A study of capacity fade of the $LiCoO_2$/graphite battery during the temperature storage process at 45°C under the different SOCs

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Equations (1)-(11)

2.1. Battery storage system

The M1254 battery from Guangdong Microelectronics New Energy Co., Ltd. was selected for the study. The battery uses LCO as the cathode (0.0326 $g \cdot cm^{-2}$) and graphite as the anode (0.0148 $g \cdot cm^{-2}$), $LiPF_6$-based electrolyte with a standard capacity of 63 mAh and the polyethylene separator coated with alumina.

Initial capacity (expressed as C_0) calibration method: Under the condition of 25±1.5°C, the battery is charged to 4.2 V at 0.75 C, then kept at 4.2 V constant voltage until the cut-off current is 2mA. Then the battery is discharged to 3.0 V at 0.2 C for 3 cycles, and the average discharge capacity of the three cycles is the initial capacity of the battery.

Battery 45°C storage method: After the battery is charged to different SOCs, its impedance, and open circuit voltage are tested. Then the battery is stored in a thermostat at 45±1.5°C for the corresponding time (1 month, 2 months, 3 months, and 6 months).

Measurement of the ***Retention capacity*** (expressed as C_1) of the battery: After the battery storage time reaches, the battery is removed and the impedance and open circuit voltage are tested. The battery is stored in a thermostat at 25±1.5°C for 0.5 h and then discharged to 3.0 V at 0.2 C to test the retention capacity after storage.

Measurement of the ***Recovery capacity*** (expressed as C_2) of the battery: After testing the retention capacity, the battery is charged to 4.2 V at 0.75 C, then kept 4.2 V constant voltage until the cut-off current is 2 mA, and then discharged to 3.0 V at 0.2 C. The battery is then discharged to 3.0 V at 0.2 C for three cycles, and the average of three cycles of discharge capacity is taken as the recovery capacity of the battery after storage.

Storage fading capacity (expressed as C_f) of the battery = Initial capacity - Retained capacity

Restored capacity (expressed as C_{re}) of the battery = Recovery capacity - Retained capacity

Lost capacity (expressed as C_{lost}) of the battery = Initial capacity - Recovery capacity

We define the calculation formula of the rate of retained capacity and the rate of recovery capacity for different SOCs as follows.

Calculation formula of the rate of retained capacity：

$$\text{The rate of retained capacity} = \frac{\text{Retained capacity} + \text{Initial capacity} - \text{Capacity of SOC}}{\text{Initial capacity}}$$

Calculation formula of the rate of recovery capacity：

$$\text{The rate of recovery capacity} = \frac{\text{Recovered capacity}}{\text{Initial capacity}}$$

2.2 Disassemble the battery and test

The battery is stored in a 45°C thermostat (POELAB, BLH-300), and charged and discharged in a 25°C battery test cabinet (Neware CT-4008T-5V1A). The voltage and internal resistance of the battery are tested by an internal resistance tester (HIOKI, Battery Hi Tester 3561), and the electrochemical impedance spectrum (EIS) curves of the battery in the 10 MHz-100 kHz range before and after storage are obtained by an electrochemical workstation (Donghua DH7006). For battery disassembly, the cells are disassembled in a glove box ($O_2 \leq 0.01$ ppm, water ≤ 0.01 ppm). The disassembled electrodes and separators are soaked in dimethyl carbonate (DMC, 98% purity) (10 mL pipette dose) for 1 h, and then cleaned with 10 mL DMC. Samples are analyzed by scanning electron microscopy (SEM MIRA4 LMH), energy dispersive spectrometry (EDS, Ultim Max 40), X-ray diffraction (XRD, PANalytical Empyren), X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha), transmission electron microscopy (TEM, JEOL 2100F, JEOL).

2.3 Dissolution and detection of anode

The disassembled and cleaned anode is dried in an oven at 60 - 80°C. The weight of the whole anode is weighed and then put into a beaker, 5 mL of concentrated nitric acid (68%) is added to the beaker, and 15 mL of deionized ultrapure water is added at the same time. The beaker is heated to 100°C and stirred for 15 minutes. When the anode is completely dissolved, the volume is fixed to 500 mL, and the content of lithium and cobalt in the fixed solution is determined by the AAS method.

