Supplemental Information

Stability of Solid Electrolyte Interphase and Calendar Life of Lithium Metal Batteries

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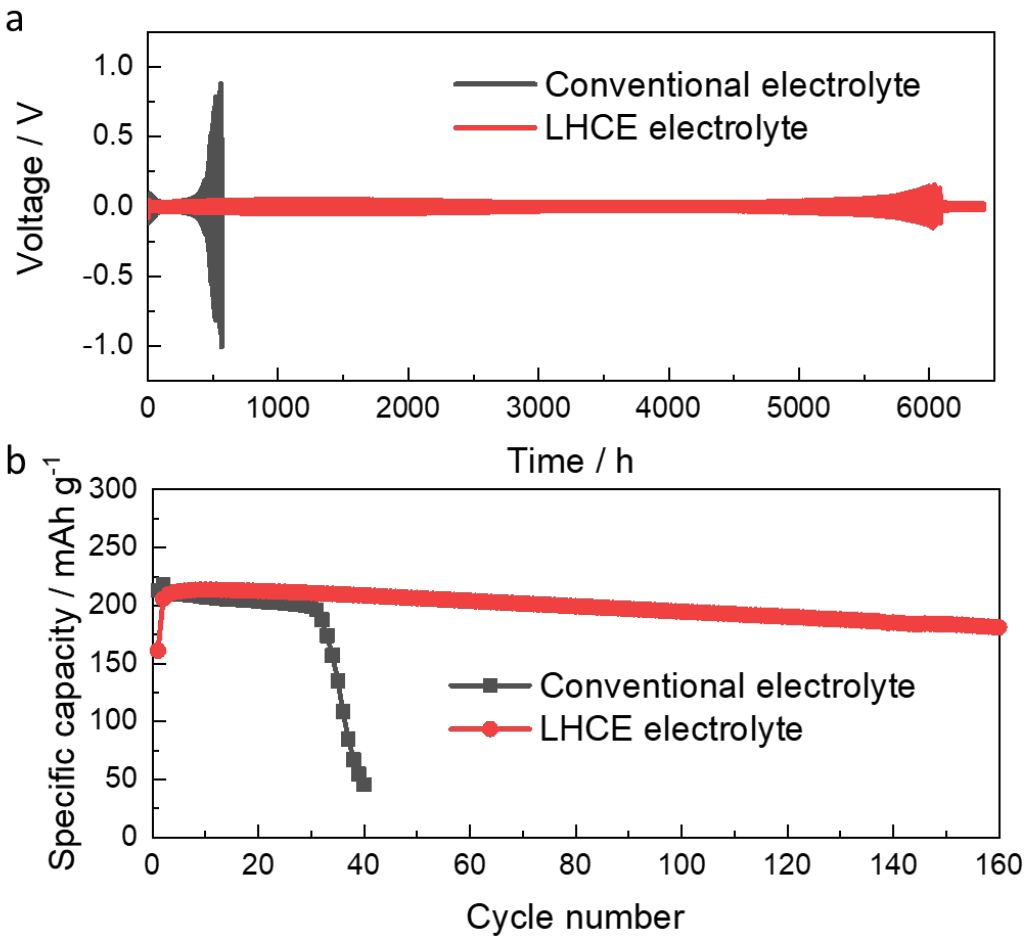
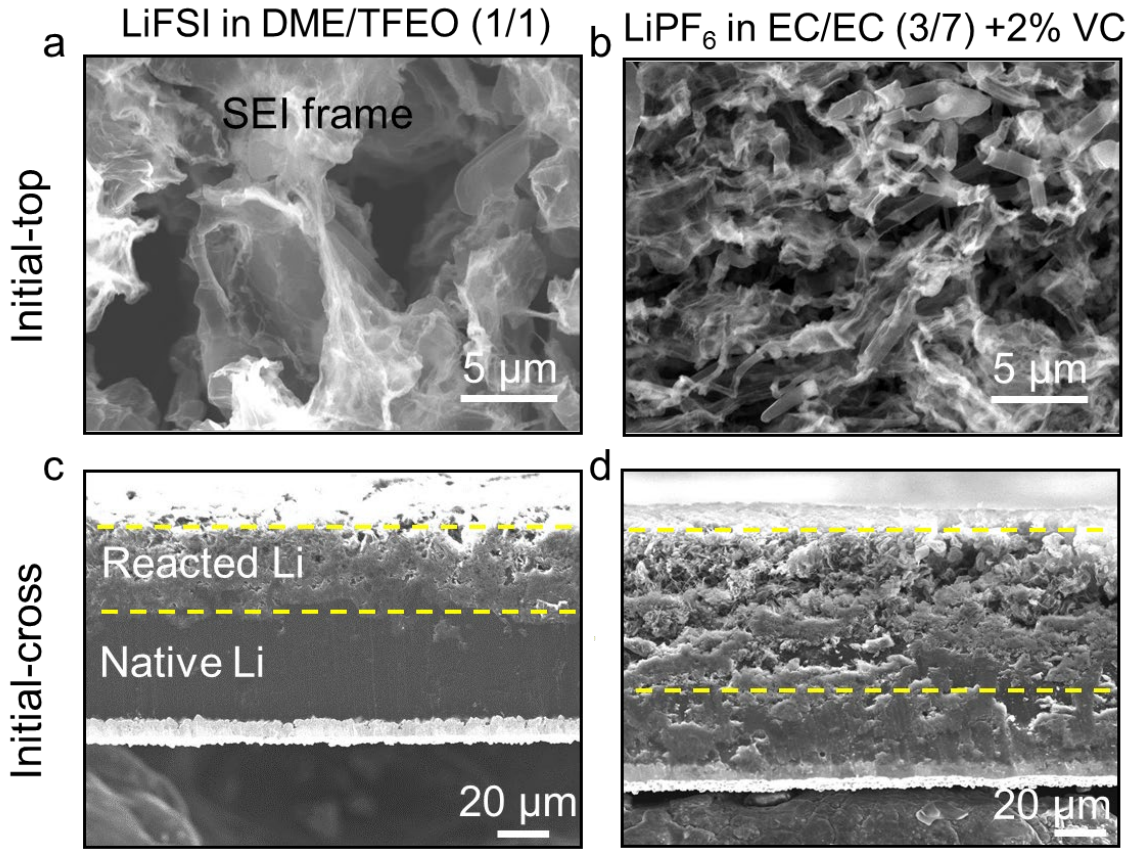
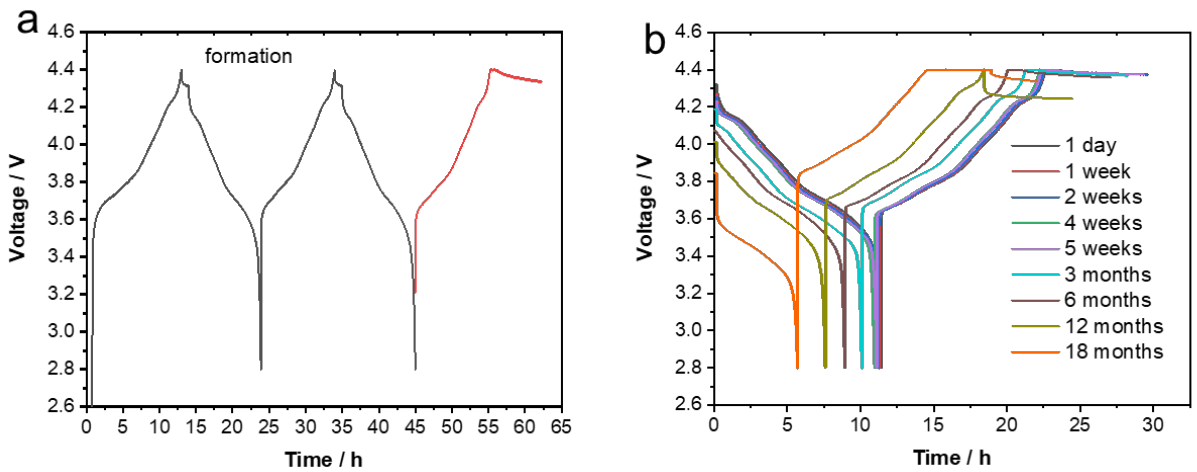


