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# Supplementary Information for

## Creep-type All-solid-state Cathode Achieving Long Life

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## 1 Section 1. Supplementary Text

### 2 Calculation Details of density and porosity

$$3 \quad \rho_C = \frac{m_C}{V_C} = \frac{m_C}{S \cdot h_C} \quad (1)$$

$$4 \quad \varphi_C = \frac{V_C - V_0}{V_C} = \left(1 - \frac{\rho_C}{\rho_0}\right) \cdot 100\% \quad (2)$$

5  $\rho_C$  is the actual density of the cathode by measuring,  $m_C$ ,  $V_C$ ,  $h_C$  and  $\varphi_C$  represents the  
6 mass, volume, height the porosity of the cathode, respectively.  $V_0$  and  $\rho_0$  is the  
7 theoretical volume and density of cathode material.

$$8 \quad \rho_0 = \frac{1}{\frac{x}{\rho_a} + \frac{y}{\rho_b}} \quad (3)$$

9  $x$  and  $y$  are the mass ratios of Se and MSe in Se-MSe composite cathode, for different  
10 proportions, Se-MSe would also be written as Se-yMSe.  $\rho_a$  and  $\rho_b$  are the theoretical  
11 density of Se (4.81 g/cm<sup>3</sup>) and MSe (6.52 g/cm<sup>3</sup>). All determined densities and  
12 porosities are susceptible to errors, as high as 10%, due to the inaccurate determination  
13 of composite cathode thickness.

14

### 15 Calculation of Energy density.

16 The calculation model of the energy density of the Se electrode was according to  
17 the previous works by Erik J. Berg<sup>1</sup> and Meiyang Li<sup>2</sup>. For the Liquid Li-ion batteries  
18 (LLIBs), the cathode consists of 60 wt.% active material (AM, Se, 4.81 g/cm<sup>3</sup>) and 30  
19 wt.% conductive carbon (Super P (SP), 2.25 g/cm<sup>3</sup>) and 10 wt.% binder (1.8 g/cm<sup>3</sup>)  
20 with 30 vol.% porosity filled with liquid electrolyte (1M LiPF<sub>6</sub> in EC: EMC, 1.22  
21 g/cm<sup>3</sup>). The cathode of traditional all-solid-state batteries (ASSBs) contains 40 wt.%  
22 AM and 50 wt.% SE (Li<sub>6</sub>PS<sub>5</sub>Cl, 1.64 g/cm<sup>3</sup>) and 10 wt.% SP<sup>2</sup>, i.e. 40 wt.% Se +50 wt.%  
23 SE +10 wt.% SP (Se-50SE-10SP). The all-electrochemical-active (AEA) all-solid-state  
24 Se-MSe cathodes in this work only contain Se and Mo<sub>6</sub>Se<sub>8</sub> two phases in different  
25 proportions without SE and SP. The theoretical specific capacity of Se is 675 mAh/g  
26 and Mo<sub>6</sub>Se<sub>8</sub> is 89 mAh/g which exhibits a stable capacity of 80 mAh/g in ASSBs (Fig.  
27 S3). Porosity is obtained by measuring the thickness of the electrode at different  
28 pressures (Table. S4, S5). Theoretical densities come from Material Project Database.

29 The density of cathode in LLIBs:

$$30 \quad \rho_{cathode} = \left( \frac{1}{\frac{0.6}{\rho_{Se}} + \frac{0.3}{\rho_{CC}} + \frac{0.1}{\rho_{Binder}}} \right) \cdot (1 - \varphi) + \rho_{LE} \cdot \varphi \quad (4)$$

31 The density of cathode in traditional ASSBs:

$$32 \quad \rho_{cathode} = \frac{1}{\frac{0.4}{\rho_{Se}} + \frac{0.5}{\rho_{SSE}} + \frac{0.1}{\rho_{CC}}} \cdot (1 - \varphi) \quad (5)$$

33 The density of Se-MSe cathode:

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34 
$$\rho_{Se-MSe} = \frac{1}{\frac{x}{\rho_{Se}} + \frac{y}{\rho_{MSe}}} \cdot (1 - \varphi) \quad (6)$$

35 Specific capacity of cathode in LIBs and SSBs:

36 
$$C_{cathode} = \frac{C_{Se} \cdot m_{se}}{m_{cathode}} \quad (7)$$

37 Specific capacity of Se-MSe cathode:

38 
$$C_{cathode} = \frac{C_{Se} \cdot m_{se} + C_{MSe} \cdot m_{Mse}}{m_{cathode}} \quad (8)$$

39 Specific energy of cathode:

40 
$$E_G = \int C_{cathode} dV = C_{cathode} \cdot V_{average} \quad (Wh/kg) \quad (9)$$

41 Volumetric energy density of cathode:

42 
$$E_V = \frac{C_{cathode} \cdot V_{average} \cdot m_{cathode}}{V_0} \quad (Wh/L) \quad (10)$$

43  $V_{average}$  is the average voltage of material during discharge.

44 Active utilization of Se in Se-MSe cathode:

45 
$$\varepsilon = \frac{C_{cathode} - C_{MSe} \cdot y}{C_{Se} \cdot x} \cdot 100\% \quad (11)$$

46

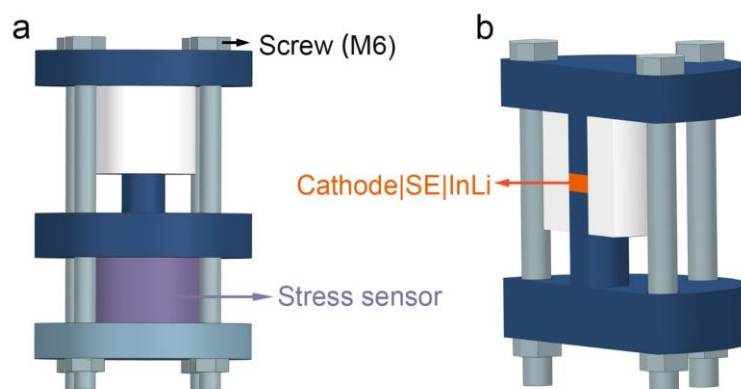
47 Supplementary Note

48 The hardness of lithiated InLi alloy ( $E \sim 46$  GPa,  $H \sim 1.8$  GPa,  $T_m \sim 600$  °C) increase  
 49 with increasing Li content<sup>3</sup>. And it should be noted that InLi alloy is brittle at low  
 50 temperature without viscosity below about 200°C<sup>4</sup>. Furthermore, in contrast with many  
 51 other intermetallic compounds, LiIn alloy don't experience the defect softening  
 52 phenomenon even at high homologous temperatures even at temperatures up to 450 °C  
 53 ( $\sim 0.8 T_m$ ), even though Indium ( $E = 12.7$  GPa,  $T_m = 156.6$  °C) is similar to Li and prone  
 54 to creep and stress relaxation<sup>5</sup>.

55 In addition, even though the practical ASSBs might eventually use Li foil as the  
 56 anode, the creep of Li foil only improves the contact condition between the Li and SSE,  
 57 while not affects the microstructural evolution within the cathode.

58

59 Section 2. Screening for creepable cathode materials



60

61 **Fig. S1** | Schematic diagram of ASSBs mold. (a) Initial stack stress measurement device  
62 with stress sensors. (b) Cross-section of the ASSBs test setup.

63 For this stainless-steel mold, the torque force of the screw translates into stack pressure  
64 on the ASSBs. The initial stacking pressure exerted by an M6 screw gram is about  
65 100MPa (~8 kN) tested by stress sensor. It is worth noting that shear stress may vary  
66 with the applied external because the microscopic forces on individual particles are  
67 anisotropic and depend on the local stress environment. Currently, it is difficult to  
68 measure internal microscopic stresses inside ASSBs experimentally, since prior  
69 computational simulations have demonstrated that shear stress in particles tends to be  
70 higher than external stack stress<sup>6,7</sup>.

71

72 **Table S1.** Physical properties of common electrode materials.

Materials	Shear Modulus (GPa)	Melting Point		T <sub>298 K</sub> /T <sub>M</sub>	T <sub>343 K</sub> /T <sub>M</sub>	Ref.
		T <sub>M</sub> (K)				
LCO	80	1373		0.22	0.25	8
NCM111	78	1373		0.22	0.25	8
LMO	77	1273		0.23	0.27	8
LFPO	45.5	1273		0.23	0.27	9
S	6.82	385.8		0.77	0.89	10
Se	3.7	493.8		0.60	0.69	10
Si	62	1683		0.18	0.20	11
Sn	18	504.9		0.59	0.68	12
Ga	18	302.8		0.98	1.13	12
Ge	41	1211.2		0.25	0.28	11
Te	16	722.5		0.41	0.47	10
Sb	20	903.6		0.33	0.38	13
In	4.4	429.6		0.69	0.80	12

73 The mechanical data and melting points without reference of these materials are  
 74 obtained from the Material Project website.

75

76

77

78 **Table S2.** Electrochemical and structural properties of common electrode materials.

<b>Material</b>	<b>Capacity (mAh/g)</b>	<b>Voltage (V)</b>	<b>Density (g/cm<sup>3</sup>)</b>	<b>Volumetric capacity (mAh/cm<sup>3</sup>)</b>	<b>Relative volume change (%)</b>	<b>Ref.</b>
<b>LCO</b>	274	3.9	4.97	1363	2	14,15
<b>NCM111</b>	280	3.9	4.76	1333	2	14,15
<b>LMO</b>	148	4.1	4.25	629	5.6	15,16
<b>LFPO</b>	170	3.4	3.6	612	7	15
<b>Li<sub>2</sub>S</b>	1166	2.28	1.66	1936	79	15
<b>Li<sub>2</sub>Se</b>	578	2.07	2.87	1658.86	98	15
<b>Li<sub>15</sub>Si<sub>4</sub></b>	1857	0.4	0.63	1167	270	17
<b>Li<sub>22</sub>Sn<sub>4</sub></b>	790	0.38	2.58	2038	255	15
<b>Li<sub>2</sub>Ga</b>	641	0.6	2.98	1910	160	18
<b>Li<sub>22</sub>Ge<sub>4</sub></b>	1143	0.4	2.04	2332	240	15
<b>Li<sub>2</sub>Te</b>	379	1.86	3.4	1288	104.7	15,19
<b>Li<sub>3</sub>Sb</b>	564	0.87	2.98	1680	135	20
<b>Li<sub>13</sub>In<sub>3</sub></b>	801	0.2	2.47	1978	134	21
<b>Li</b>	3860	0	0.534	2061	∞	
<b>Li<sub>4</sub>Mo<sub>6</sub>Se<sub>8</sub></b>	89	2.2	6.52	580.3	11.2	22

79

80 The homogenous temperature  $T_H$  indicates that, under some stress circumstances, both  
81 S and Se can creep at room temperature. Given Se and S have comparable volumetric  
82 capacity (3253 mA h/cm<sup>3</sup> for Se and 3467 mA h/cm<sup>3</sup> for S), but compared to S ( $5 \times 10^{-28}$   
83 S/cm)<sup>23</sup>, Se has a significantly higher electrical conductivity ( $10^{-3}$  S/cm)<sup>24</sup>, which  
84 means that Se can occupy a much higher active content in the electrode than S,  
85 indicating that Se as the active material promises superior electrochemical performance  
86 for all-solid-state cathode.