Equations (1)-(4):

Under 30% SOC: y=-0.01289+0.03731x R^2(COD)=0.99257 **(1)**

Under 50% SOC: y=0.00244+0.01244x R^2(COD)=0.98718 **(2)**

Under 75% SOC: y=0.04653+0.01226x R^2(COD)=0.98796 **(3)**

Under 100% SOC: y=0.02603+0.0195x R^2(COD)=0.99273 **(4)**

Where x represents storage time, it is calculated on a monthly basis. COD is the coefficient of determination in Origin, also known as the goodness of fit. When the value of R^2 is closer to 1, the higher the relevant equation reference value; Instead, the value of R^2 is closer to 0, the lower the reference value is.

Equations (5)-(8):

Under 30% SOC: y=100.31179-2.40643x R^2(COD)=0.97008 **(5)**

Under 50% SOC: y= 98.075-2.39x R^2(COD)= 0.98546 **(6)**

Under 75% SOC: y= 96.65893-2.31214x R^2(COD)= 0.99285 **(7)**

Under 100% SOC: y= 98.73179-1.90643x R^2(COD)= 0.97718 **(8)**

Where x represents storage time, it is calculated on a monthly basis.

Equations (9)-(11):

The content of Li in the anode: y=0.96821+0.16143x R^2 (COD) =0.99118 **(9)**

The content of Co in the anode: y=0.02639+0.01429x R^2 (COD) =0.98565 **(10)**

Li mass in anode / Li mass lost in capacity: y=0.9914+0.05036x R^2（COD）=0.99696 **(11)**

Where x represents storage time, it is calculated on a monthly basis.

Table S1 Capacity data under 0% SOC stored 1-3 months at 45℃

Initial capacity /mAh	Charge capacity /mAh	Voltage before storage/V	Storage time	Retained capacity/mAh	Voltage after storage/V	Recovery capacity	Rate of Retained capacity	Rate of recovery capacity
66.1	0	3.3348	1 month	0	2.9532	64.7	0%	97.88%
66.1	0	3.3355	2 months	0	0.6522	13.15	0%	19.89%
65.9	0	3.3345	3 months	0	-0.013	0.005	0%	0.008%

Table S2 Capacity data under different SOCs stored 1-6 months at 45°C

Initial capacity /mAh	Charge capacity /mAh	Storage time	SOC	Retained capacity /mAh	Recovery capacity	Rate of retained capacity	Deviation of retained capacity ratio	Rate of recovery capacity	Deviation of recovery capacity ratio
65.29	19.59	1 month	30%	16.74	64.46	95.64%	1.47%	98.73%	1.15%
62.1	31.1		50%	26.7	59.8	92.91%	0.49%	96.30%	0.48%
62.95	47.25		75%	40.65	59.7	89.52%	0.15%	94.84%	0.12%
61.93	61.93		100%	55.58	60.32	89.75%	0.78%	97.40%	0.25%
65	19.5	2 months	30%	13.36	61.88	90.56%	1.79%	95.40%	1.26%
64.05	32.05		50%	24	59.65	87.43%	0.58%	93.13%	0.17%
63.75	47.85		75%	38.1	58.45	84.71%	0.26%	91.69%	0.22%
62.5	62.5		100%	53.3	59.25	85.28%	0.51%	94.80%	0.5%
65	19.5	3 months	30%	9.6	59.7	84.77%	0.56%	91.85%	0.76%
64.88	32.45		50%	20.43	58.45	81.47%	0.67%	90.10%	0.24%
64.65	48.5		75%	35.4	57.78	79.74%	0.16%	89.36%	0.29%
61.4	61.4		100%	49.35	56.6	80.37%	1.05%	92.18%	0.71%
65.4	19.6	6 month	30%	3.4	56.5	75.23%	1.16%	86.39%	0.32%
66.0	33.0		50%	13.93	55.5	71.11%	0.74%	84.09%	0.45%

65.87	49.4	s	75%	27.97	54.67	67.47%	1.1%	83.00%	0.93%
62.18	62.18		100 %	45.33	54.50	72.90%	1.45%	87.65%	1.16%