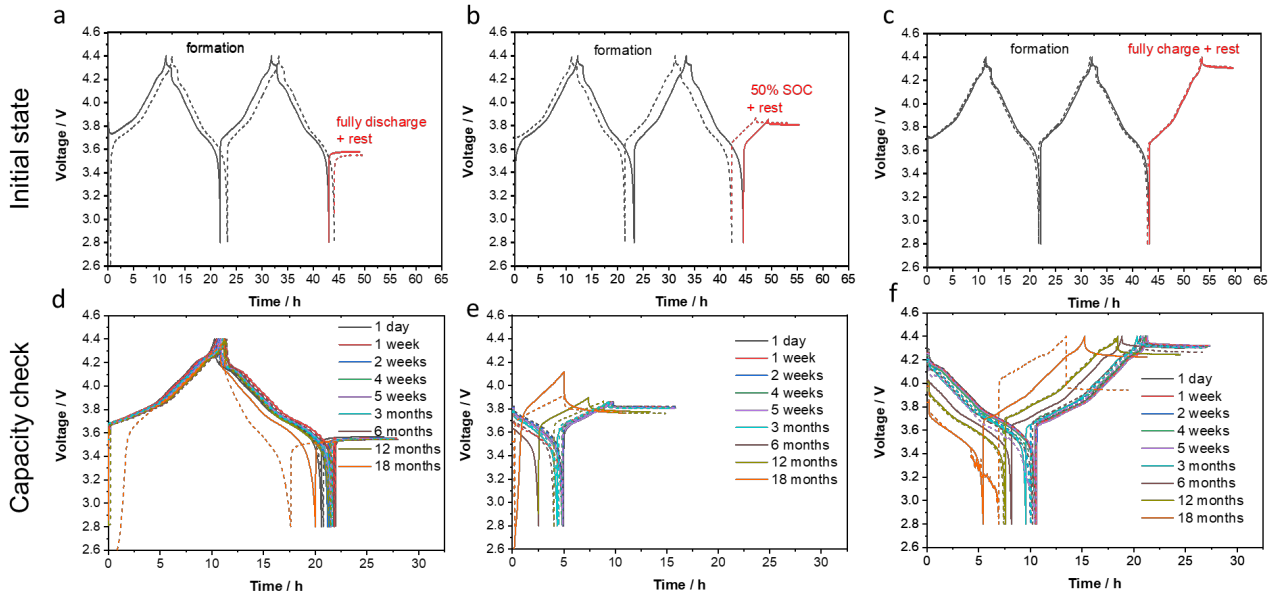
Supplemental Information Fig. 1. (a) Voltage profiles of Li||Li cells as a function of cycling time obtained at a current density of 0.5 mA cm^{-2} and a capacity of 1 mAh cm^{-2} for each plating or stripping step. (b) Cycling performance of Li||NMC811 cells at C/10 charge and C/3 discharge. The cathode loading of NMC811 was 4.2 mAh cm^{-2}.



