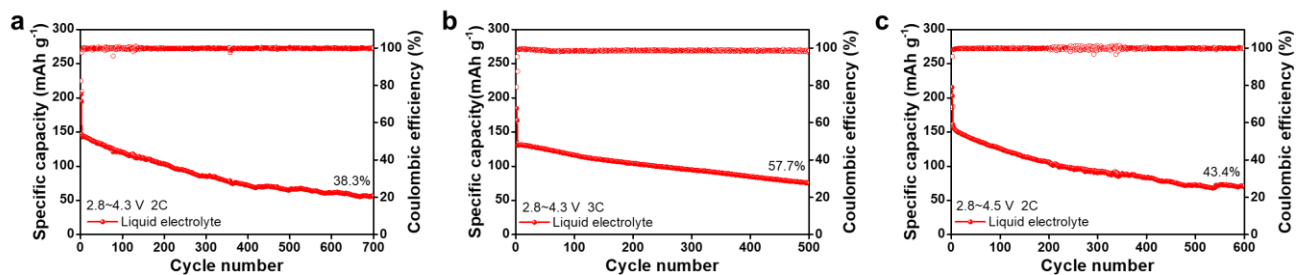
Supplementary Figure 34. EIS of Li|PVDF|NCM811 and Li|PVMS-15|NCM811 cells before rate tests.



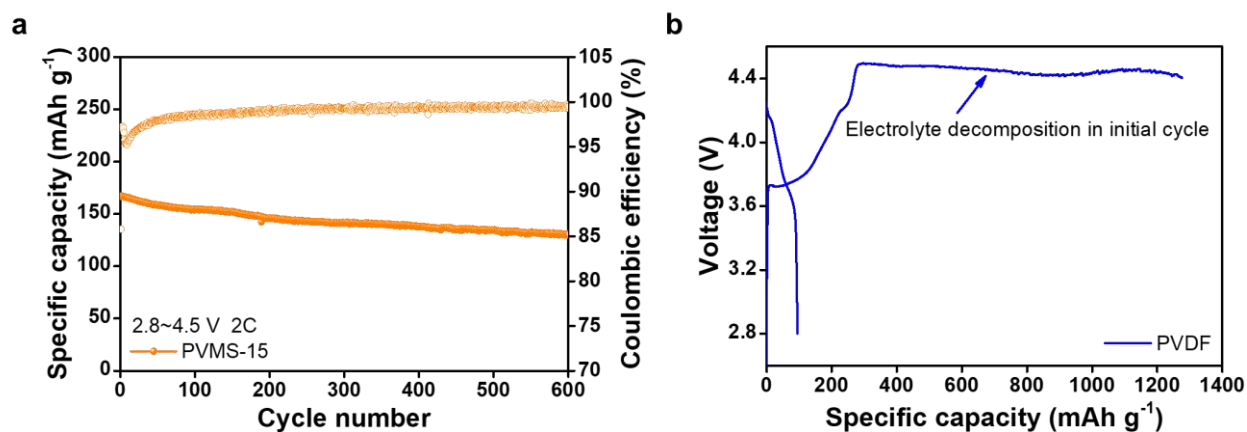
Supplementary Figure 35. Charge/discharge curves at different rates of Li|PVMS-15|NCM811 (a) and Li|PVDF|NCM811 (b) cells.



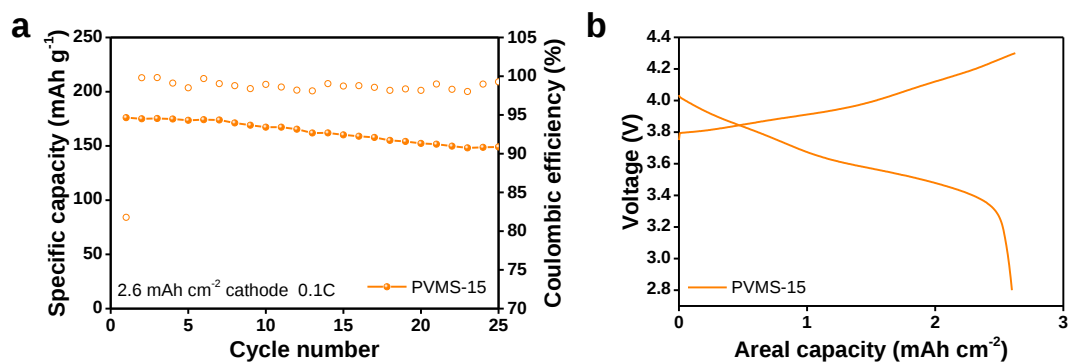
Supplementary Figure 36. EIS of Li|PVDF|NCM811 and Li|PVMS-15|NCM811 cells after rate tests.