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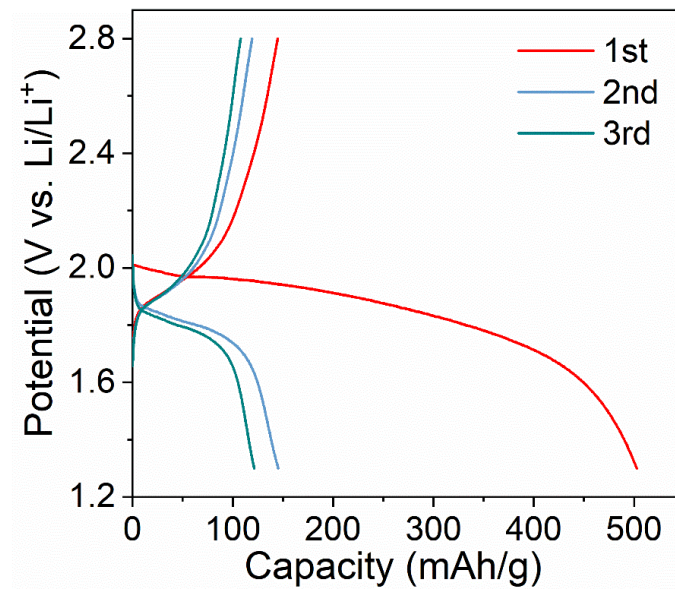
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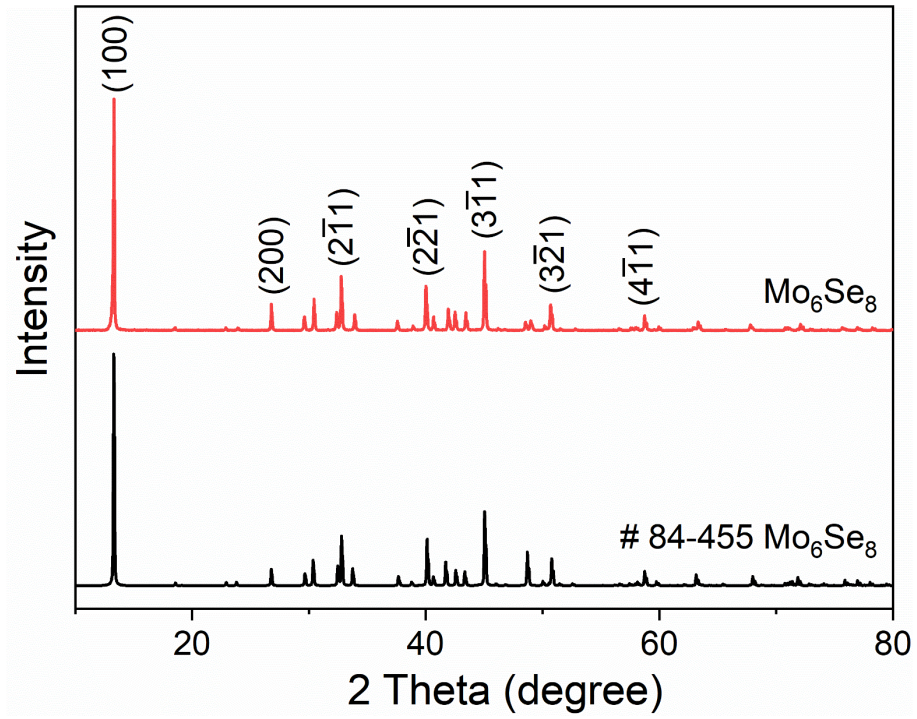
96 Section 3. Construct creep-type all-solid-state cathodes



97

98 **Fig. S2** | The galvanostatic charge-discharge curves of Se-50SE-10SP composite  
99 cathodes.

100 Large volume changes of Se during charging and discharging process in conventional  
101 all-solid-state selenium electrodes without structural design may end up in  
102 electrochemical capacity loss owing to particles contact failure.

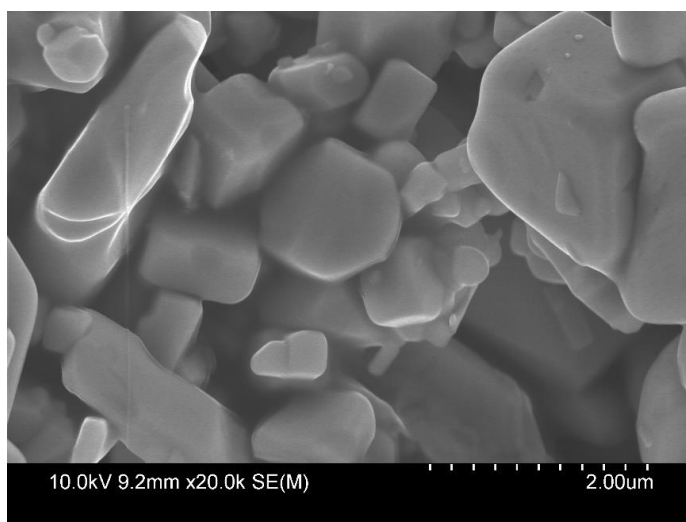


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104 **Fig. S3** | The XRD patterns of the Mo<sub>6</sub>Se<sub>8</sub> sample.

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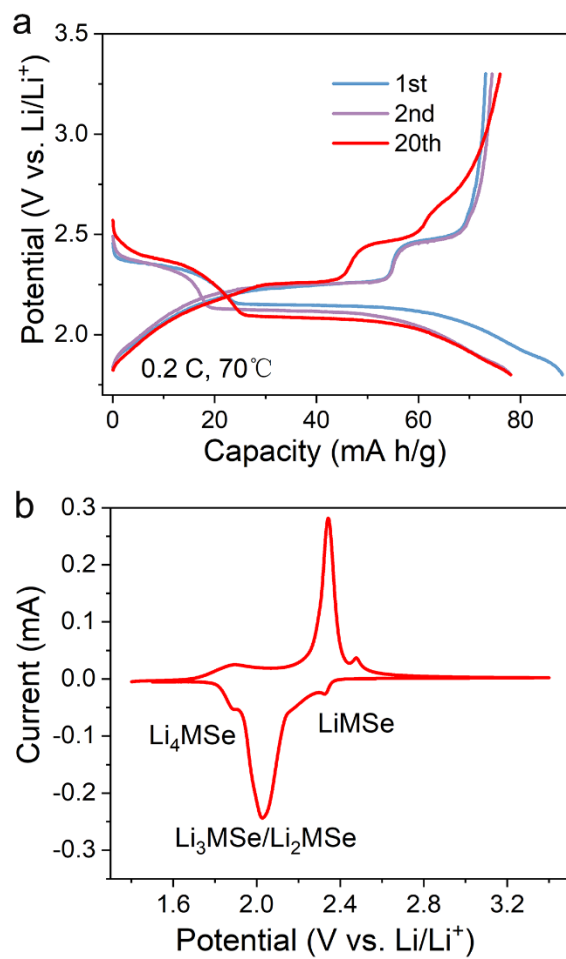




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107 **Fig. S4** | SEM image of Mo<sub>6</sub>Se<sub>8</sub>.

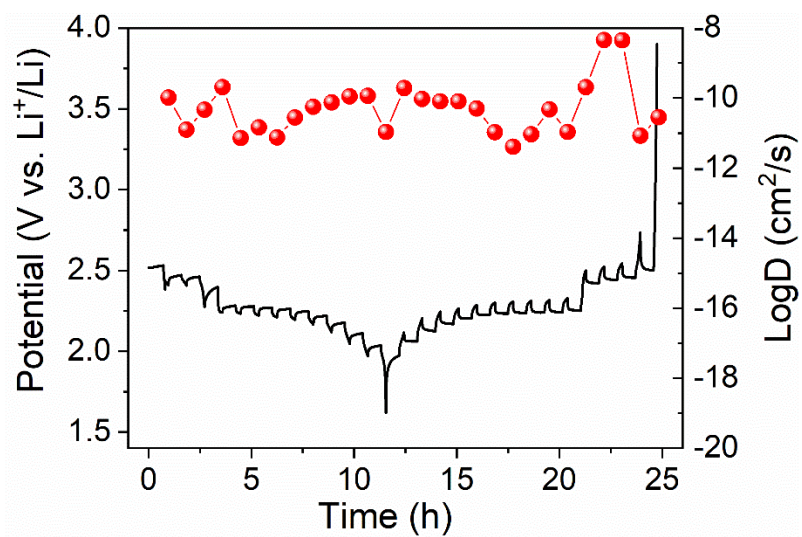
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110 **Fig. S5** | Electrochemical performance of Mo<sub>6</sub>Se<sub>8</sub> in ASSBs. (a) The galvanostatic  
111 charge-discharge curves of Mo<sub>6</sub>Se<sub>8</sub> for the 1st, 2nd, and 20th cycles. (b) Cyclic  
112 voltammetry of Mo<sub>6</sub>Se<sub>8</sub> electrode between 1.4-3.4 V at a scan rate of 0.5 mV/s.

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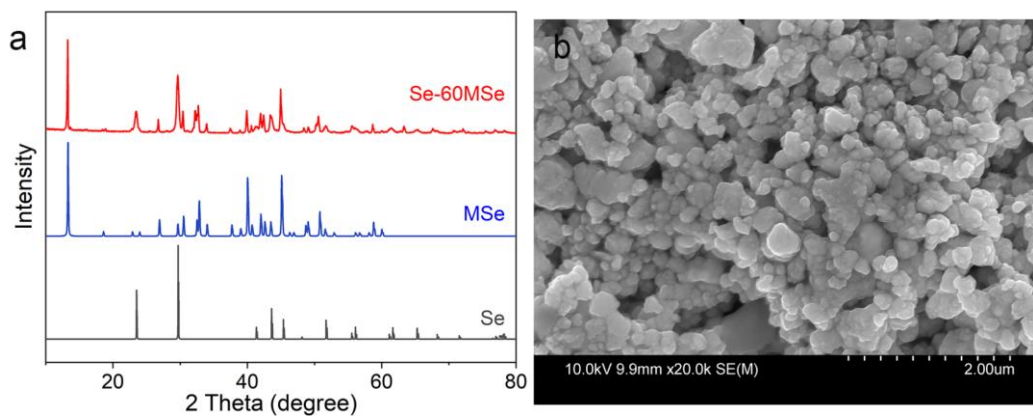
115 **Fig. S6** | The Li-ion diffusion coefficients of Mo<sub>6</sub>Se<sub>8</sub> were obtained from GITT.

116

117 **Table S3.** Details of electronic conductivity measurements of Mo<sub>6</sub>Se<sub>8</sub> and Super P  
 118 using four-pin probe method under different pressure.