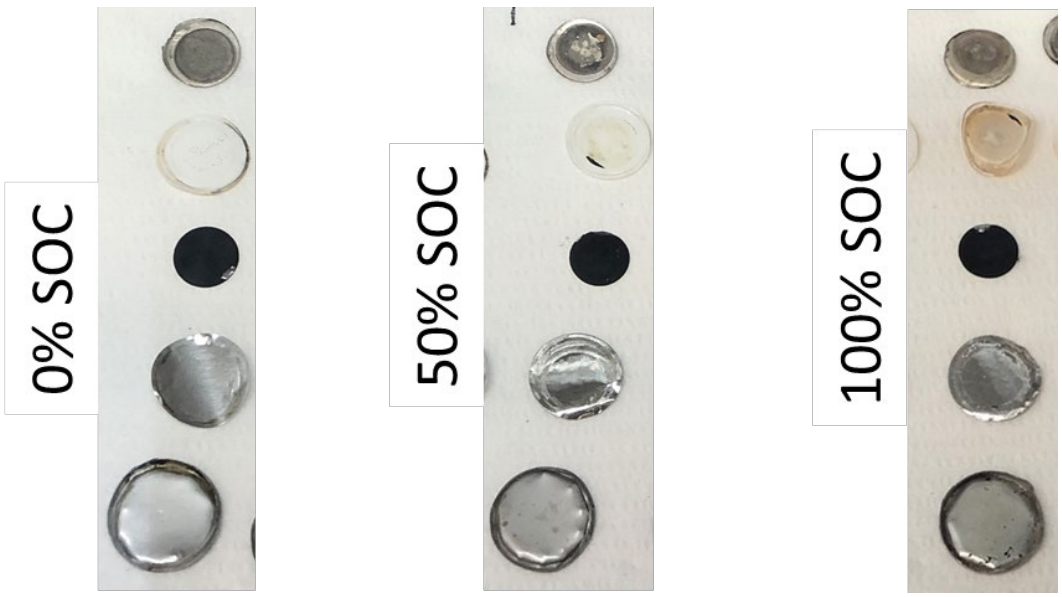
Supplemental Information Fig. 2. (a, b) Top views and (c, d) cross-sectional views of SEM images of Li metal electrodes collected from Li||NMC811 cells after two formation cycles using (a, c) advanced fluorinated orthoformate-based LHCE and (b, d) conventional carbonate electrolyte.