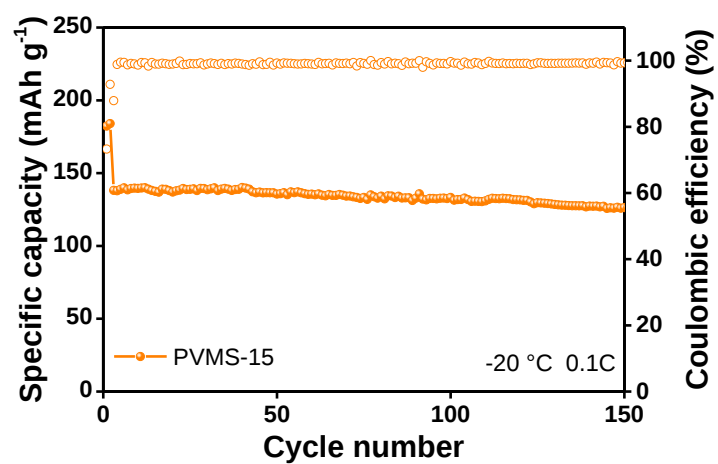
Supplementary Figure 37. Cycling stability of commercial liquid Li||NCM811 cells at 2.8~4.3 V, 2C (a), 2.8~4.3 V, 3C (b) and 2.8~4.5V, 2C (c).



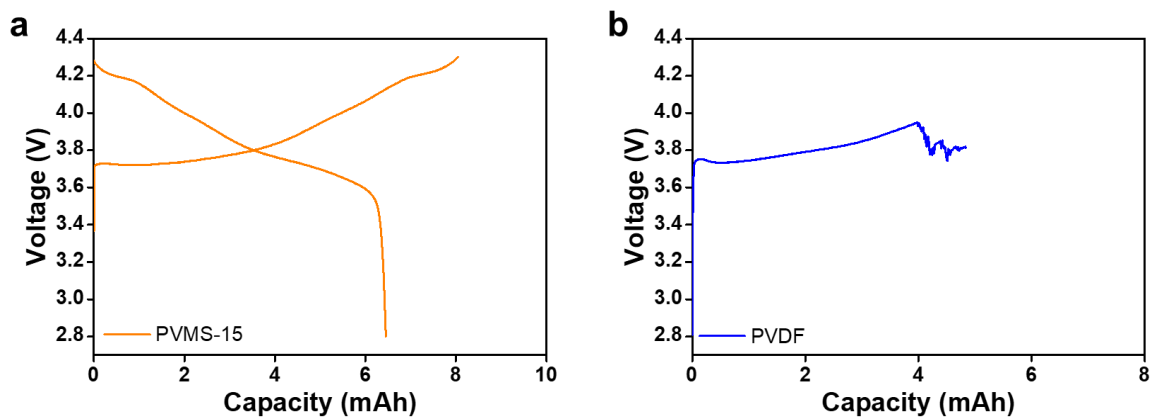
Supplementary Figure 38. Electrochemical performance of the batteries under cut-off voltage of 4.5 V. a Cycling stability of the Li|PVMS-15|NCM811 cells. **b** Charge/discharge curve of the Li|PVDF|NCM811 cells.



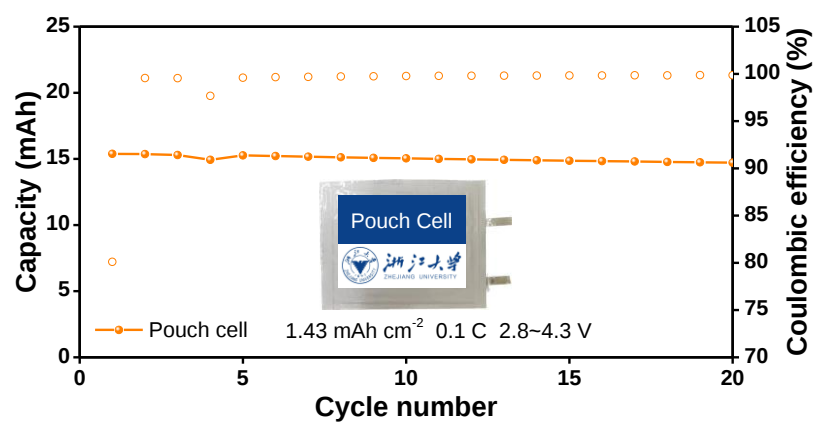
Supplementary Figure 39. Electrochemical performance of the Li||NCM811 coin cells with 2.6 mAh cm^{-2} cathode at 0.1C . a Cycling stability. b Charge/discharge curve.