Table S3 Data of voltage and Internal resistance under different SOCs stored for 1-6 months at 45℃

Voltage before storage/V	Internal resistance /mΩ	Storage time	SOC	Voltage after storage/V	Internal impedance /mΩ	Rate of change of internal impedance
3.7844	365.05	1 month	30%	3.7527	377.7	3.47%
3.834	348.95		50%	3.818	367.6	5.34%
3.9848	368.6		75%	3.9277	380.7	3.28%
4.181	374.68		100%	4.1385	456.3	21.78%
3.7862	355.2	2 months	30%	3.7273	388.5	9.37%
3.8372	375.25		50%	3.8138	431.8	15.07%
3.9855	382.55		75%	3.9156	413.35	8.05%
4.1805	369		100%	4.1155	478.99	29.81%
3.7852	370.05	3 months	30%	3.6945	415.1	12.17%
3.8361	362.43		50%	3.793	430.03	18.65%
3.9861	364.9		75%	3.8984	439.15	20.35%
4.187	395.2		100%	4.0974	535.47	35.49%
3.7811	321.52	6 months	30%	3.5662	419.5	30.47%
3.8263	320.33		50%	3.7498	466.8	45.72%
3.9793	326.9		75%	3.8607	522.23	59.75%
4.1883	332.33		100%	4.0702	532.5	60.23%

Table S4 EIS fit data before storage and after 1-6 months of storage under 100% SOC at 45°C

Storage time	R_s (Ω·cm²)	Y_f ($S \cdot s^n \cdot cm^{-2}$)	n	R_f (Ω·cm²)	Y_{dl} ($S \cdot s^n \cdot cm^{-2}$)	n	R_{ct} (Ω·cm²)	W $S \cdot s^{0.5}$	ave err (%)	chi squared
Before storage	0.27	1.002×10^{-2}	0.95	0.21	6.49×10^{-3}	0.68	0.299	3.64	1.93	5.2×10^{-4}
1 month	0.32	1.148×10^{-2}	0.92	0.407	1.07×10^{-2}	0.60	1.02	2.95	2.02	4.2×10^{-4}
2 months	0.33	1.349×10^{-2}	0.81	0.415	2.10×10^{-2}	0.61	1.20	2.11	2.15	5.7×10^{-4}
3 months	0.38	1.873×10^{-2}	0.97	0.425	2.29×10^{-2}	0.52	1.48	3.04	1.13	1.8×10^{-4}
6 months	0.47	2.029×10^{-2}	0.98	0.462	2.52×10^{-2}	0.59	1.79	1.932	0.96	3.5×10^{-4}

Table S5 Data of Rs, R_f and R_{ct} under different SOCs stored for 1-6 months at 45°C

SOC	Storage time	R_s (Ω)	R_f (Ω)	R_{ct} (Ω)
0%	Before the storage	0.274	0.412	0.864
30%	1 month	0.376	0.639	1.92
	2 months	0.355	0.664	2.15
	3 months	0.382	0.691	2.32
	6 months	0.389	0.739	2.46
50%	1 month	0.362	0.533	1.51
	2 months	0.347	0.549	1.82
	3 months	0.377	0.563	2.03
	6 months	0.306	0.578	2.27
75%	1 month	0.302	0.462	1.32
	2 months	0.328	0.484	1.55
	3 months	0.343	0.502	1.79
	6 months	0.369	0.531	2.01
100%	1 month	0.322	0.407	1.02
	2 months	0.334	0.415	1.20
	3 months	0.381	0.425	1.48
	6 months	0.473	0.462	1.79