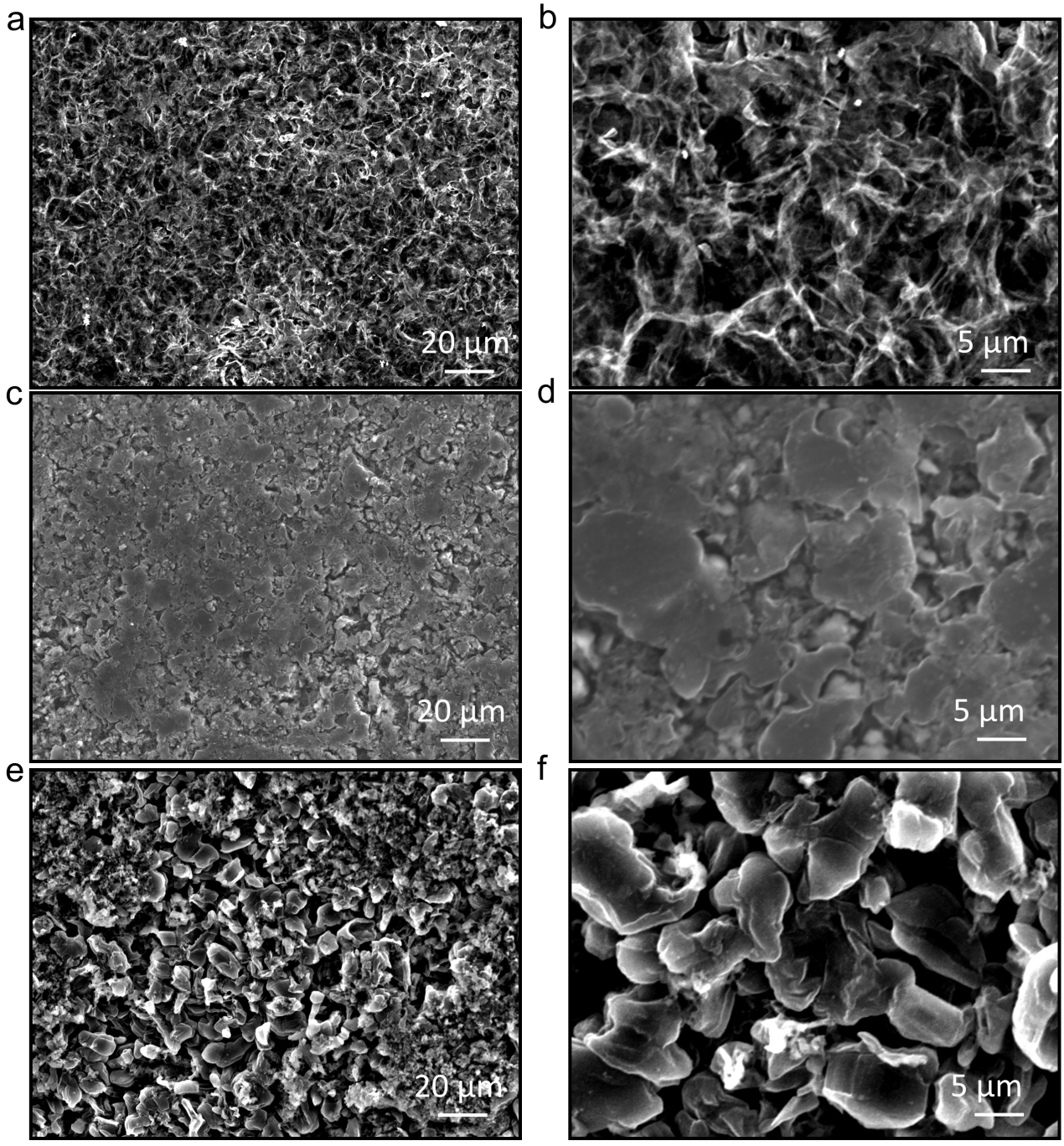
Supplemental Information Fig 3. Electrochemical performance of cells at 100% SOC with an additional CV step at 4.4 V. (a) Voltage profiles of a cell during the formation process and rest conditions and (b) after storage for different time periods within 18-month storage at 30 °C.