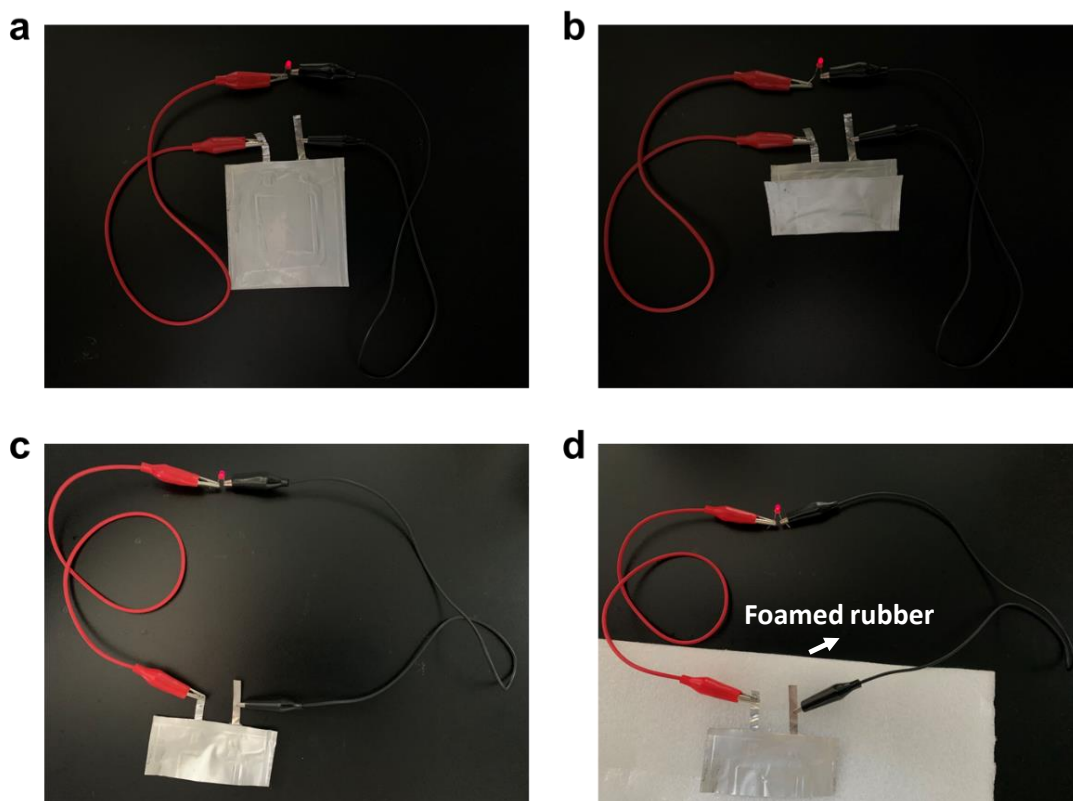
Supplementary Figure 40. Cycling stability of the Li|PVMS-15|NCM811 full cells at -20°C.



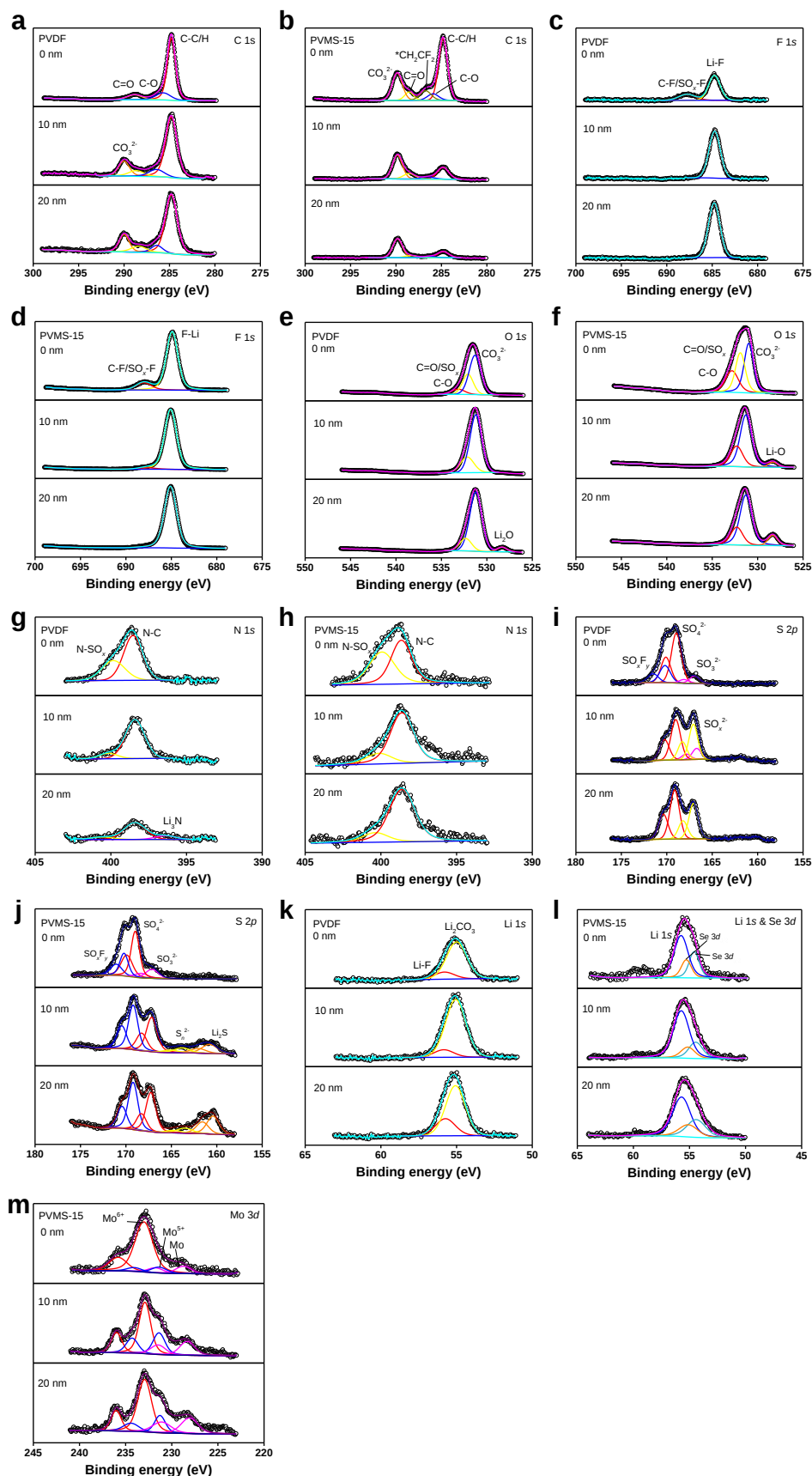
Supplementary Figure 41. Electrochemical tests of single layer pouch cells. Charge/discharge curve of Li|PVMS-15|NCM811 (a) and Li|PVDF|NCM811 (b) pouch cell.