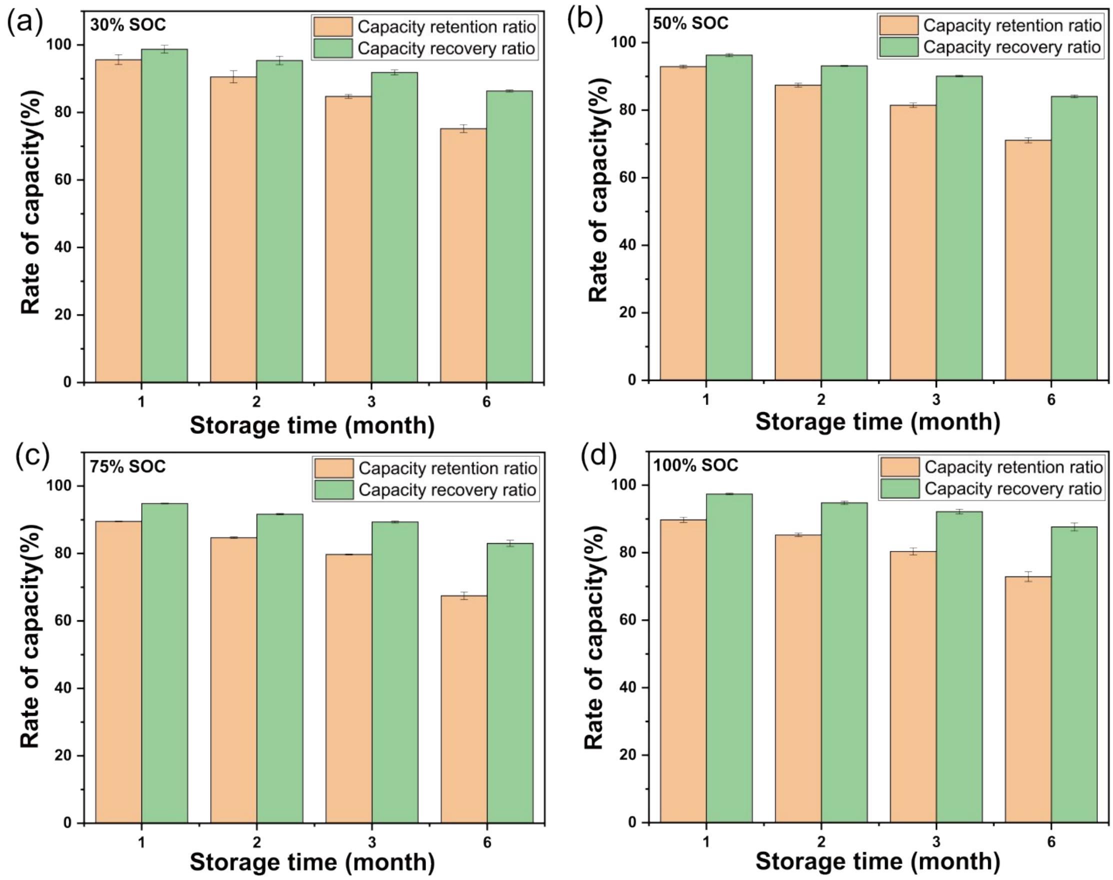

Figure S1 Capacity deviation diagram for capacity retention ratio and capacity recovery ratio under different SOCs stored for 1 to 6 months at 45°C.

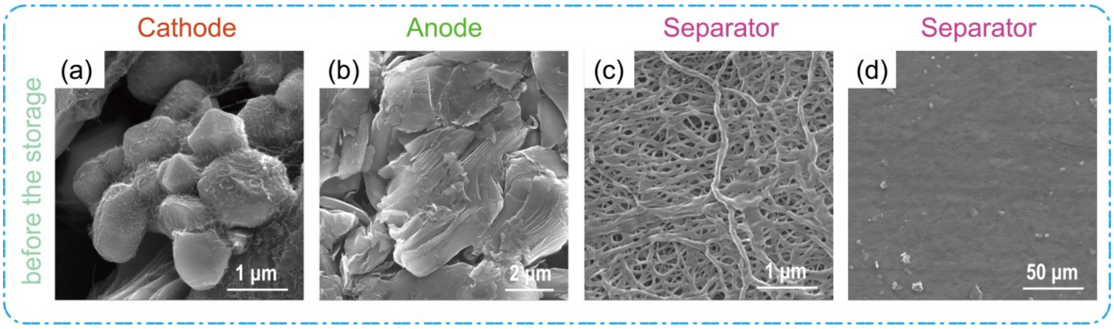

Figure S2 (a) Electron micrographs of the cathode at size 1 μm. **(b)** SEM of anode at size 2 μm. **(c)-(d)** separator at size 1 μm and 50 μm, separately.