<b>Material</b>	<b>Pressure [MPa]</b>	<b>Thickness [mm]</b>	<b>Conductivity [S/cm]</b>	<b>Density [g/cm<sup>3</sup>]</b>
<b>Mo<sub>6</sub>Se<sub>8</sub></b>	9.55	1.87	32.45	3.44
	19.10	1.78	59.62	3.61
	28.65	1.74	85.32	3.70
	38.20	1.71	110.72	3.76
	47.75	1.68	132.91	3.85
	57.30	1.65	154.18	3.90
<b>Super P</b>	9.55	4.84	12.95	0.71
	19.10	4.21	18.80	0.82
	28.65	4.86	23.57	0.89
	38.20	3.62	27.69	0.95
	47.75	3.43	31.45	1.00
	57.30	3.29	34.77	1.05

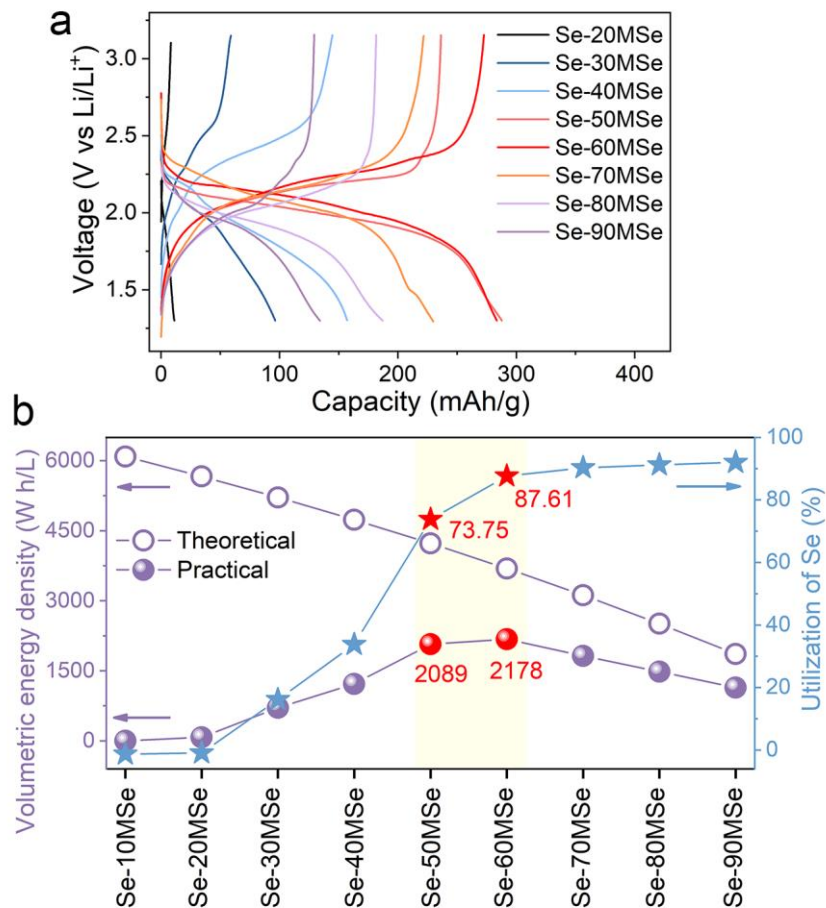
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122 **Fig. S7** | (a) The XRD patterns and (b) SEM image of Se-60MSe powder.

123 As illustrated by the XRD patterns, there are no new phases generated after the ball-  
124 milling mixing process, which suggests no reaction between Se and MSe, and the  
125 constructed Se-60MSe cathode remains a stable phase structure.

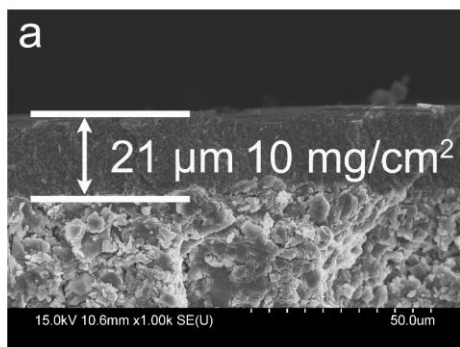


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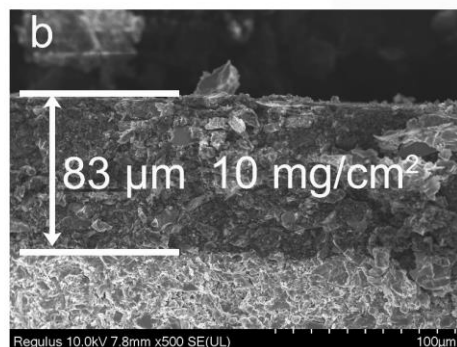
127 **Fig. S8** | Comparison of electrochemical performance of Se-MSe with different mixing  
 128 ratios. (a) The galvanostatic charge-discharge curves of Se-MSe composite electrodes  
 129 for the 2nd cycle. (b) Corresponding volumetric energy density and active capacity  
 130 utilization of Se for Se-MSe electrodes. Active capacity utilization of Se is calculated  
 131 as shown in part [Calculation of Energy density](#).

132

133



Se-60MSe



Se-50SE-10SP

134

135 **Fig. S9** | Cross-sectional SEM images of (a) Se-60MSe and (b) Se-50SE-10SP cathodes  
136 with the same mass loading of 10 mg/cm<sup>2</sup>.

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**Table S4.** Details for calculation of the density and porosity of Se-MSe composite cathodes in different proportions under different pressures.

	Cathode	$m_c$ [mg]	$\rho_0$ [g/cm <sup>3</sup> ]	Pressure/ MPa			
				0	100	270	360
$h_c$ [mm]				2.53	1.23	1.13	1.11
$\rho_c$ [g/cm <sup>3</sup> ]	Se-10MSe	390	4.94	1.96	4.04	4.40	4.48
$\varphi_c$ [%]				28.67	18.23	10.99	9.39
$h_c$ [mm]				3.76	1.79	1.63	1.6
$\rho_c$ [g/cm <sup>3</sup> ]	Se-20MSe	580	5.08	1.97	4.13	4.53	4.62
$\varphi_c$ [%]				61.29	18.69	10.71	9.03
$h_c$ [mm]				3.61	1.78	1.66	1.61
$\rho_c$ [g/cm <sup>3</sup> ]	Se-30MSe	590	5.22	2.08	4.22	4.53	4.67
$\varphi_c$ [%]				60.12	19.12	13.28	10.58
$h_c$ [mm]				3.65	1.79	1.69	1.62
$\rho_c$ [g/cm <sup>3</sup> ]	Se-40MSe	600	5.37	2.09	4.27	4.52	4.72
$\varphi_c$ [%]				61.03	20.54	15.84	12.20
$h_c$ [mm]				3.52	1.78	1.69	1.59
$\rho_c$ [g/cm <sup>3</sup> ]	Se-50MSe	600	5.54	2.17	4.29	4.52	4.81
$\varphi_c$ [%]				60.78	22.43	18.30	13.17
$h_c$ [mm]				5.21	2.93	2.72	2.60
$\rho_c$ [g/cm <sup>3</sup> ]	Se-60MSe	995	5.71	2.43	4.31	4.66	4.88
$\varphi_c$ [%]				57.38	24.61	18.36	14.60
$h_c$ [mm]				3.36	1.77	1.63	1.55
$\rho_c$ [g/cm <sup>3</sup> ]	Se-70MSe	600	5.89	2.27	4.32	4.69	4.93
$\varphi_c$ [%]				61.39	24.71	20.41	16.30
$h_c$ [mm]				3.07	1.69	1.59	1.49
$\rho_c$ [g/cm <sup>3</sup> ]	Se-80MSe	600	6.09	2.49	4.52	4.81	5.13
$\varphi_c$ [%]				59.10	24.30	21.03	15.73
$h_c$ [mm]				2.98	1.57	1.49	1.43
$\rho_c$ [g/cm <sup>3</sup> ]	Se-90MSe	600	6.30	2.56	4.87	5.13	5.34
$\varphi_c$ [%]				59.26	22.68	18.53	15.11

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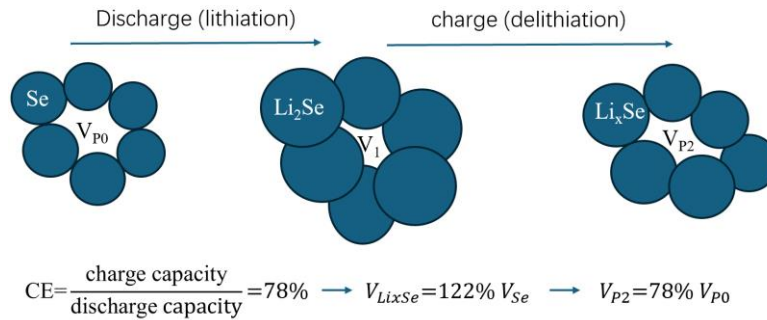
143 **Table S5.** Details for calculation of the density and porosity of Se-50SE-10SP  
 144 composite cathodes.

	Cathode	$m_c$ [mg]	$\rho_0$ [g/cm <sup>3</sup> ]	Pressure/ MPa			
				0	100	270	360
$h_c$ [mm]				6.08	3.69	3.04	2.55
$\rho_c$ [g/cm <sup>3</sup> ]	Se-SE-SP	300	2.31	0.63	1.04	1.26	1.50
$\varphi_c$ [%]				72.8	54.9	45.5	35.1

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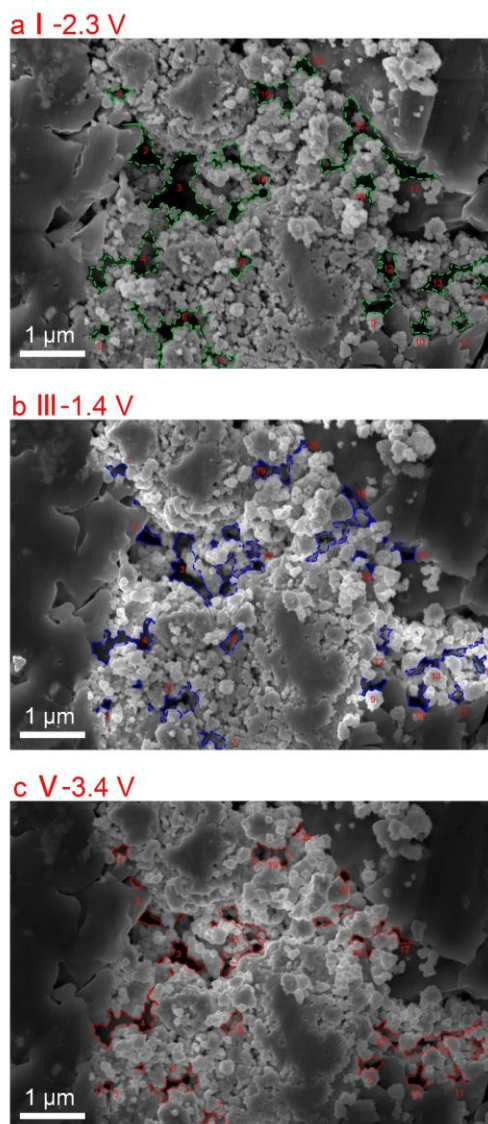
147 **Section 4. In situ observation of creep behavior of Se**



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149 **Fig. S10** | Schematic of the volume change of Se particles during (de)lithiation and the  
 150 corresponding pore size.