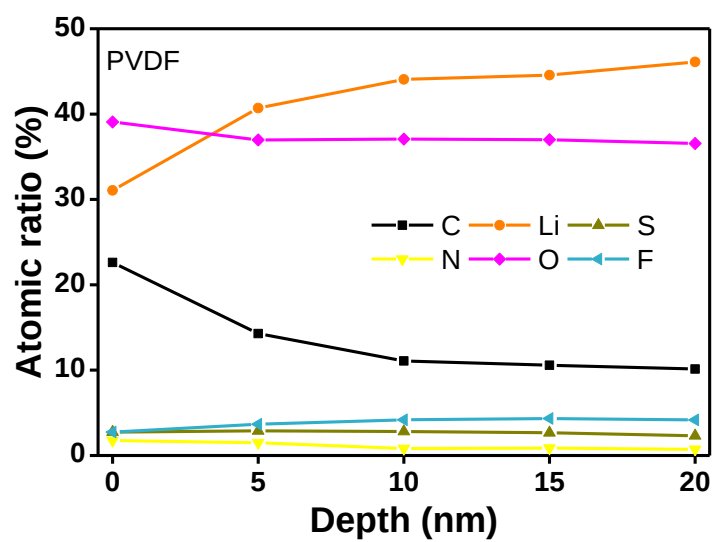
Supplementary Figure 42. Cycling stability of the Li|PVMS-15|NCM811 solid-state pouch cells.



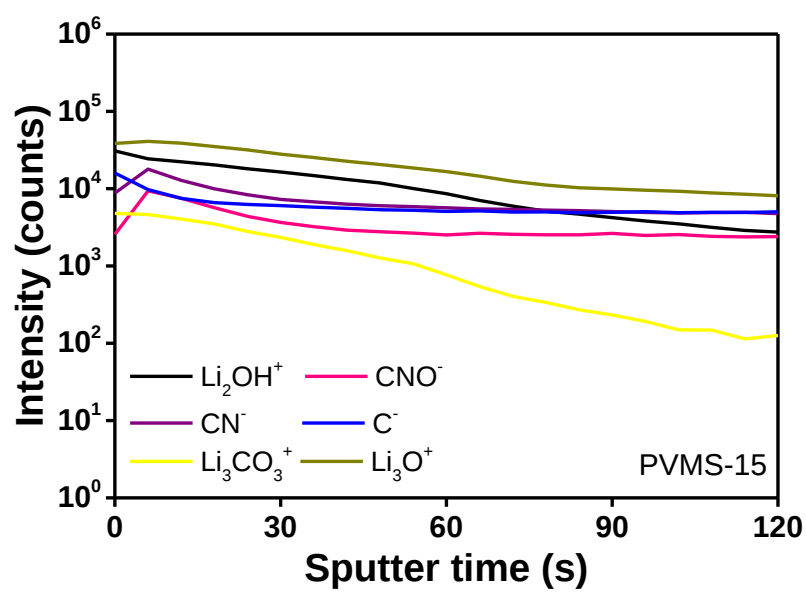
Supplementary Figure 43. Optical photographs of pouch cells using PVMS-15 electrolyte. a Optical photograph of Li|PVMS-15|NCM811 pouch cell. **b** Flexible test. **c** Cutting test. **d** Puncturing test.