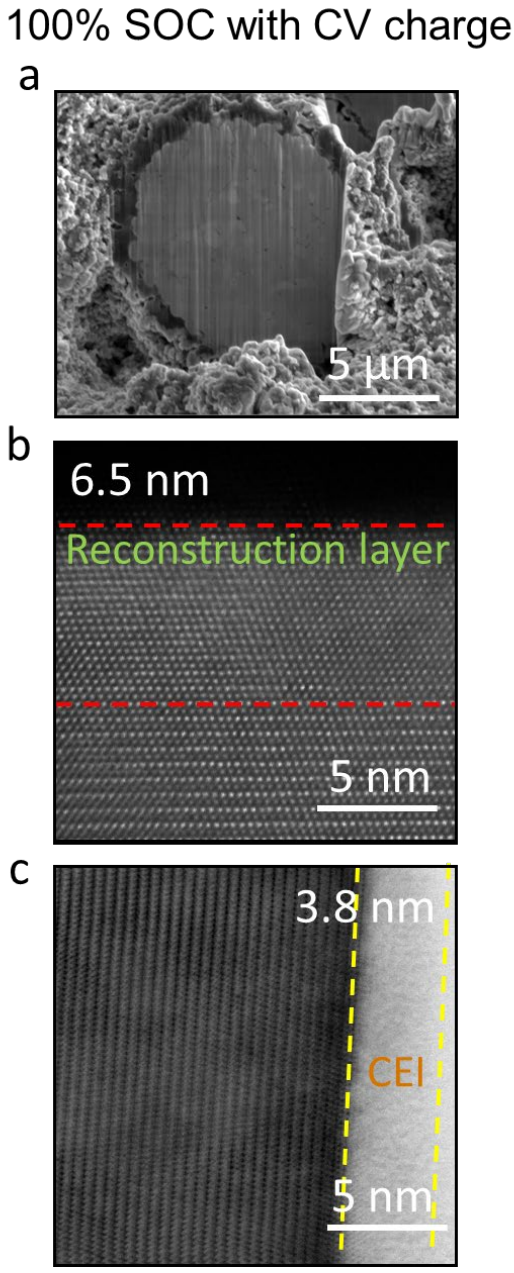
Supplemental Information Fig. 4. Voltage profiles of two parallel cells, where the solid lines are for the cells shown in the manuscript and dashed lines represent the results for the second cell.



Supplemental Information Fig. 5. Photos of the cell components after 18-month storage at 30 °C.



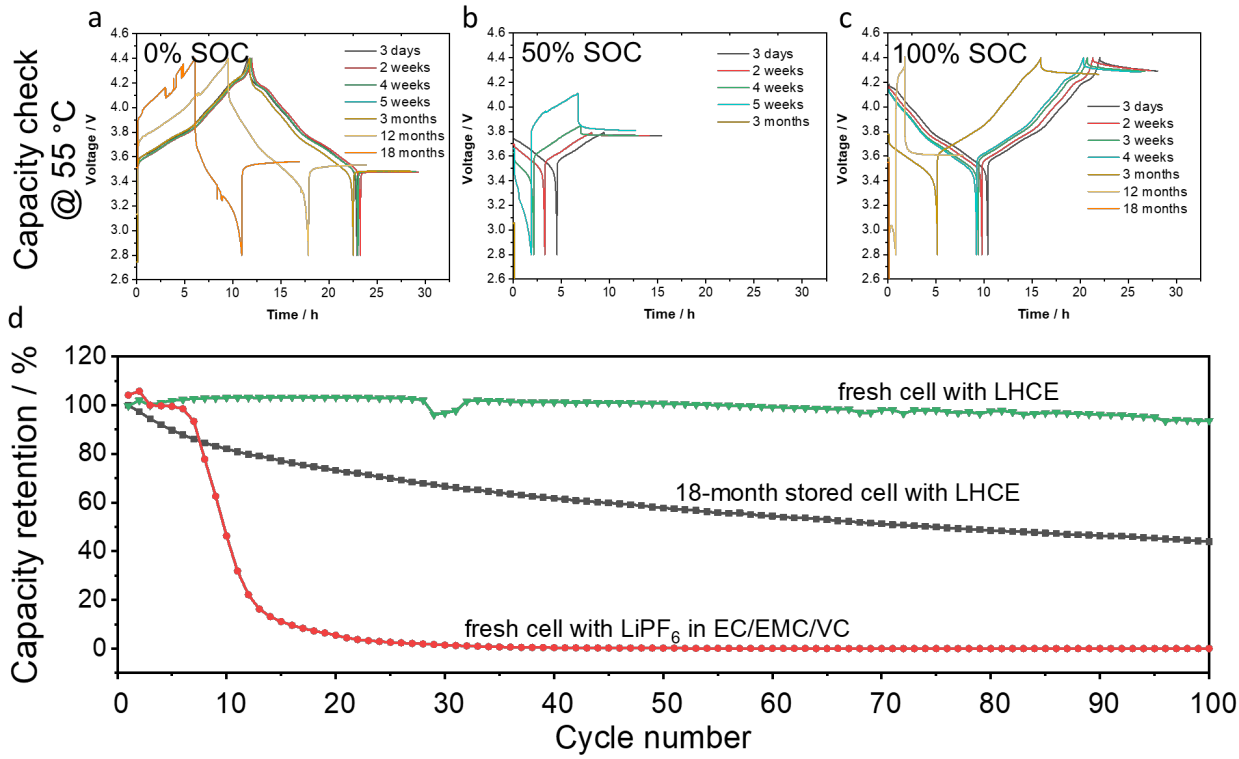
Supplemental Information Fig. 6. Top-view SEM images of Li metal electrodes at two different resolutions collected from cells stored at (a, b) 0% SOC, (c, d) 50% SOC, and (e, f) 100% SOC for 18 months.