151 The coulombic efficiency (CE) is obtained by discharge (lithiation) capacity divided by  
 152 charge (delithiation) capacity. That is, if plastic deformation is not considered, after one  
 153 cycle of charging and discharging, the degree of lithiation of Se is 22% compared to  
 154 the initial state, i.e., the volume of Se increases by about 22% ( $\Delta V_{Se/Li_2Se} = 98\%$ ),  
 155 approximating the relative shrinkage of the pores by 22%. This is to imply that at the  
 156 end of charging, the pore size is approximated to be 78% of the initial state. Thus, the  
 157 volume change of porosity can be used to correspond to the volume change to validate  
 158 the creep mechanism, even though there will be minor variances in the local  
 159 environment, and we present the change of 20 pores to emphasize static tendency.



160

161 **Fig. S11** | The morphology evolution of region I of the Se-60MSe cathode varies with  
162 different states of charge, corresponding to various creep changes of Se. The complete  
163 evolution in Movie S1.

164 We illustrate the evolution of the particle contacts by altering the pore sizes during  
165 charging and discharging process for the in-situ SEM observant ion. The area  
166 of the 20 pores in the initial condition of the Se-MSe cathode, after discharging to 1.4  
167 V and after charging to 3.4 V are compared (the area data were obtained using histogram  
168 statistics from Photoshop).

169 If without creep deformation, the electrode pores theoretically shrink during discharge  
170 (lithiation) and re-expand to 78% of the volume of the initial state after end of charge  
171 (delithiation). However, most of the actual pore sizes after the end of charge are much  
172 smaller than 78% of the initial state (Fig. 3d in main text), indicating that Se creep into  
173 the pores to induce the pores further shrink.

174

175 **Table S6.** Material properties used to simulate the creep of composite electrodes.

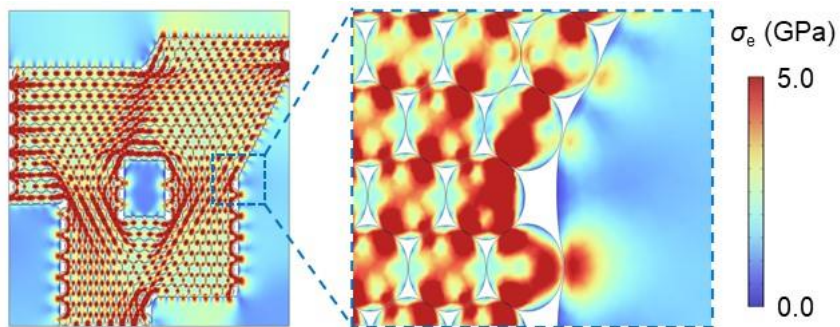
<b>Parameter (unit)</b>	<b>Value</b>
Young's modulus of LCO <sup>25</sup> (Pa)	$1.91 \times 10^{11}$
Young's modulus of Se (Pa)	$1.8 \times 10^{10}$
Young's modulus of Li <sub>2</sub> Se (Pa)	$1.27 \times 10^{10}$
Young's modulus of MSe (Pa)	$3.76 \times 10^{10}$
Young's modulus of Li <sub>4</sub> MSe (Pa)	$2.25 \times 10^{10}$
Poisson's ratio of LCO (1)	0.3
Poisson's ratio of Se (1)	0.3
Poisson's ratio of MSe (1)	0.3
Stress exponent of Se (Li <sub>2</sub> Se) (1)	7 (4.9)
Creep rate coefficient of Se (1/s)	$1 \times 10^3$
Reference stress of Se (Li <sub>2</sub> Se) (Pa)	$6.9 \times 10^9$ ( $4.8 \times 10^9$ )

176 The Young's modulus of Se, Li<sub>2</sub>Se, MSe, and Li<sub>4</sub>MSe listed in Table S6 are obtained  
 177 from the nanoindentation test in Fig. S22-S25, and the Young's modulus of LCO is from  
 178 the previous reports<sup>25</sup>.

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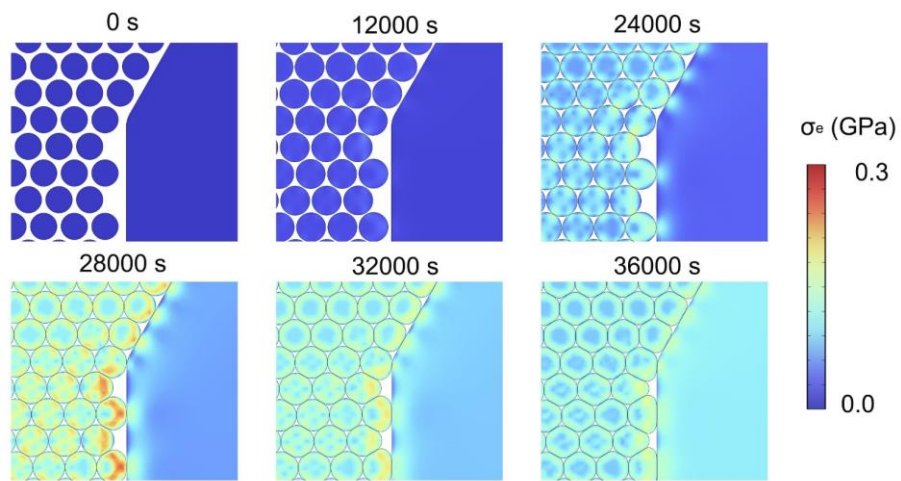


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183 **Fig. S12** | The deformation and equivalent stress in the fully lithiated LCO-MSe cathode.

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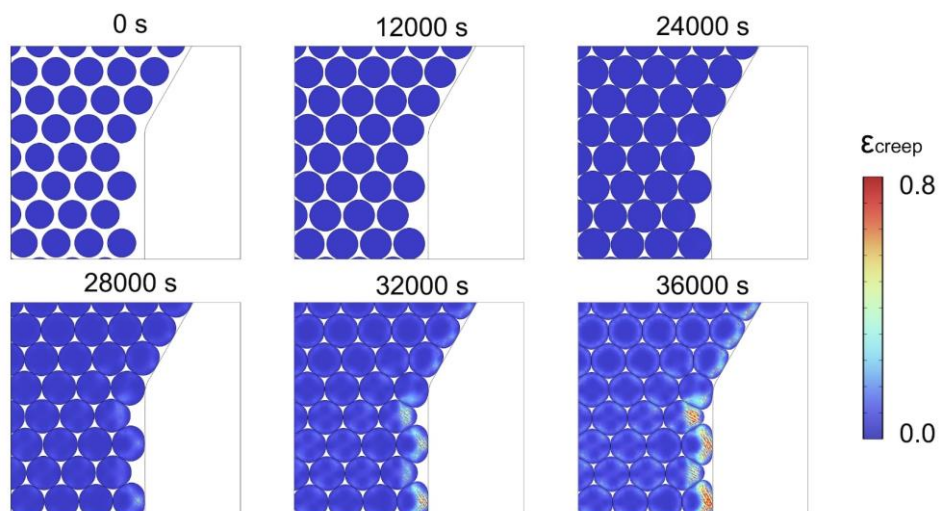
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187 **Fig. S13** | The equivalent stress in the Se-MSe cathode during its lithiation.

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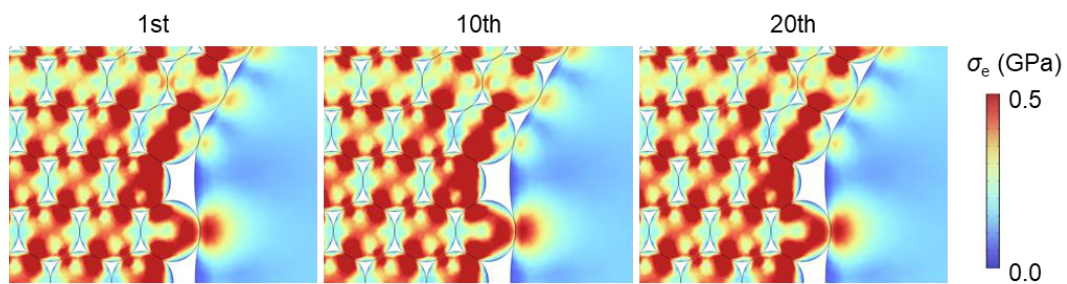


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190 **Fig. S14** | The magnitude (color contour) and direction (arrows) of the creep strain in  
191 the Se particles during the lithiation of the Se-MSe cathode.

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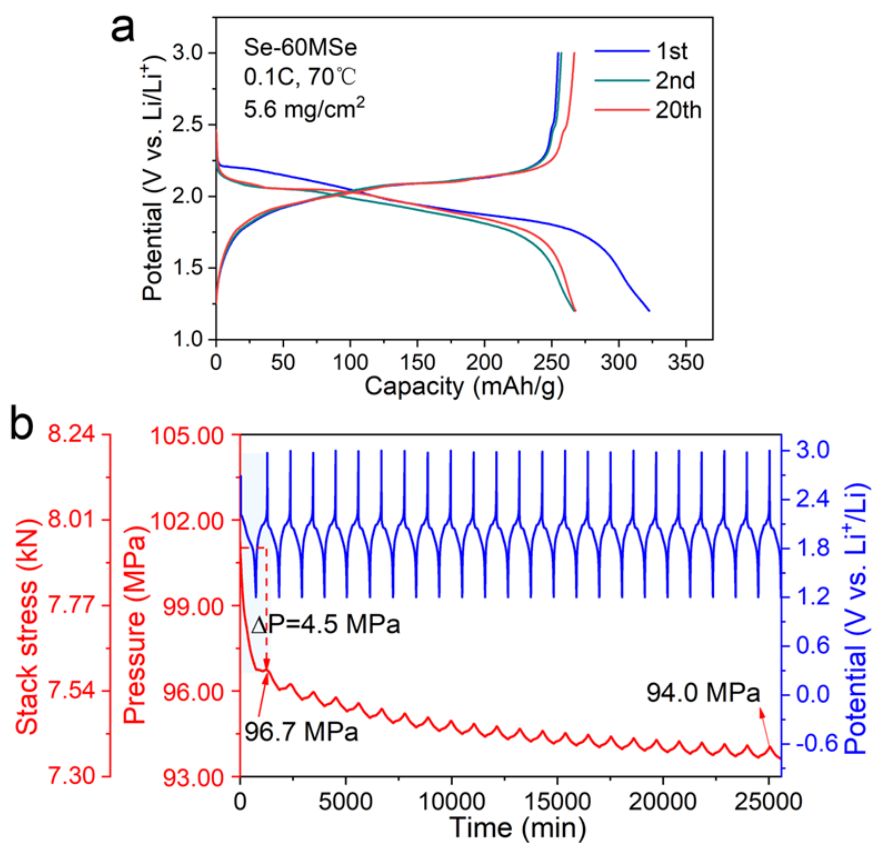


194

195 **Fig. S15** | The deformation and equivalent stress in the LCO-MSe cathode at different  
196 cycles.