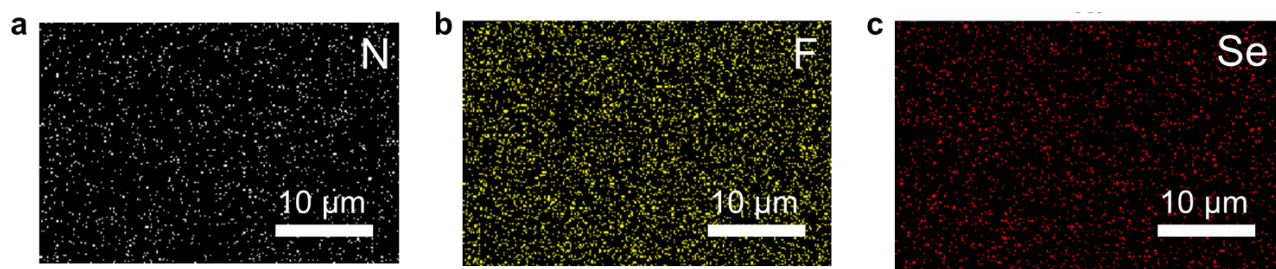
Supplementary Figure 44. XPS spectra of C 1s (a, b), F 1s (c, d), O 1s (e, f), N 1s (g, h), S 2p (i, j), Li 1s (k), Li 1s & Se 3d (l) and Mo 3d (m) for the SEI using PVDF and PVMS-15 electrolytes.



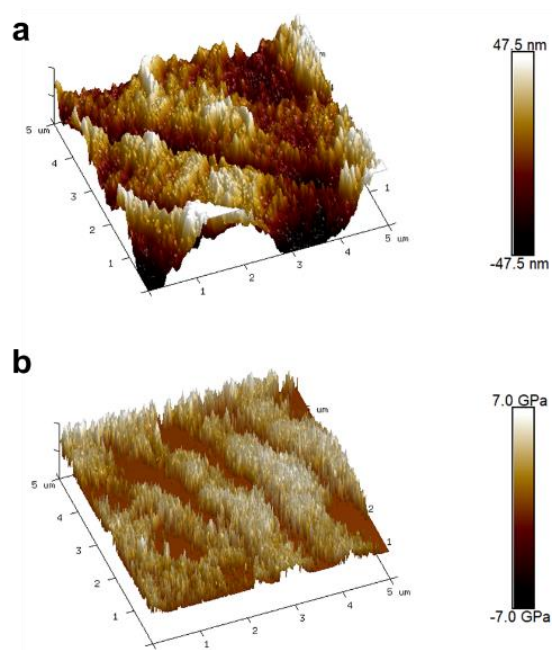
Supplementary Figure 45. Atomic ratios of the SEI at different sputter time with the PVDF electrolyte.



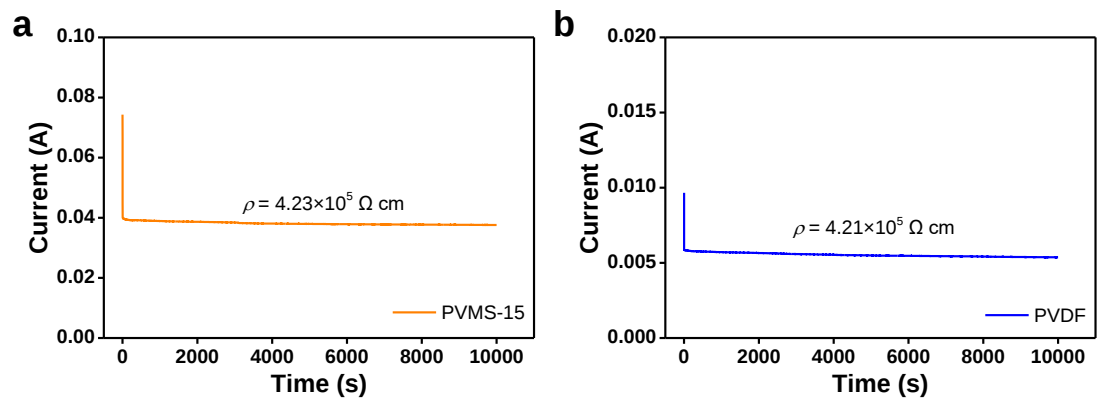
Supplementary Figure 46. TOF-SIMS depth profiles of secondary ion fragments in the formed SEI by PVMS-15 electrolyte.