Supplemental Information Fig. 7. Structural and CEI properties of the NMC811 particles in Li||NMC811 cells after 18-month storage at 30 °C and at 100% SOC with additional CV charge step, (a) FIB-SEM, (b) HAADF-STEM and (c) ABF-STEM images.

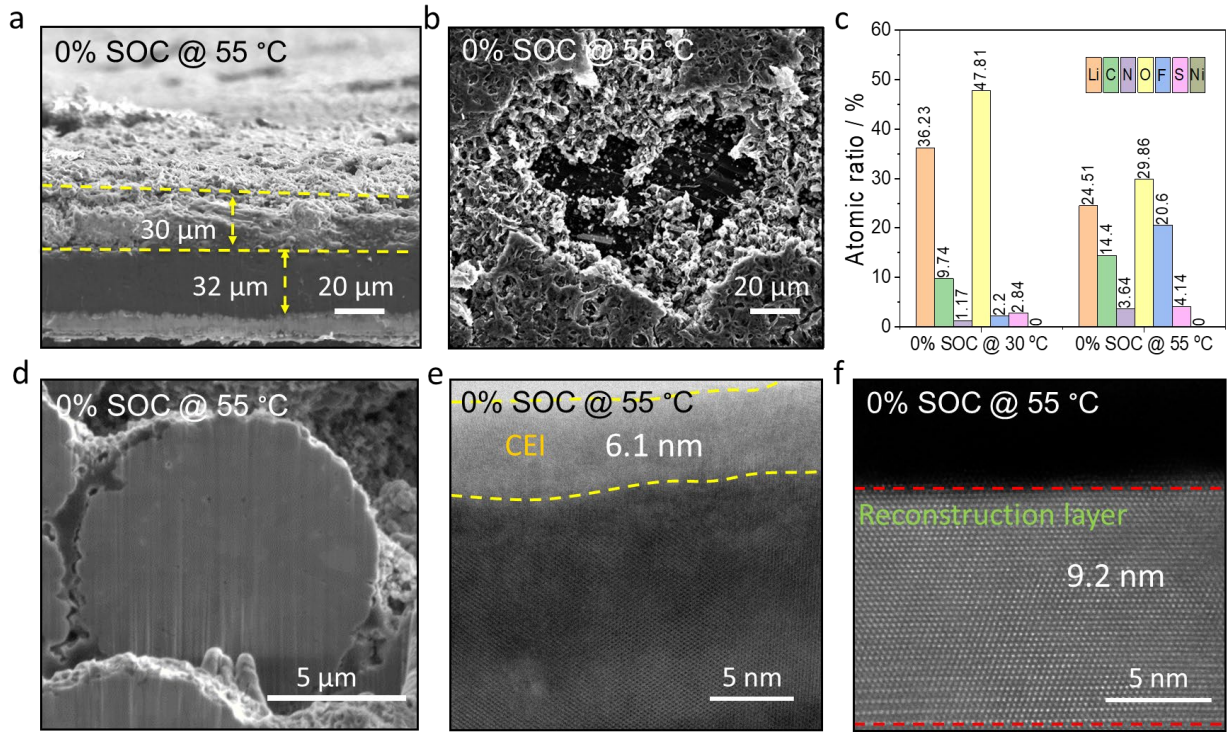
Storage performance at elevated temperature