197





198

199 **Fig. S16** | Operando pressure measurement for Se-60MSe|LPSC|InLi ASSB. (a)  
 200 Galvanostatic curves of the battery. (b) Galvanostatic cycling of the battery along with  
 201 the measured stack-pressure changes. The pressure at  $t = 0$  is 101.2 MPa.

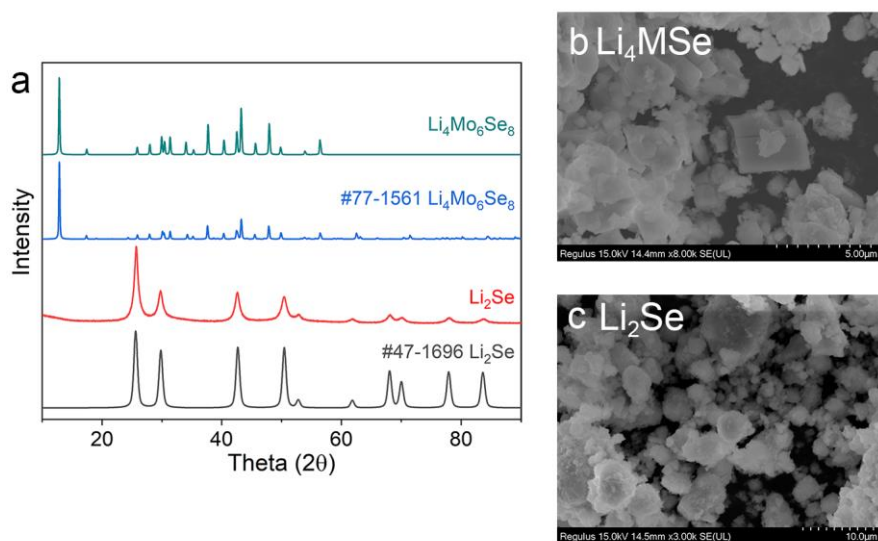
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208

209 **Fig. S17** | Structural and morphological characterization for  $\text{Li}_2\text{Se}$  and  $\text{Li}_4\text{MSe}$  obtained  
210 by chemical prelithiation. (a) XRD patterns of  $\text{Li}_2\text{Se}$  and  $\text{Li}_4\text{MSe}$ . SEM images of (b)  
211  $\text{Li}_4\text{MSe}$  and (c)  $\text{Li}_2\text{Se}$ .

212



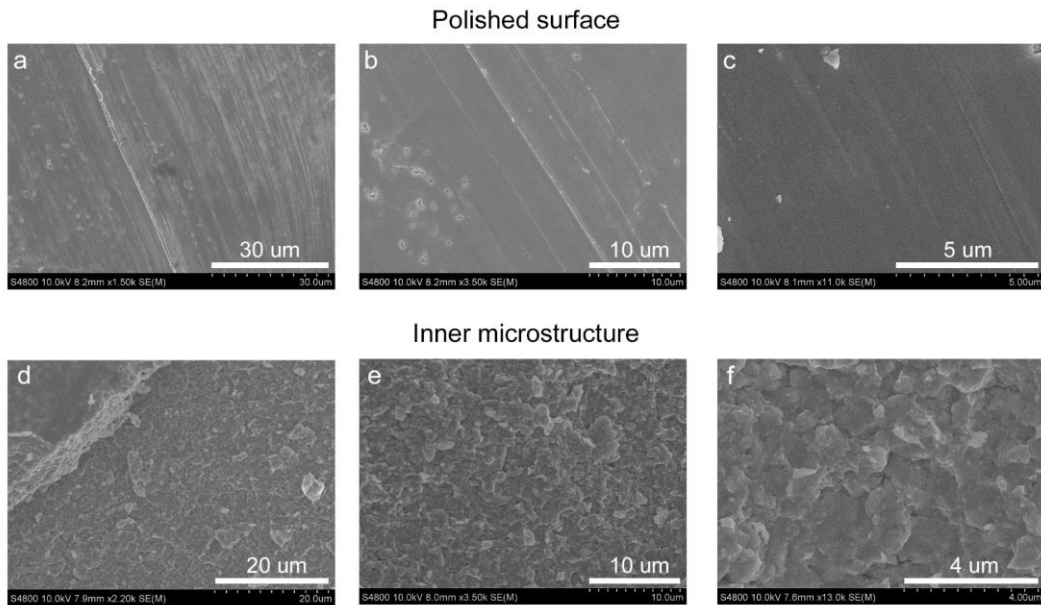
213

214 **Fig. S18** | Digital photo of polished samples for nanoindentation. Black zone is sample,  
215 and transparent part is epoxy resin for cold inlay with sample fixed.

216 Li<sub>2</sub>Se and Li<sub>4</sub>MSe exhibit higher strain-rate sensitivity exponent and considerably  
217 lower hardness and Young's modulus after lithiation in comparison to Se and MSe (Fig.  
218 S21-S24). This tendency is consistent with earlier research on the development of Si  
219 hardness, elastic modulus, and strain-rate sensitivity exponent with lithiation degree<sup>26</sup>.

220

221



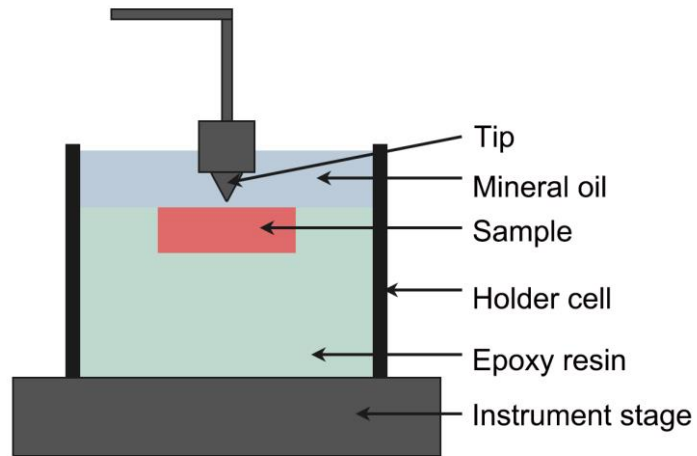
222

223 **Fig. S19** | The surface morphology of cold-pressed Se samples used for nanoindentation.  
224 (a-c) The polished surface and (d-f) inner microstructure.

225

226 The Se pellet has a much dense contact in particles without invisible pores and cracks,  
227 consistent with its high relative density of 95.65% (measured by Archimedes method).

228 The Young's modulus and hardness measured from such dense pellet should be close  
229 to the material's intrinsic properties.



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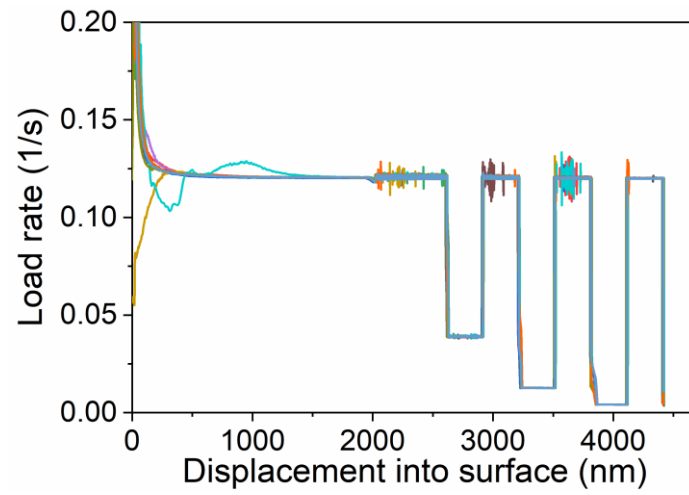
231 **Fig. S20** | Schematic of specialized fluid cell with mineral oil to prevent the sulfide  
232 sample from being exposed to air during nanoindentation.

233 The schematic diagram's height of the liquid cell has been expanded for ease of  
234 understanding. In the actual device, the liquid bath is 1 mm high to protect the tip of the  
235 nanoindentation from being impacted. And the mineral oil is well anchored in the liquid  
236 cell due to its high surface tension.

237

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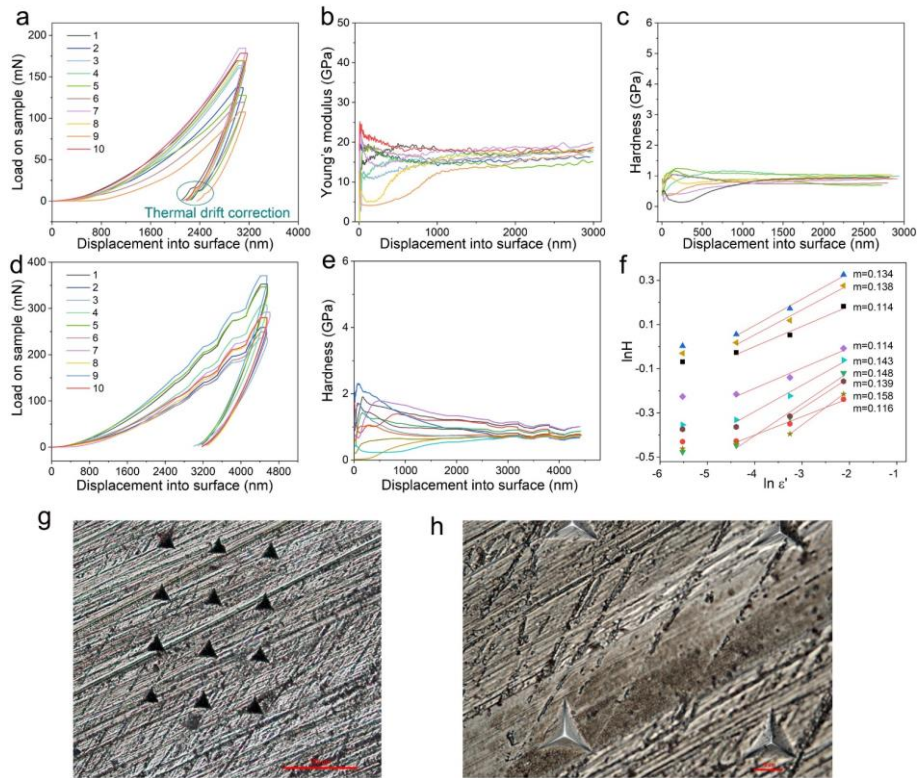
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241 **Fig. S21** | Nanoindentation strain-rate jump experiment by four different applied strain  
242 rates at corresponding displacement.