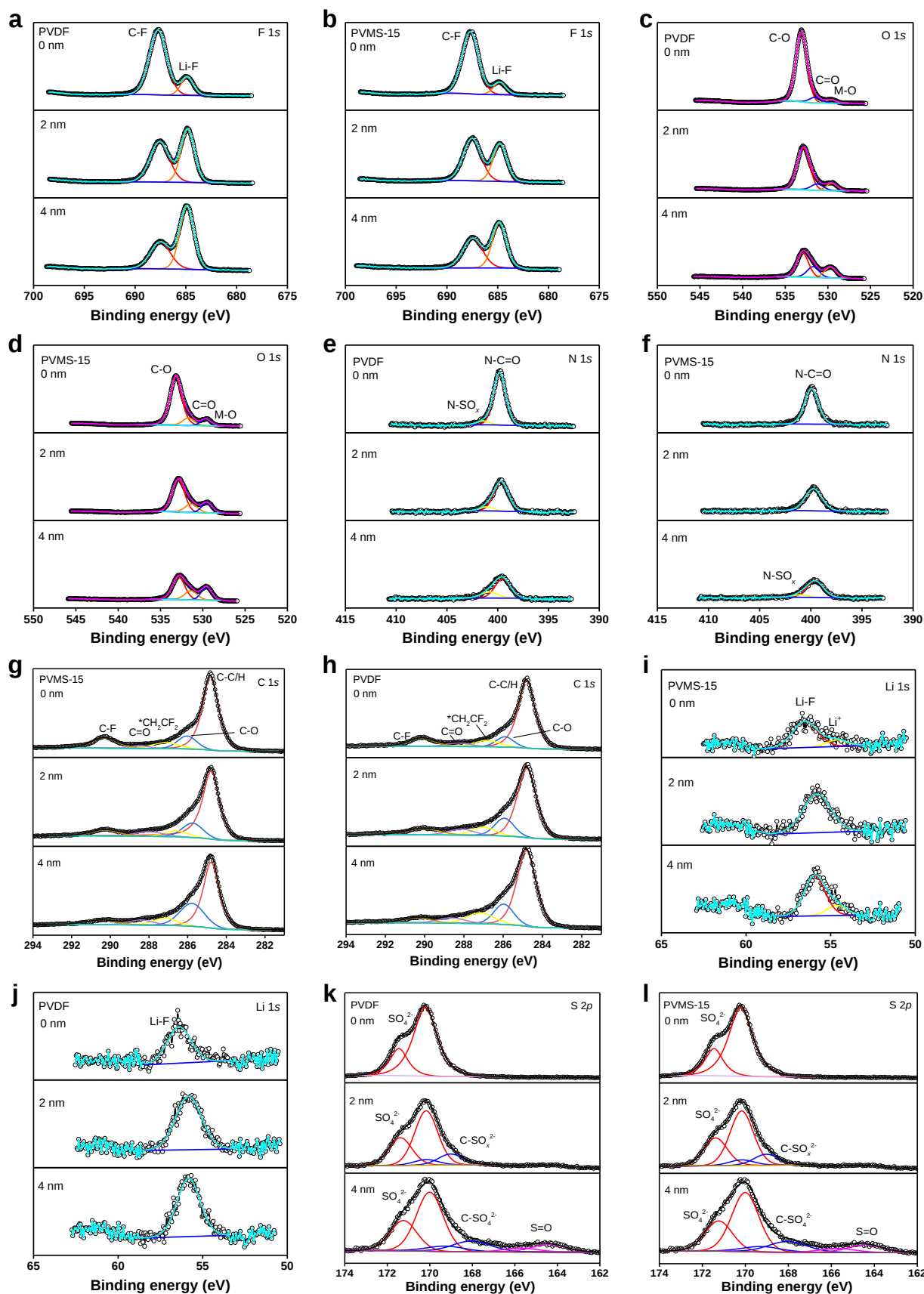
Supplementary Figure 47. Element EDS mappings of N (a), F (b) and Se (c) of SEI formed by the PVMS-15 electrolyte.