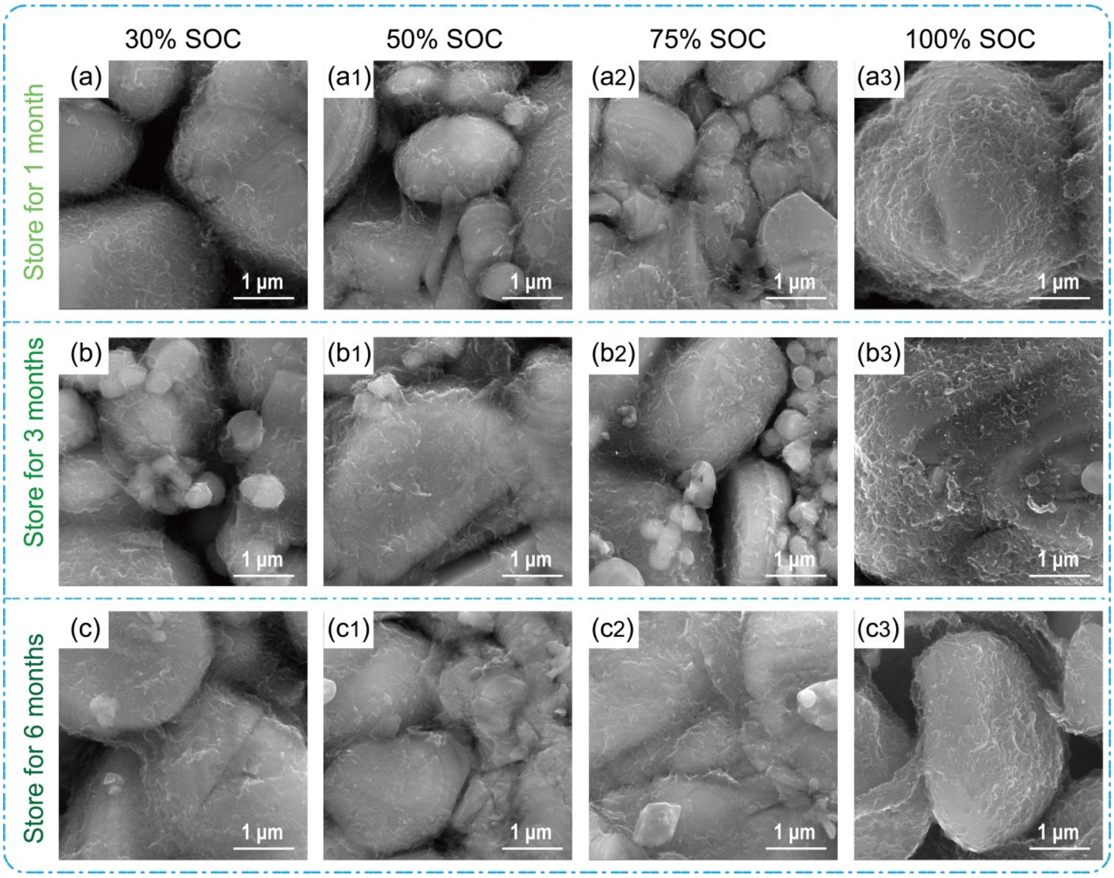

Figure S3 (a) SEM of the cathode (alumina coated separator side) of 30% SOC store for 1 month at size 1 μm. **(a1)-(a3)** SEM of the cathode under 50% SOC, 75% SOC and 100% SOC store for 1 months. **(b)-(b3)** SEM of the cathode of different SOCs stored for 3 months. **(c)-(c3)** Stored for 6 months.

