Supplementary Materials:

Figure S1: TG profiles of LZT/SN-SPE and SN-SPE; Figure S2: Electrochemical impedance curves of (a) LZT/SN-SPE and (b) SN-SPE at various temperature; Figure S3: Nyquist plots of the symmetric Li cells with (a) LZT/SN-SPE and (b) SN-SPE before and after polarization. Steady-state current measurement of the symmetric Li cells with (c) LZT/SN-SPE and (d) SN-SPE; Figure S4. XPS spectra of F 1s for the cycled lithium metal anode in Li|LZT/SN-SPE|Li; Figure S5. EIS evolution when cycling a Li|LZT/SN-SPE|Li cell at room temperature with a current density of 1 mA $cm^{-2}$; Figure S6. Charge/discharge curves of LFP|LZT/SN-SPE|Li; Table S1 The electrochemical performance comparison of the LZT/SN-SPE with the other published works for ASSLBs.

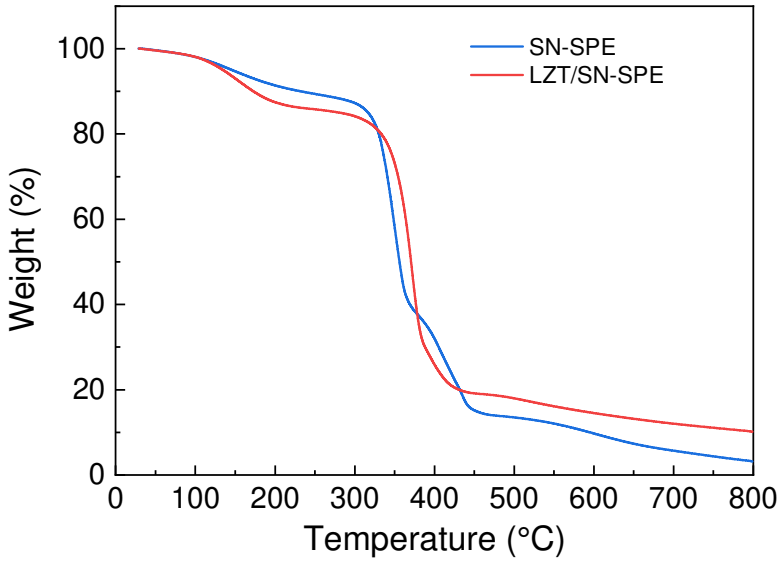


Figure S1. TG profiles of LZT/SN-SPE and SN-SPE

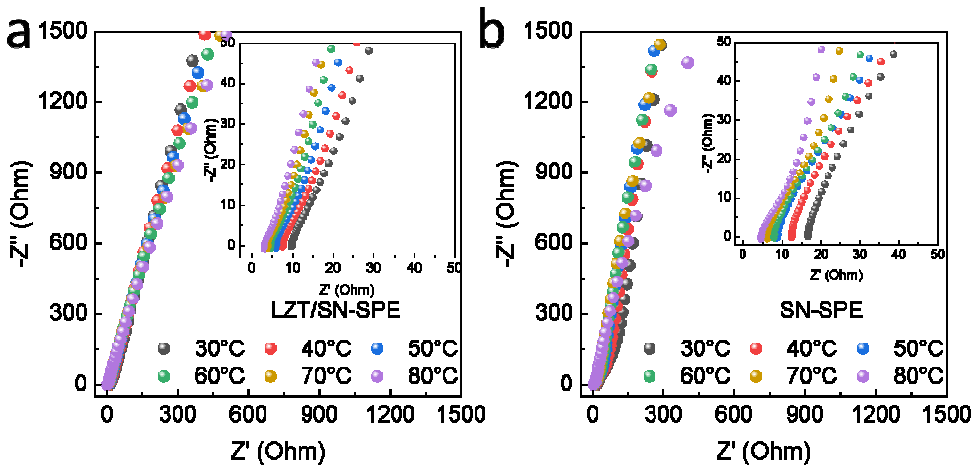


Figure S2. Electrochemical impedance curves of (a) LZT/SN-SPE and (b) SN-SPE at various temperature.