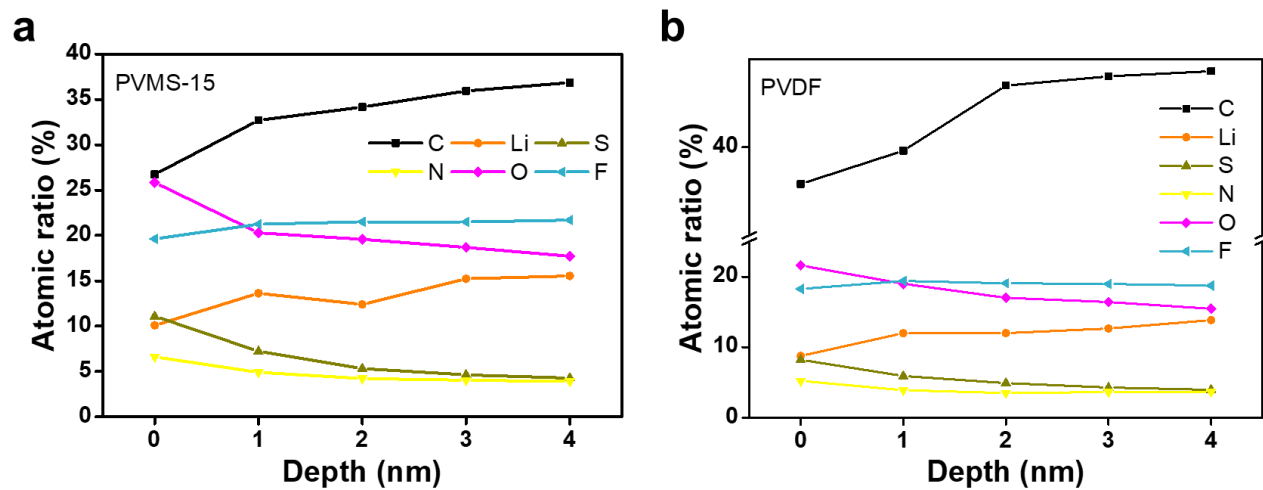
Supplementary Figure 48. 3D AFM images of roughness (a) and Young's modulus (b) tests of the SEI using the PVDF electrolyte.



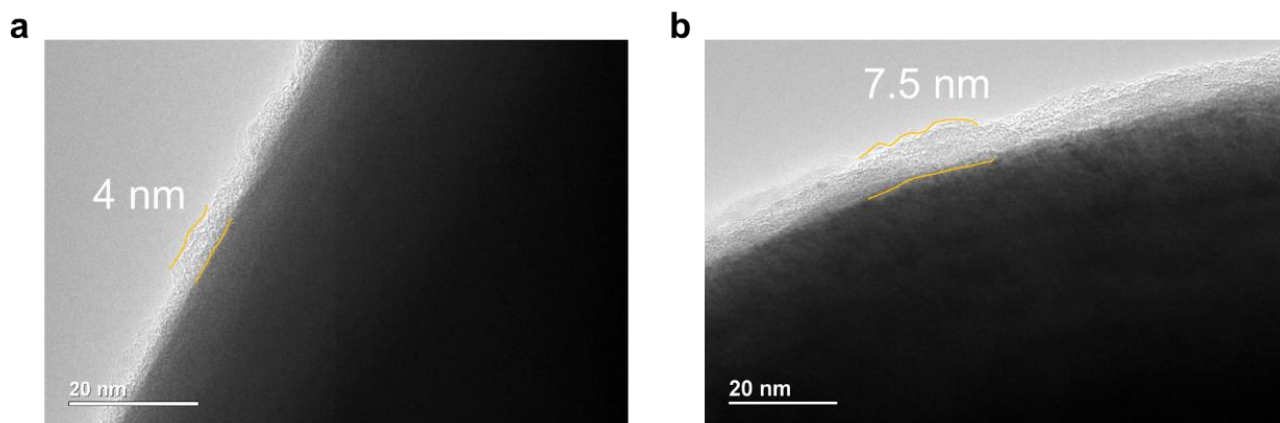
Supplementary Figure 49. Current-time curves of the Li|SEI|SS cells for the electronic conductivity of the SEI in PVMS-15 (a) and PVDF (b) electrolytes.



Supplementary Figure 50. XPS spectra of F 1s (a, b), O 1s (c, d), N 1s (e, f), C 1s (g, h), Li 1s (i, j) and S 2p (k, l) for the CEI using PVDF and PVMS-15 electrolytes.



Supplementary Figure 51. Atomic ratios of the CEI at different sputter time with the PVMS-15 (a) and PVDF (b) electrolytes.



Supplementary Figure 52. CEI images. TEM images of the CEI using PVMS-15 (a) and PVDF (b) electrolytes.

Supplementary Tables

Supplementary Table 1. Calculation details of β -phase PVDF in the electrolytes.

Electrolyte	Average A_β	Average A_α	Average β -phase PVDF content (%)
PVDF	0.1598	0.1891	39
PVMS-10	0.2014	0.1430	52
PVMS-15	0.2422	0.1057	64
PVMS-20	0.2891	0.0661	77

Supplementary Table 2. Electronic conductivities of the electrolytes.

Electrolyte	Electronic conductivity (S cm ⁻¹)
PVDF	6.82×10 ⁻¹¹
PVMS-10	2.08×10 ⁻¹⁰
PVMS-15	3.09×10 ⁻¹⁰
PVMS-20	3.51×10 ⁻¹⁰

Supplementary Table 3. Comparison of electronic conductivities of the PVMS-15 electrolyte with other reported electrolyte systems.