The degradation of Li||NMC811 cells was further investigated by storing the cells at 55 °C for up to 18 months. Supplemental Information Fig. 8a shows the electrochemical performance of a cell stored at 0% SOC. 94.7% capacity was recovered after the first three months with only negligible cell polarization. After 18-month storage, the recovered capacity was 42.9%, with an overpotential of ~0.3 V at the beginning of charging. For the cell stored at 50% SOC, capacity loss from self-discharge increased quickly in the first month, followed by a large overpotential of about 0.4 V after 5-week storage and cell failure after 3 months (the test was terminated by voltage protection of −5 V caused by a large cell resistance) (Supplemental Information Fig. 8b). As summarized in Supplemental Information Table 2, the self-discharge rate in this condition is 1.9–7.19% / day, which is more than 10 times those of similar cells stored at 30 °C. When the cell was stored fully charged to 100% SOC, the storage performance (Supplemental Information Fig. 8c) became much better than that of those stored at 50% SOC: the self-discharge rate at 100% SOC was 1.18–2.96% / day, which is about half the rate of those stored at 50% SOC. In addition, the polarization of the cell stored at 100% SOC is significantly smaller than those of the cells stored at 50% SOC. In short, the calendar life of Li||NMC811 cells stored at 55 °C follows the same order of 0% SOC > 100% SOC > 50% SOC that was observed at 30 °C; it also correlates with the rankings of the porosities and surface areas of the Li deposited in cells stored at the 50% SOC > 100% SOC > 0% SOC.



Supplemental Information Fig. 8. Electrochemical performance of cells at different states of charge (SOCs) at 55 °C and cycling stability of the cells after 18-month storage in optimal conditions. (a-c) Voltage profiles of the cells during the storage at different elapsed times within 18-month storage at 55 °C and at different SOCs: (a) 0% SOC, (b) 50% SOC, and (c) 100% SOC. (d) Capacity retention of the cell cycled after 18-month storage at 0% SOC at 30 °C compared to fresh cells using LHCE and conventional carbonate electrolyte.

Supplemental Information Fig. 9 shows Li structure and SEI properties for the accelerated Li degradation at 55 °C. In particular, some apparent pits (~10 μm) were found on Li metal stored at 55 °C (Supplemental Information Fig. 9b), which is possibly related to the accelerated Li corrosion at the defects in the SEI. As a result, the continuous Li corrosion at these defects is exacerbated over the long-term storage and finally produced these open pits at 55 °C while defects on the SEI are negligible at 30 °C. Therefore, elevated temperature (such as 55 °C) is detrimental to the calendar life of LMBs. Supplemental Information Fig. 9 also shows the NMC811 structure after 18-month storage at 0% SOC at 55 °C. Unlike the cathode stored at 30 °C at the same SOC, the secondary particle remained crack free (Supplemental Information Fig. 9d) while the CEI thickness (6.1 nm, Supplemental Information Fig. 9e) and reconstruction layer thickness (9.2 nm, Supplemental Information Fig. 9f) observed at 55 °C are four times and six times as thick as those observed at 30 °C (Figs. 5g and 5d), respectively.



Supplemental Information Fig. 9. Electrode structures after 18-month storage at 55 °C at 0% SOC. (a-c) Li structure and (f) SEI compositions of the Li metal anode. (d-f) Structural and interphase properties of the NMC811 particles (d) FIB-SEM, (e) HAADF-STEM and (f) ABF-STEM images.

Supplemental Information Table 1. Summary of cell performance at different elapsed times within 18-month storage at 30 °C or 55 °C in terms of charge capacity and discharge capacity for all cells, capacity recovery for cells stored at 0% SOC, and self-discharge capacity loss and self-discharge rate for cells stored at 50% SOC and 100% SOC.