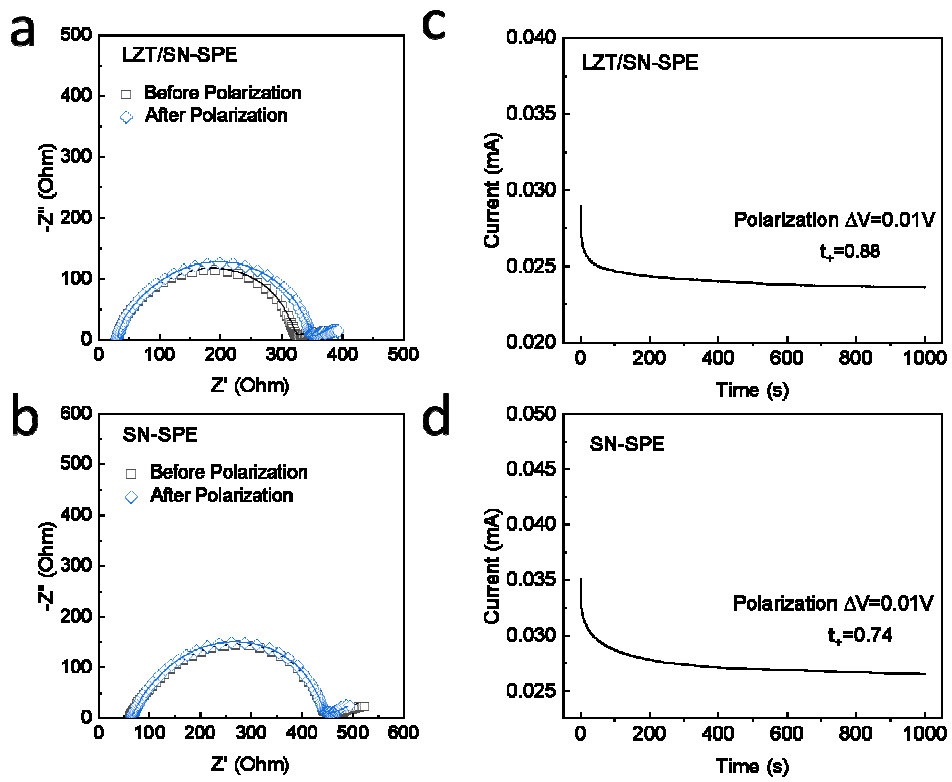


Figure S3. Nyquist plots of the symmetric Li cells with (a) LZT/SN-SPE and (b) SN-SPE before and after polarization. Steady-state current measurement of the symmetric Li cells with (c) LZT/SN-SPE and (d) SN-SPE.

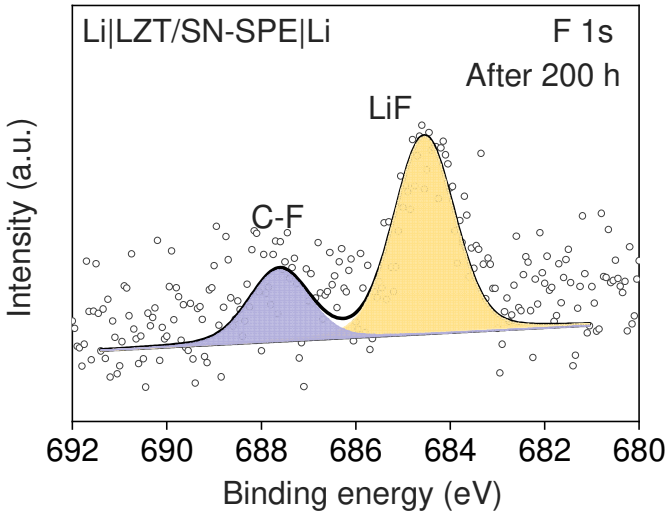


Figure S4. XPS spectra of F 1s for the cycled lithium metal anode in Li|LZT/SN-SPE|Li.

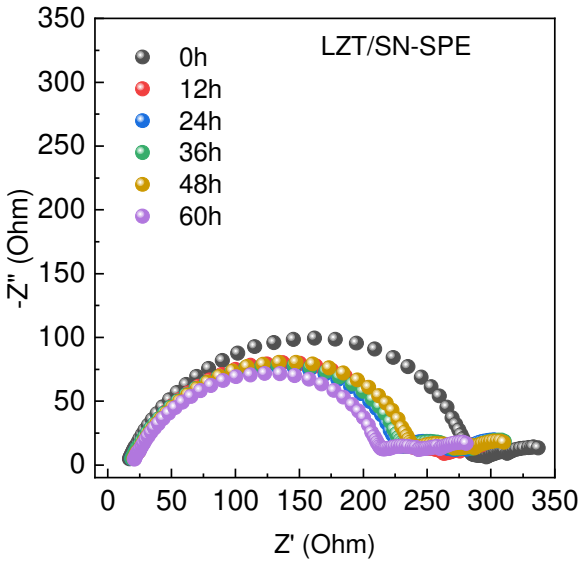


Figure S5. EIS evolution when cycling a Li|LZT/SN-SPE|Li cell at room temperature with a current density of 1 mA $cm^{-2}$.