Electrolyte	Electronic conductivity (S cm ⁻¹)	Ref.
Li ₂ In _{1/3} Sc _{1/3} Cl ₄	4.7×10 ⁻¹⁰	8
Li ₃ YCl ₆	2.8×10 ⁻⁹	9
PEO/PVDF/LiTFSI /TiO ₂	10 ⁻¹⁰	10
LiTFSI/EmimFSI/ PMMA/LLZO	3.14×10 ⁻¹⁰	11
Li ₃ PS ₄	5×10 ⁻⁹	12
LiF-Li ₁₀ GeP ₂ S ₁₂	2.42×10 ⁻⁹	13
LiNbOCl ₄	5.22×10 ⁻¹⁰	14
PEO/LiTFSI/GDC	5.5×10 ⁻¹⁰	15
LLZO/Li ₃ AlF ₆	1.27×10 ⁻⁸	16
PI/LLZTO/PVDF	3.73×10 ⁻¹⁰	17
PEO/LiTFSI/carbon	6.83×10 ⁻⁹	18
PVMS-15	3.09×10 ⁻¹⁰	This work

Supplementary Table 4. Calculated lattice parameters for Li₂Se, LiOH, Li₂CO₃, and Li₂O.

Crystals	Calculated	Reported	Space Group
Li ₂ Se	a= b=c=5.89 Å $\alpha=\beta=\gamma=90^\circ$	a=b=6.02 Å $\alpha=\beta=\gamma=90^\circ$	Fm3m (No. 225)
LiOH	a=b=3.51 Å c= 4.11 Å $\alpha=\beta=\gamma=90^\circ$	a=b=3.59 Å c=4.41 Å $\alpha=\beta=\gamma=90^\circ$	P4/nmm (No.129)
Li ₂ CO ₃	a=8.37 Å b=5.02 Å c=6.32 Å $\alpha=\gamma=90^\circ$ $\beta=114.08^\circ$	a=8.42 Å b=5.04 Å c=6.35 Å $\alpha=\gamma=90^\circ$ $\beta=114.24^\circ$	C2/c (No. 15)
Li ₂ O	a= b=c=4.55 Å $\alpha=\beta=\gamma=90^\circ$	a=b=c=4.66 Å $\alpha=\beta=\gamma=90^\circ$	Fm3m (No. 225)

Supplementary Table 5. Calculated surface energies along different orientations for Li₂Se, LiOH, Li₂CO₃, and Li₂O.

Crystals	Surfaces	Surface energy (J m ⁻²)
Li ₂ Se	002	2.07
	111	0.64
LiOH	001	0.25
Li ₂ CO ₃	002	0.17
Li ₂ O	111	0.99
	110	1.16

Supplementary Table 6. Comparison of our developed batteries with other reported batteries.

Electrolyte	Ionic conductivity ($\times 10^{-4}$ S cm $^{-1}$)	Areal capacity (mAh cm $^{-2}$)	Current density (mA cm $^{-2}$)	Thickness (μ m)	Cathode material	Cut-off Voltage (V)	Cycle number	Ref.
PVDF/LLZTO	5	0.342	0.1	100	LCO	4.2	120	19
PVDF- <i>b</i> -PTFE/LLTO	1.38	0.45	0.225	61	NCM532	4.35	550	20
PVDF-HFP/LiTFSI	1.24	0.378	0.075	100	NCM532	4.3	200	21
PVDF-HFP/LiTFSI	2.7	0.36	0.36	—	NCM811	4.2	800	22
P(VDF-TrFE-CTFE)/LiTFSI	3.1	0.272	0.136	70	LFP	4.2	200	23
PVDF/BTO/LLTO	8	0.288	0.288	67	NCM811	4.3	1500	24
P(VDF-TrFE-CTFE)/(Pyr13-TFSI)	5.75	0.17	0.17	130	LFP	4.2	1000	25
PEO/SN/FEC	10.1	0.34	0.17	300~400	LFP	3.9	2000	26
IL/VEC/OFHDOD A /LiTFSI	13.7	0.187	0.099	100~200	NCM532	4.5	200	27
COF/LiClO $_4$	1.2	0.17	0.17	80~100	LFP	4.2	750	28
COF/LiTFSI	1.65	0.425	0.1	32	LFP	3.8	130	29
PVMS-15	6.5	0.36	1.08	80	NCM811	4.3	2000	This work
PVMS-15	6.5	0.36	0.72	80	NCM811	4.5	600	This work
PVMS-15	6.5	1.44	0.288	80	NCM811	4.3	100	This work
PVMS-15	6.5	2.6	0.26	80	NCM811	4.3	25	This work

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