243

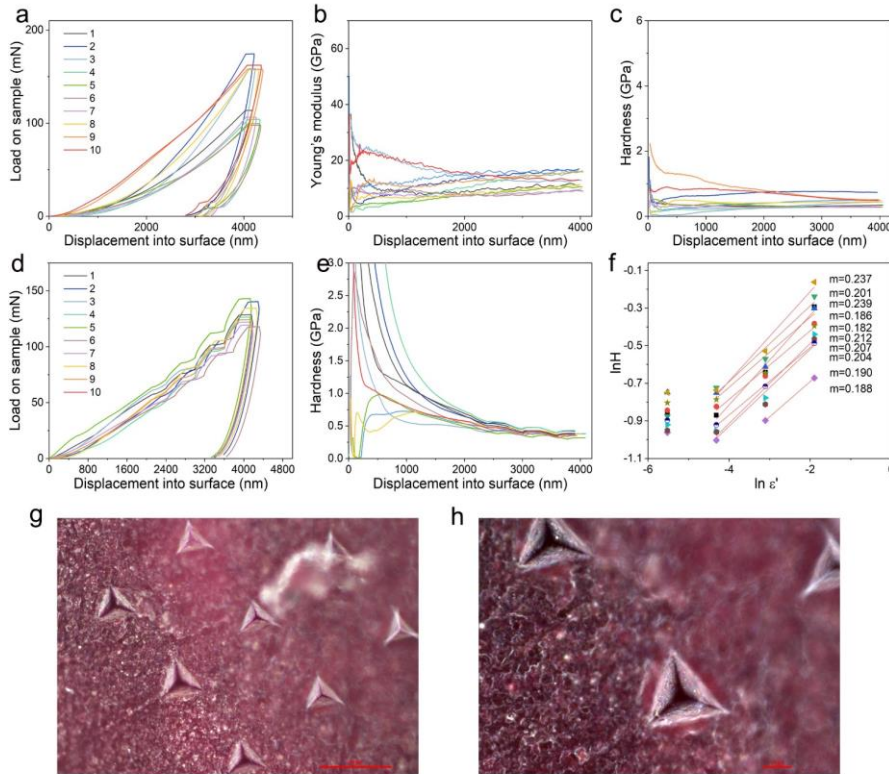


244

245 **Fig. S22 | Mechanical characteristics of Se sample by nanoindentation test.** (a-c)  
 246 Displacement control mode for measurement of *E* and *H* by maintaining a constant  
 247 strain rate of 0.05 s<sup>-1</sup>. Using the Oliver-Pharr method, (a) the corresponding load–  
 248 displacement curves and the calculated (b) *E* and (c) *H*. (d-f) Nanoindentation strain-  
 249 rate jump experiment with four different applied strain rates. (d) Corresponding load–  
 250 displacement curves, (e) the measured *H*, and (f) the calculated strain-rate sensitivity  
 251 exponent *m* for Se. (g, h) Residual topography after nanoindentation experiments by  
 252 microscopy. Scale bar: 100 μm for (g), 10 μm for (h).

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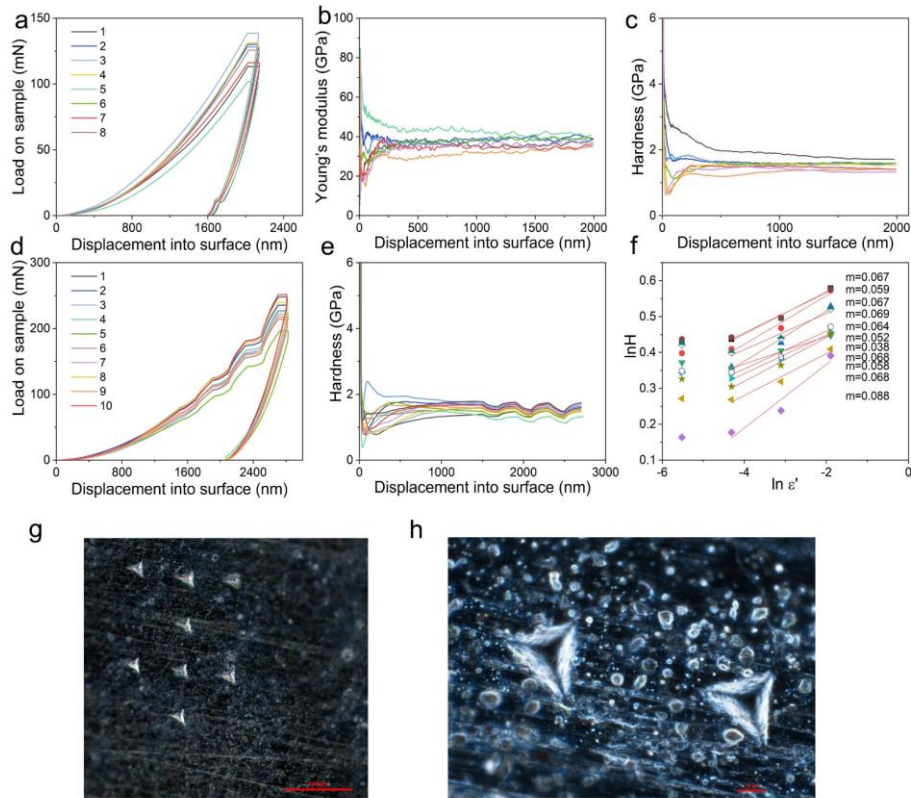


255

256 **Fig. S23** | Mechanical characteristics of Li<sub>2</sub>Se sample by nanoindentation test. (a-c)  
 257 Displacement control mode for measurement of E and H by maintaining a constant  
 258 strain rate of 0.05 s<sup>-1</sup>. Using the Oliver-Pharr method, (a) the corresponding load-  
 259 displacement curves and the calculated (b) E and (c) H. (d-f) Nanoindentation strain-  
 260 rate jump experiment with four different applied strain rates. (d) Corresponding load-  
 261 displacement curves, (e) the measured H, and (f) the calculated strain-rate sensitivity  
 262 exponent *m* for Li<sub>2</sub>Se. (g, h) Residual topography after nanoindentation experiments by  
 263 microscopy. Scale bar: 50 μm for (g), 10 μm for (h).

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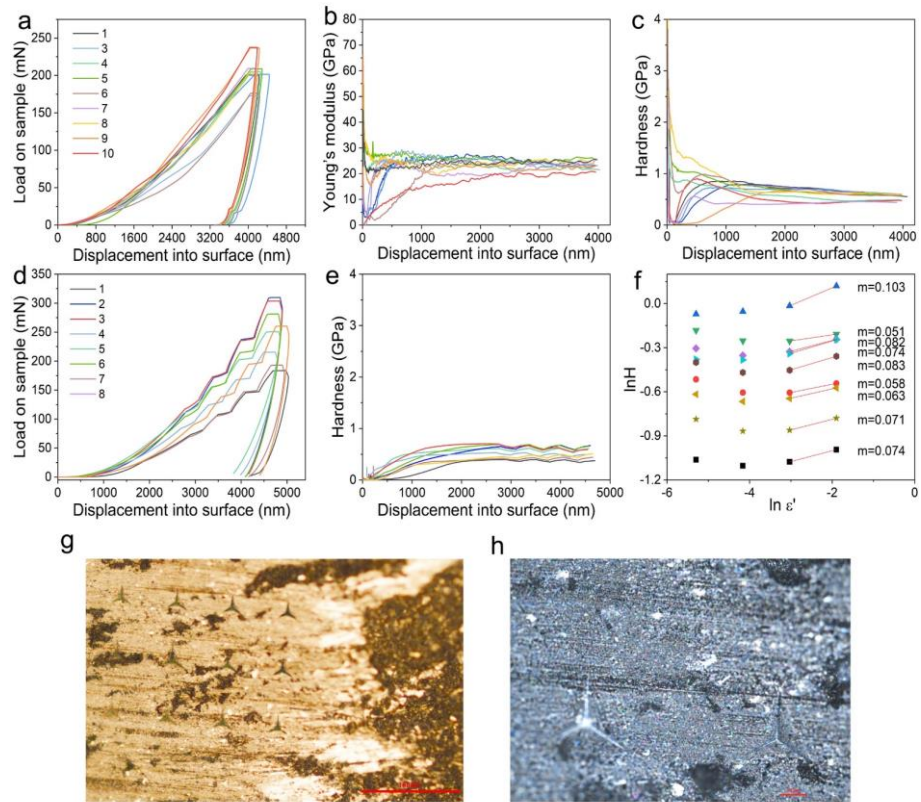




265

266 **Fig. S24** | Mechanical characteristics of MSe sample by nanoindentation test. (a-c)  
 267 Displacement control mode for measurement of  $E$  and  $H$  by maintaining a constant  
 268 strain rate of  $0.05 \text{ s}^{-1}$ . Using the Oliver-Pharr method, (a) the corresponding load–  
 269 displacement curves and the calculated (b)  $E$  and (c)  $H$ . (d-f) Nanoindentation strain-  
 270 rate jump experiment with four different applied strain rates. (d) Corresponding load–  
 271 displacement curves, (e) the measured  $H$ , and (f) the calculated strain-rate sensitivity  
 272 exponent  $m$  for MSe. (g, h) Residual topography after nanoindentation experiments by  
 273 microscopy. Scale bar: 100  $\mu\text{m}$  for (g), 10  $\mu\text{m}$  for (h).

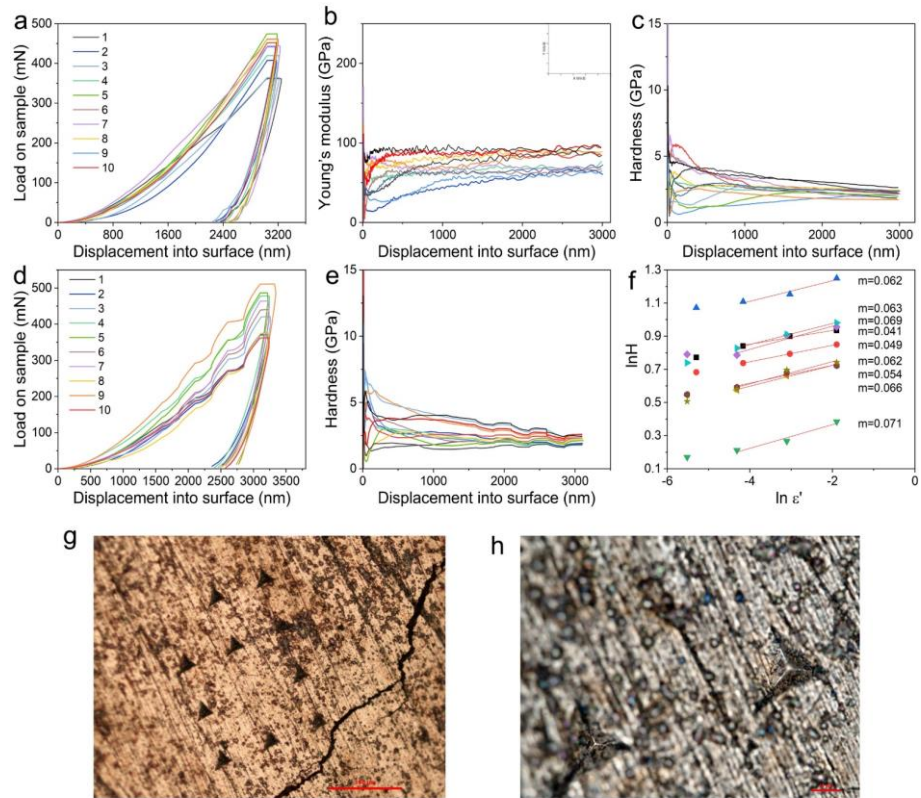
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275

276 **Fig. S25** | Mechanical characteristics of Li<sub>4</sub>MSe sample by nanoindentation test. (a-c)  
 277 Displacement control mode for measurement of E and H by maintaining a constant  
 278 strain rate of 0.05 s<sup>-1</sup>. Using the Oliver-Pharr method, (a) the corresponding load–  
 279 displacement curves and the calculated (b) E and (c) H. (d-f) Nanoindentation strain-  
 280 rate jump experiment with four different applied strain rates. (d) Corresponding load–  
 281 displacement curves, (e) the measured H, and (f) the calculated strain-rate sensitivity  
 282 exponent *m* for Li<sub>4</sub>MSe. (g, h) Residual topography after nanoindentation experiments  
 283 by microscopy. Scale bar: 100 μm for (g), 10 μm for (h).