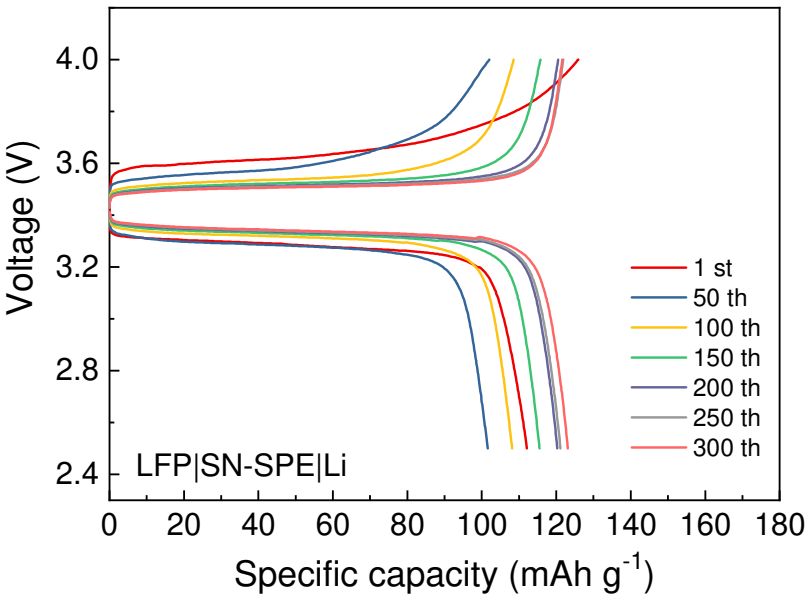


Figure S6. Charge/discharge curves of LFP|LZT/SN-SPE|Li.

Table S1 The electrochemical performance comparison of the LZT/SN-SPE with the other published works for ASSLBs.

| **Ref.** | **Sample** | **Anode\|Cathode** | **Cycle performance** | **capacity decay rate** | **Capacity (mAh $g^{-1}$)** | **Rate(C)** |
|---|---|---|---|---|---|---|
| **Our work** | LZT/SN-SPE | Li\|LFP | 420 cycles, 98.6% at 1C | 0.003% | 136.63 | 0.5 |
| | | | | | 136.56 | 1 |
| | | | | | 126.69 | 2 |
| | | | | | 118.36 | 3 |
| | | | | | 106.03 | 5 |
| | | | | | 92.40 | 8 |
| [7] | LiTFSI/SN/PTFE/LLZTO | Li\|LFP | 200 cycles, 90.3% at 0.2C | 0.048% | 157 | 0.1 |
| | | | | | 153 | 0.2 |
| | | | | | 142 | 0.3 |
| | | | | | 133 | 0.5 |
| | | | | | 115 | 1 |
| [14] | LCPE-60 | Li\|LFP | 240 cycles, | 0.031% | 157 | 0.1 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | | 92.6% at 0.5C | | 153 | 0.2 |
| | | | | | 146 | 1 |
| | | | | | 140 | 2 |
| | | | | | 131 | 3 |
| | | | | | 86 | 5 |
| [16] | IPLL-SSE | Li\|LFP | 200 cycles, 84% at 1C | 0.08% | 169.5 | 0.2 |
| | | | | | 160.5 | 0.3 |
| | | | | | 141.1 | 0.5 |
| | | | | | 125.8 | 1 |
| | | | | | 106.3 | 2 |
| [23] | PVDF-HFP/SN/LiTFSI | Li\|LFP | 300 cycles, 98% at 0.5C | 0.007% | 162 | 0.1 |
| | | | | | 164 | 0.2 |
| | | | | | 160 | 0.5 |
| | | | | | 157 | 1 |
| | | | | | 148 | 2 |
| [24] | LLZTO@SN/PAN | Li\|LFP | 500 cycles, 87% at 0.2C | 0.026% | 163 | 0.1 |
| | | | | | 160 | 0.2 |
| | | | | | 150 | 0.5 |
| | | | | | 126 | 1 |
| | | | | | 72 | 2 |
| [41] | TPU/LLZTO/SN | Li\|LFP | 100 cycles, 88% at 0.5C | 0.12% | 168 | 0.1 |
| | | | | | 163 | 0.2 |
| | | | | | 150 | 0.5 |
| | | | | | 135 | 1 |
| | | | | | 121 | 2 |
| | | | | | 66 | 5 |
| [48] | SN-CPE | Li\|LFP | 350 cycles, 88.3% at 1C | 0.033% | 160 | 0.1 |
| | | | | | 156 | 0.2 |
| | | | | | 155 | 0.5 |
| | | | | | 149 | 1 |
| | | | | | 133 | 2 |
| [52] | PVDF–HFP-15%LLZO-LITFSI | Li\|LFP | 180 cycles, 92.5% at 0.5 C | 0.042% | 140 | 0.1 |
| | | | | | 124 | 0.2 |
| | | | | | 113 | 0.5 |
| | | | | | 100 | 1 |
| | | | | | 82 | 2 |