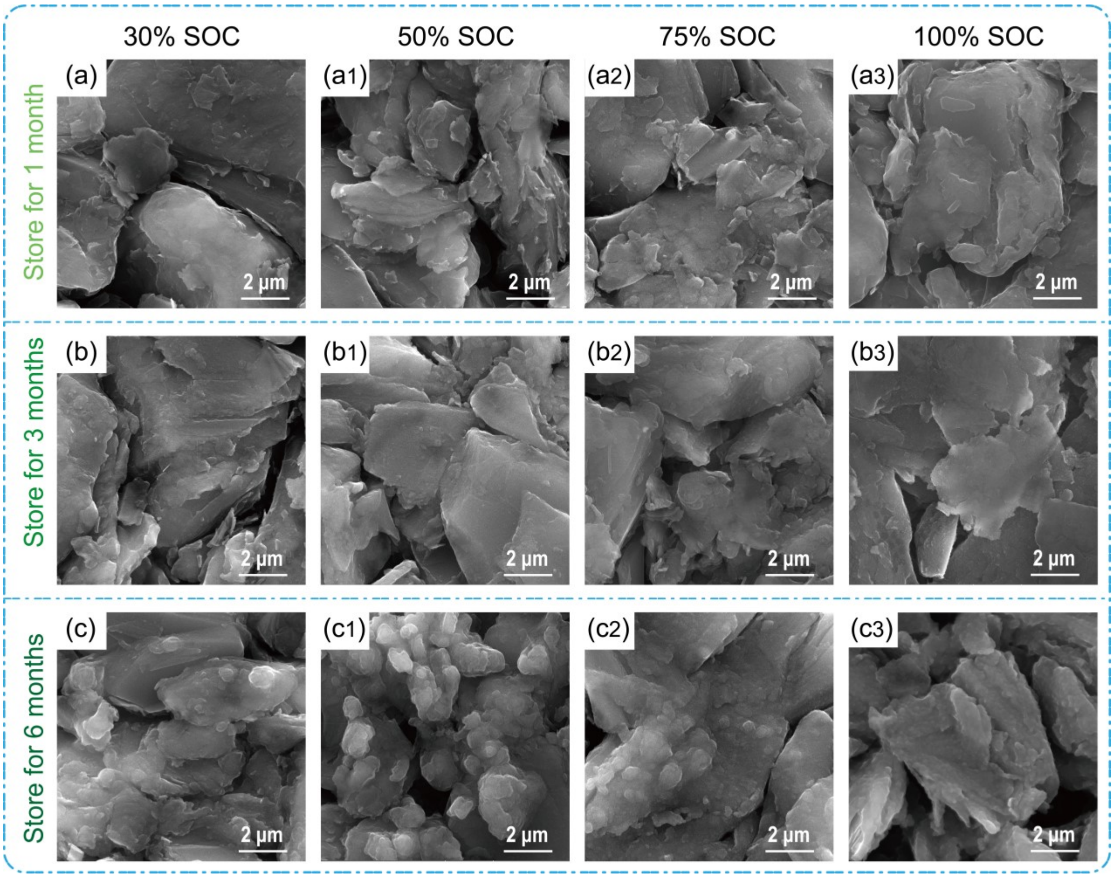

Figure S4 (a)-(a3) SEM of the anode of graphite under 30% SOC, 50% SOC, 75% SOC, and 100%SOC stored for 1 month at size 2 μm. **(b)-(b3)** Stored for 3 months. **(c)-(c3)** Stored for 6 months.