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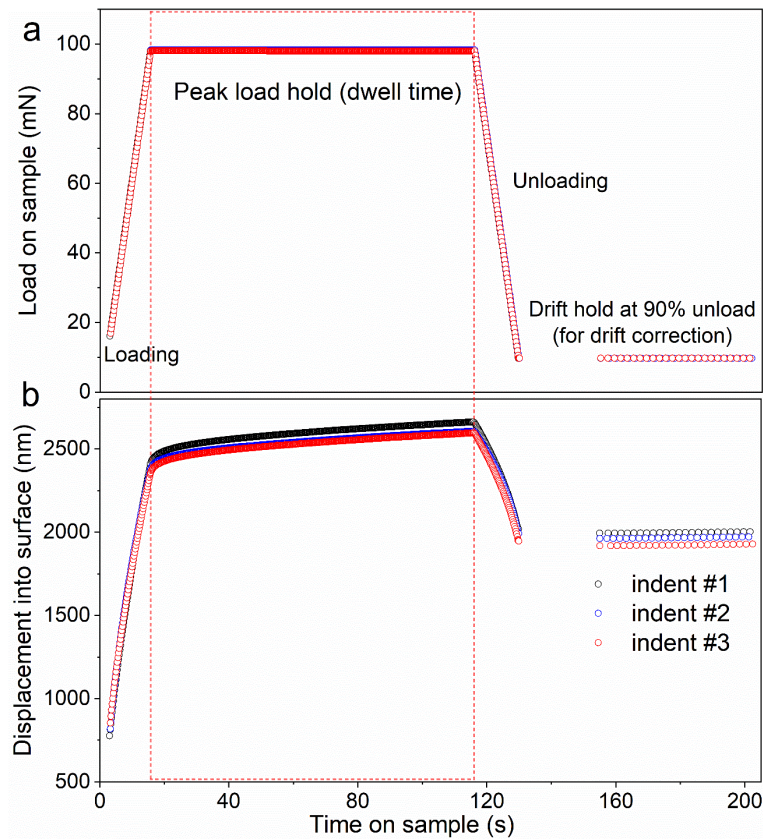


285

286 **Fig. S26** | Mechanical characteristics of FeS sample by nanoindentation test. (a-c)  
 287 Displacement control mode for measurement of E and H by maintaining a constant  
 288 strain rate of 0.05 s<sup>-1</sup>. Using the Oliver-Pharr method, (a) the corresponding load–  
 289 displacement curves and the calculated (b) E and (c) H. (d-f) Nanoindentation strain-  
 290 rate jump experiment with four different applied strain rates. (d) Corresponding load–  
 291 displacement curves, (e) the measured H, and (f) the calculated strain-rate sensitivity  
 292 exponent *m* for FeS. (g, h) Residual topography after nanoindentation experiments by  
 293 microscopy. Scale bar: 100 μm for (g), 10 μm for (h).

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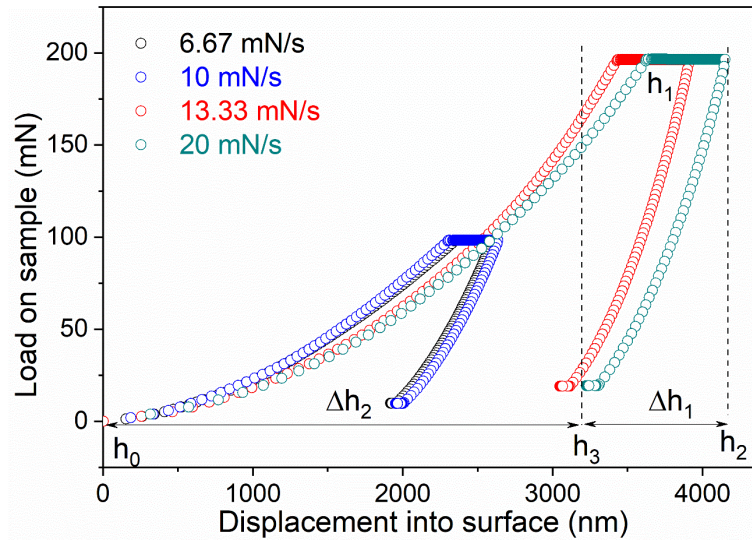
297 **Fig. S27** | The constant load and hold method for creep measurements of Se material.  
 298 The loading rate is 6.67 mN/s and the holding times is 100 s. (a) The load on the sample.  
 299 (b) The displacement into surface curves versus time on the sample. This indentation  
 300 depth trend with time is similar to the creep evolution on constant stress in previous  
 301 research<sup>27</sup>.

302

303 As illustrated in this constant load test by nanoindentation, the indentation depth  
 304 increases continuously during the long-term dwell time, indicating the viscosity feature  
 305 of Se material.

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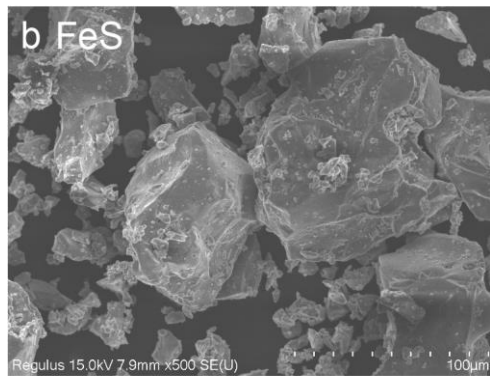
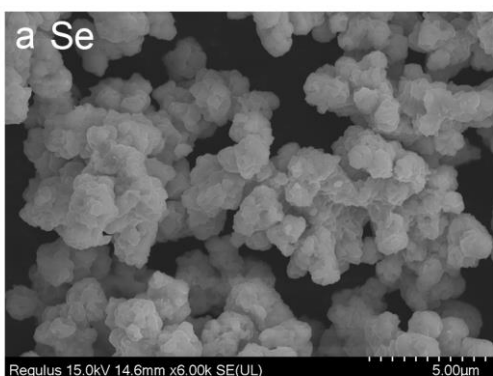
309 **Fig. S28** | Load-displacement curves of Se sample at different loading rates and  
 310 maximum loads (hold at the max load for 100 s).

311 After unloading, the indentation depth reverts from  $h_2$  to  $h_3$  ( $\Delta h_1$ ), leaving the non-  
 312 reversible part ( $\Delta h_2$ ) due to the plastic deformation, which well further demonstrates  
 313 that the Se material exhibits viscoplasticity.

314

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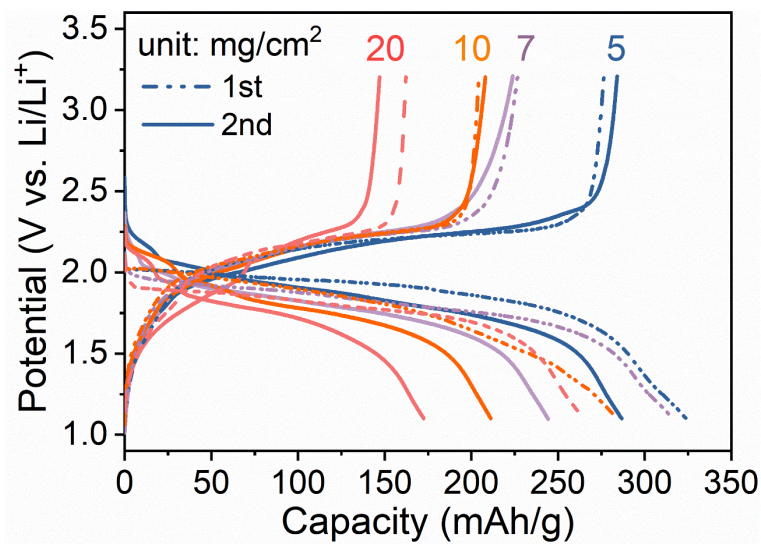
317

318 **Fig. S29** | Comparison of particle size and morphology. (a) Se, (b) FeS.

319 The morphology and size of the Se and FeS particles vary greatly, despite their similar  
320 densities (Se, 4.81 g/cm<sup>3</sup>; FeS, 4.84 g/cm<sup>3</sup>), which may have led to the FeS-MSe  
321 electrode being thicker than the Se-MSe electrode when they have the same mass  
322 loadings.

323

324 Section 6. Electrochemical performance of creep-type Se-60MSe cathode.



325

326 **Fig. S30** | The galvanostatic curves of Se-60MSe cathodes with varying loadings.

327 There are more electrochemical reaction sites in the two-phase cathode and where ions  
328 and electrons migrating in the same medium in Se-MSe cathodes significantly reduce  
329 the tortuosity factor,<sup>28</sup> benefiting the cathode kinetics with an excellent performance  
330 even at high mass loadings and great current densities.

331

332 **Table S7.** Calculation details of the energy density of Se-60MSe cathode with different  
 333 mass loadings.