Time frame	Time gap / day	Capacity recovery at 0% SOC			Self-discharge at 50% SOC				Self-discharge at 100% SOC			
		Charge capacity / mAh g^{-1}	Discharge capacity / mAh g^{-1}	Capacity recovery / %	Discharge capacity / mAh g^{-1}	Charge capacity / mAh g^{-1}	Self-discharge capacity loss / mAh g^{-1}	Self-discharge rate / % day^{-1}	Disharge capacity / mAh g^{-1}	Charge capacity / mAh g^{-1}	Self-discharge capacity loss / mAh g^{-1}	Self-discharge rate / % day^{-1}
30 °C storage												
Initial capacity			203.0			97				206.9		
1 day	1	204.8	206.8	101.9	96.2	97	0.8	0.82	208	210.2	0	-
1 week	7	208.0	208.7	102.8	94.2	97	2.8	0.41	207.3	212.8	2.9	1.38
2 weeks	5	212.0	211.7	104.3	94.9	97	2.1	0.43	208.9	213.9	3.9	0.02
4 weeks	13	213.9	212.1	104.5	94.6	97	2.4	0.19	205.7	214.4	8.2	0.04
5 weeks	9	213.8	212.8	104.8	93.7	97	3.3	0.38	207.1	214.9	7.3	0.03
3 months	47	216.9	211.8	104.3	83.7	97	13.3	0.29	187.7	215.0	27.2	0.13
6 months	96	225.4	210.2	103.5	56.4	-	40.6	0.44	150.1	213.7	64.9	0.30
12 months	177	223.4	202.5	99.8	-	97	-	-	144.1	210.5	69.6	0.18
18 months	185	220.4	181.9	89.6	0	97	97	> 0.54	105.0		105.5	0.27
55 °C storage												
Initial capacity			227.7			97				227.7		
5 day	5	220.8	227.4	99.9	87.8	97	9.2	1.90	198.9	225.6	28.9	2.53
2 weeks	9	229.9	225.4	99.0	62.3	97	34.7	3.97	190.3	220.4	35.3	1.74
4 weeks	11	227.8	223.5	98.2	39.6	97	51.4	4.82	180.0	219.2	40.4	1.66
5 weeks	9	224.8	222.5	97.7	34.2	97	62.8	7.19	176.2	215.1	43.1	2.18
3 months	55	224.8	215.7	94.7	0	0	97	> 1.82	97.0	208.7	118.1	1.00
12 months	260	181.6	167.6	73.6	-	-	-	-	13.2	18.2	195.6	0.36
18 months	180	114.7	97.6	42.9	-	-	-	-	0	-	18.2	> 0.56

Note: Self-discharge capacity loss = charge capacity (measured before the specified storage period) minus discharge capacity (measured after the specified storage period); Self-discharge rate = self-discharge capacity loss ÷ specified storage period ÷ charge capacity (measured before the specified storage period).

Supplemental Information Table 2. Summary of cell performance at 100% SOC with or without CV charge step at 4.4 V within 18-month storage at 30 °C in terms of discharge capacity, charge capacity, self-discharge capacity loss, and self-discharge rate.

Time frame	Time gap / day	Self-discharge at 100% SOC w/o CV				Self-discharge at 100% SOC w/ CV			
		Discharge capacity / mAh g^{-1}	Charge capacity / mAh g^{-1}	Self-discharge capacity loss / mAh g^{-1}	Self-discharge rate / % day^{-1}	Disharge capacity / mAh g^{-1}	Charge capacity / mAh g^{-1}	Self-discharge capacity loss / mAh g^{-1}	Self-discharge rate / % day^{-1}
Initial capacity			206.9				218.9		
1 day	1	208	210.2	0	-	224.4	227.5	0	-
1 week	7	207.3	212.8	2.9	1.38	221.8	228.3	5.7	0.36
2 weeks	5	208.9	213.9	3.9	0.02	221	229	7.3	0.64
4 weeks	13	205.7	214.4	8.2	0.04	219.4	229.7	9.6	0.32
5 weeks	9	207.1	214.9	7.3	0.03	215.8	228.2	13.9	0.67
3 months	47	187.7	215.0	27.2	0.13	198.8	227.6	29.4	0.27
6 months	96	150.1	213.7	64.9	0.30	164.5	226.7	63.1	0.29
12 months	177	144.1	210.5	69.6	0.18	148.4	216.8	78.3	0.20
18 months	185	105.0		105.5	0.27	114	-	102.8	0.26