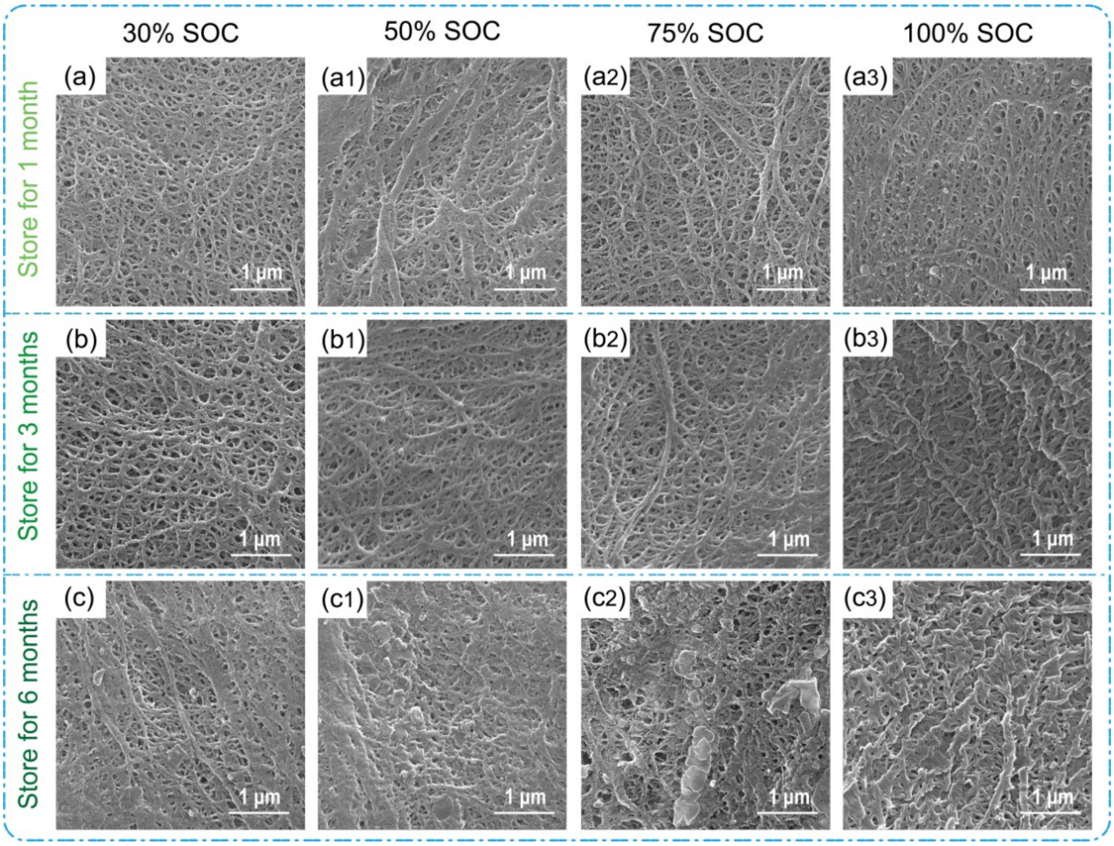

Figure S5 (a)-(a3) Electron micrographs (1 μm) of the battery separator (anode side) under 30% SOC, 50% SOC, 75% SOC, and 100% SOC stored for 1 month. **(b)-(b3)** SEM of the separator stored for 3 months. **(c)-(c3)** Stored for 6 months.