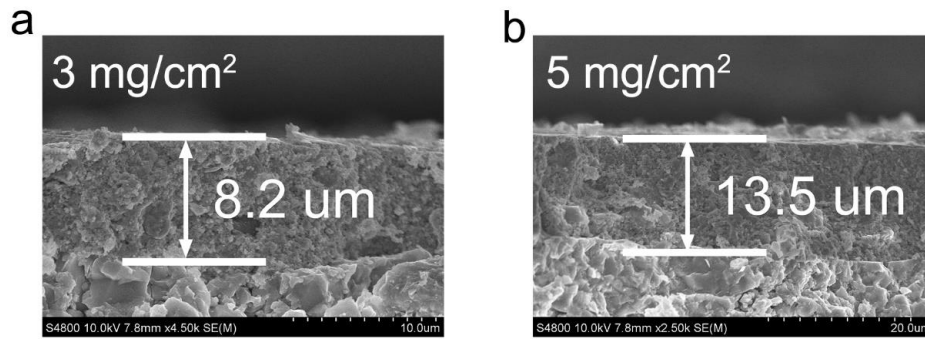
<b>Mass Loading</b> [mg/cm <sup>2</sup> ]	<b>Cycle</b>	<b>Specific Capacity</b> [mAh/g]	<b>Capacity</b> [mAh/cm <sup>2</sup> ]	<b>V<sub>average</sub></b> [V]	<b>h<sub>cathode</sub></b> [um]	<b>E<sub>G</sub></b> [Wh/kg]	<b>E<sub>V</sub></b> [Wh/L]
3	1st	323.4	0.97	2.08	8.2	688.8	<b>2460</b>
	2nd	283.5	0.85	2.10	8.2	609.5	<b>2178</b>
5	1st	321.9	1.61	2.04	13.5	672.8	<b>2432</b>
	2nd	271.9	1.36	2.03	13.5	565.6	<b>2044</b>
10	1st	286	2.86	1.97	21	569.3	<b>2505</b>
	2nd	211.4	2.11	1.94	21	410.1	<b>1949</b>

334

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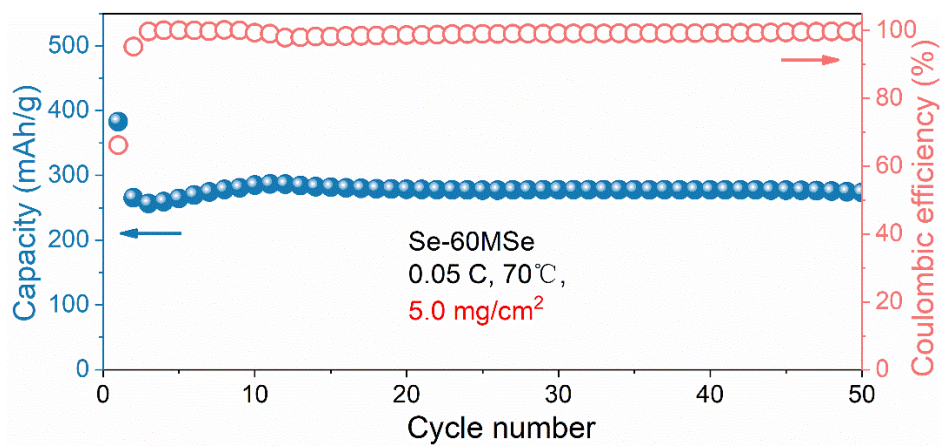


337

338 **Fig. S31** | The thickness of Se-60MSe cathode with different mass loadings. (a) 3  
339 mg/cm<sup>2</sup>, (b) 5 mg/cm<sup>2</sup>.

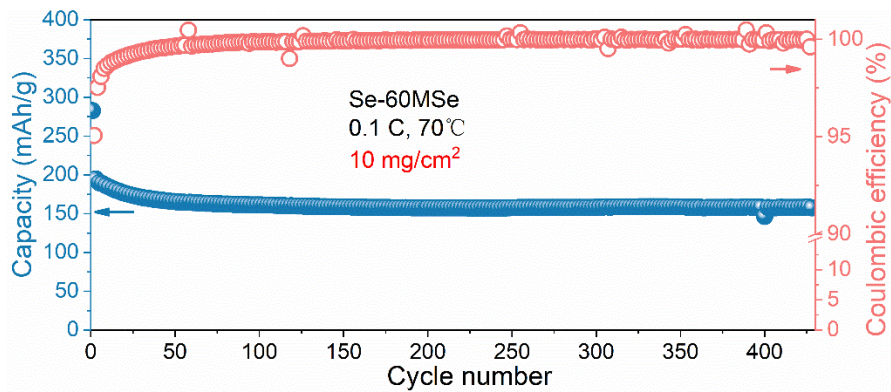
340

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342

343 **Fig. S32** | Cycling performance of Se-60MSe cathode with the mass loading of 5  
344 mg/cm<sup>2</sup>.

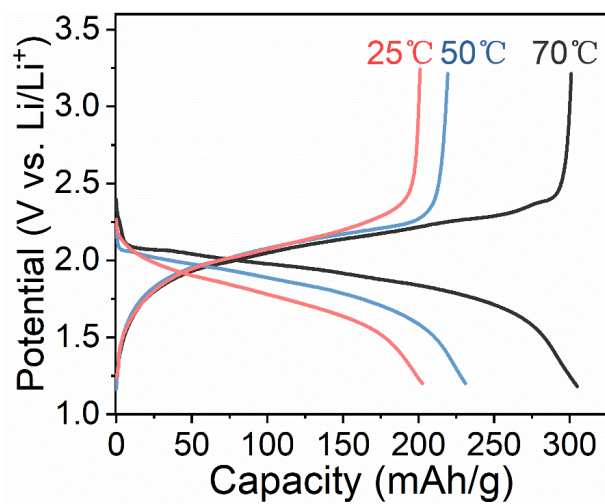


345

346 **Fig. S33** | Cycling performance of Se-60MSe cathode with the mass loading of 10  
347 mg/cm<sup>2</sup>.

348

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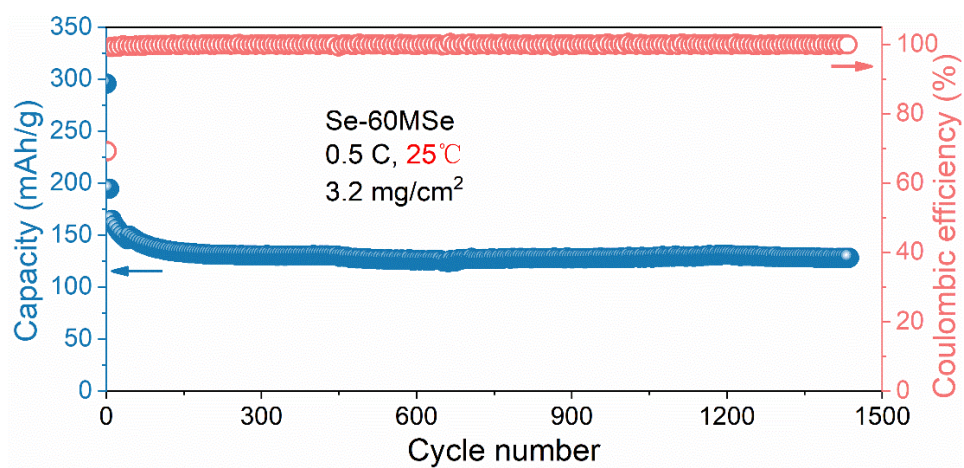


350

351 **Fig. S34** | The 2nd galvanostatic curves of Se-60MSe cathodes at different temperatures.

352

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354

355 **Fig. S35** | Cycling performance of Se-60MSe cathode at room temperature of 25°C at  
356 0.5 C.

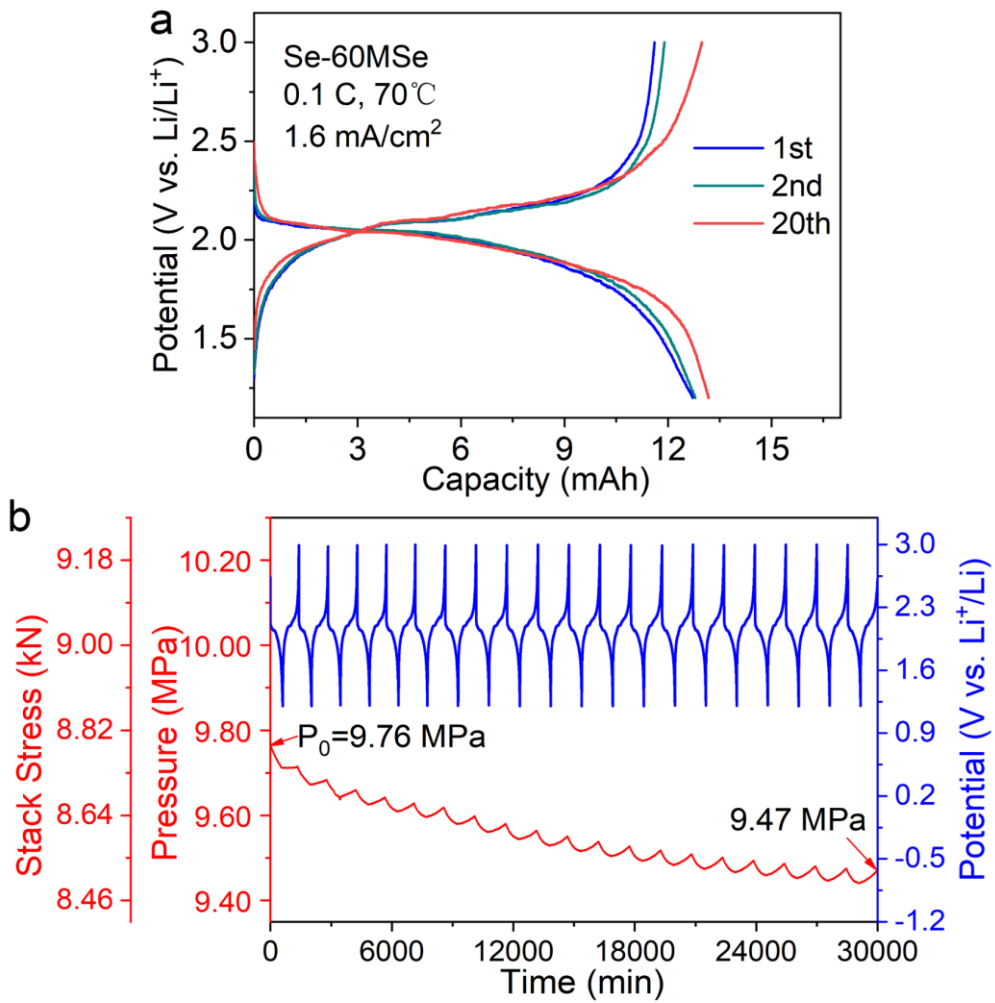
357

358 **Table S8.** Calculation details of the energy density of Se-60MSe cathode for the CT-  
 359 ASS Se-60MSe//InLi all-solid-state pouch battery.  
 360

	<b>Parameter</b>	<b>Value</b>	
<b>Se-60MSe cathode (at the cathode level)</b>	Area weight	4.69 mg/cm <sup>2</sup>	
	Area capacity	1.66 mAh/cm <sup>2</sup>	
	Thickness	18 μm	
	Average voltage (vs InLi)	1.299 V	
	Average voltage (vs Li/Li <sup>+</sup> )	1.899 V	
	Capacity	26.53 mAh	
	Weight	76.53 mg	
	Energy density		658.3 Wh/kg
			1749.3 Wh/L

361

362



363

364 **Fig. S36** | Operando pressure measurement for Se-60MSe|LPSC|InLi (3 cm×3 cm, 1.48  
 365 mAh/cm<sup>2</sup>) all-solid-state pouch cell. (a) Galvanostatic curves of the battery. (b)  
 366 Galvanostatic cycling of the battery along with the measured stack-pressure changes.  
 367 The pressure at t = 0 is 9.76 MPa.

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