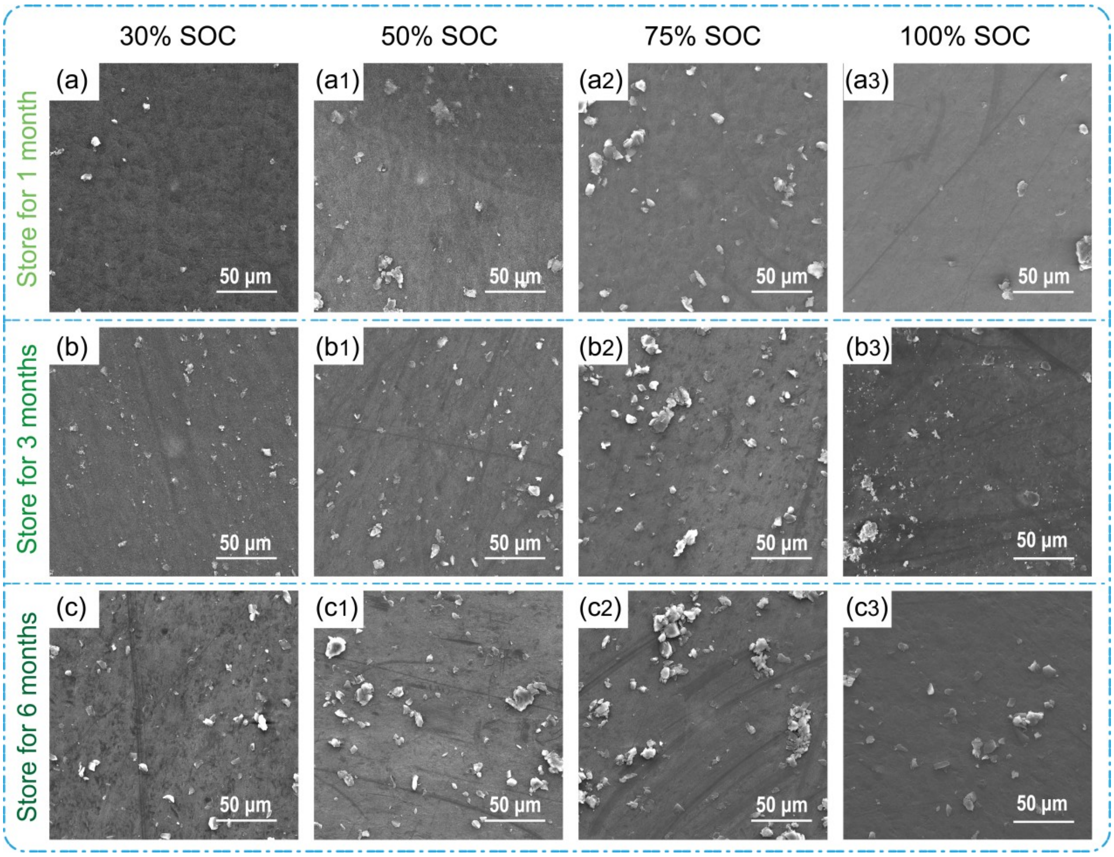

Figure S6 (a)-(a3) Electron micrographs (50 μm) of the battery separator (anode side) under 30% SOC, 50% SOC, 75% SOC, and 100% SOC stored for 1 month. **(b)-(b3)** Store for 3 months. **(c)-(c3)** Stored for 6 months.

Table S6 Quantitative analysis data of dead lithium in the anode stored at 45°C for 1-6 months

SOC	Net weight of anode/ mg	Storage time/ month(s)	Li mass in the anode/ mg	The proportion of dead Li in the anode
30%	26.26		0.267	1.017%
50%	32.76		0.401	1.224%
75%	30.53	1	0.388	1.271%
100%	255.7		2.915	1.140%
30%	33.04		0.479	1.450%
50%	33.97		0.512	1.507%
75%	31.55	3	0.481	1.525%
100%	270.8		4.035	1.490%
30%	36.64		0.748	2.041%
50%	33.46		0.704	2.104%
75%	34.76	6	0.760	2.186%
100%	35.76		0.692	1.935%

Table S7 Quantitative analysis of lithium and cobalt content in graphite anode before and after storage

Storage time/m	Initial capacity/ mAh	Recovery capacity /mAh	Lost capacity/mAh	Net weight of anode/ mg	Co mass in the anode/mg	Li mass in the anode	Increments of dead Li in the anode	The proportion of dead Li in the anode	The proportion of Co in the anode
Before the storage				261.2	0.03	2.485		0.95%	0.011%
Store for 1 month	60.9	59.4	1.5	255.7	0.095	2.915	0.43	1.14%	0.037%
Store for 2 months	62.3	59.3	3	269.1	0.15	3.375	0.89	1.25%	0.056%
Store for 3 months	60.9	55.9	5	270.8	0.20	4.035	1.55	1.49%	0.074%
Store for 6 months	62.4	55.5	6.9	254.7	0.28	4.91	2.43	1.93%	0.110%

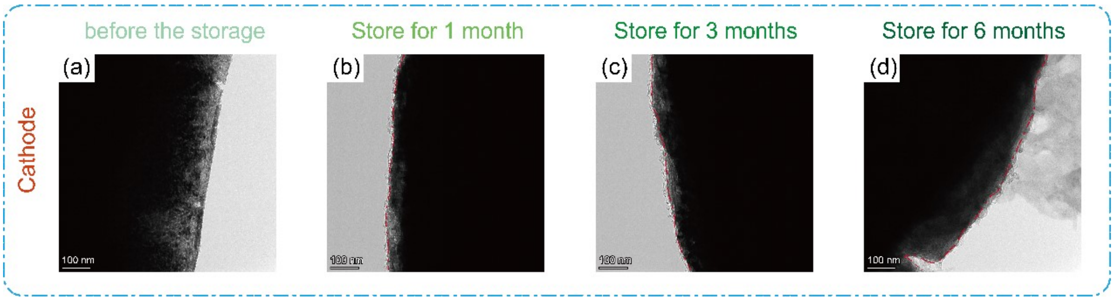

Figure S7 (a)-(d) TEM of the LCO cathode before storage, and stored for 1 month, 3 months, and 6 months under 100% SOC, respectively.