From Electrode Saturation to Structural Collapse: Unraveling the Rollover Failure in Lithium-Rich Manganese/Graphite Pouch Cell under Elevated Temperature

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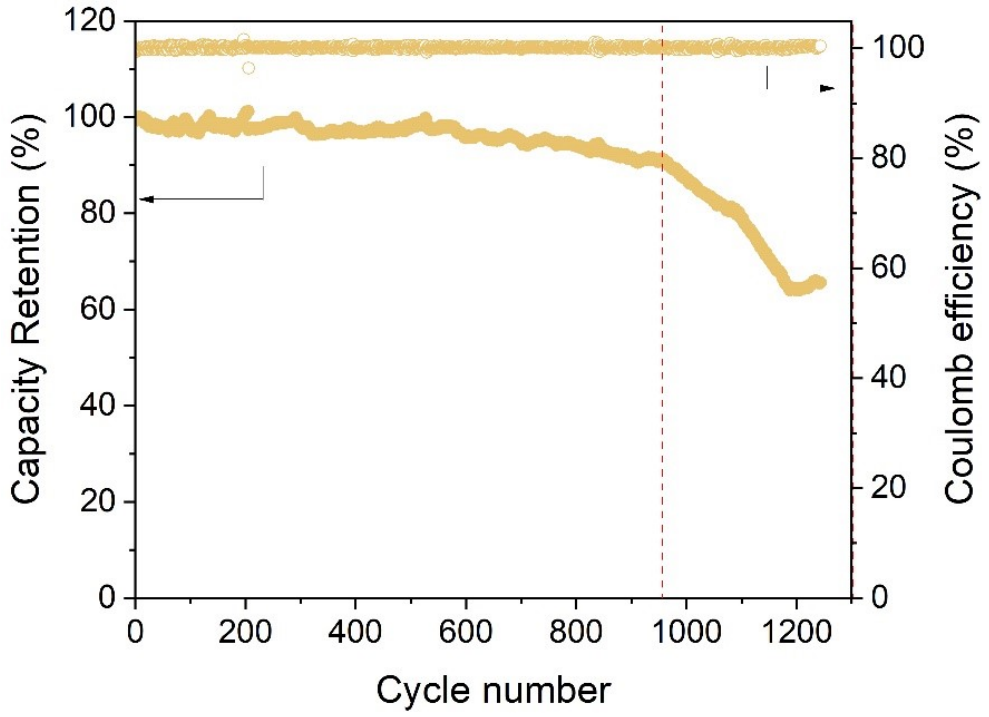

Figure S1 Electrochemical degradation of pouch-type LRMO-Gr cell at room temperature between 3 and 4.35V.

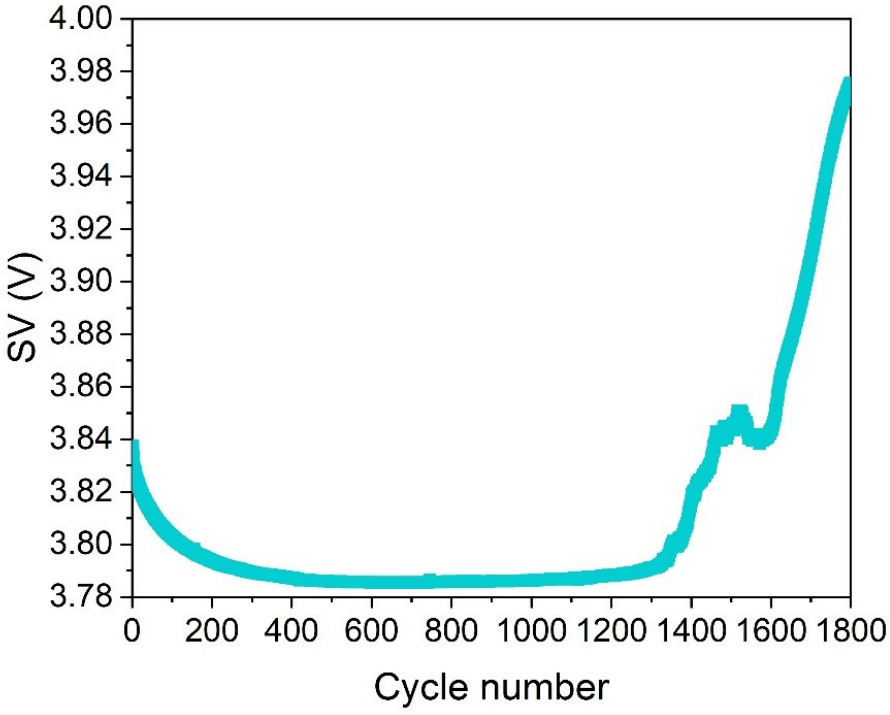

Figure S2 The change of shift voltage with cycle count (Shift voltage is the average of average charge- and discharge-voltages).

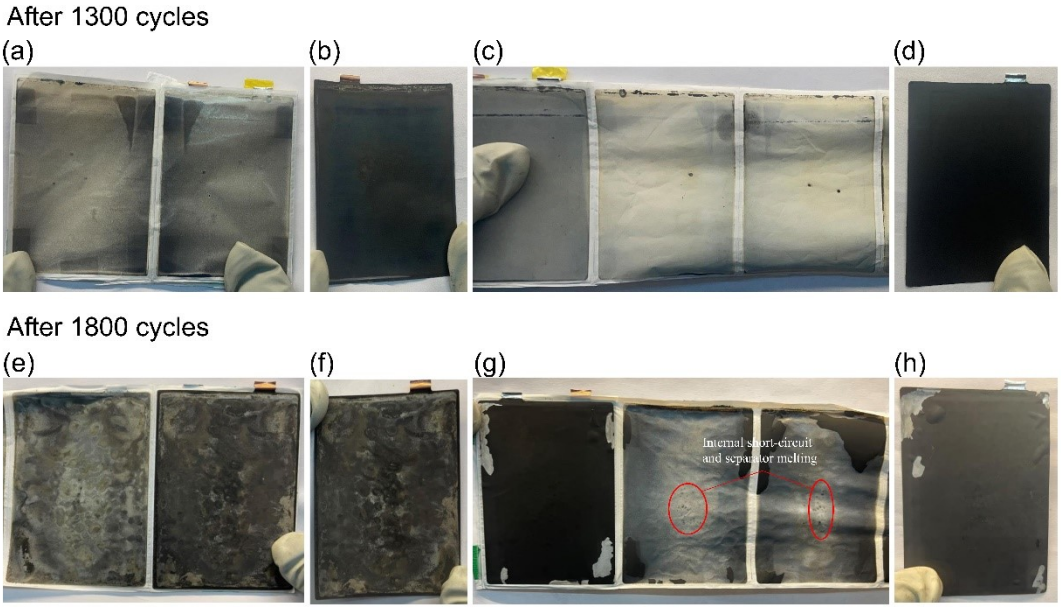

Figure S3 Optical photographs of disassembled (a-d) 1300-cycled and (e-h) 1800-cycled pouch cells at full discharge state: (a, e) separators facing the anode; (b, f) graphite anodes; (c, g) separators facing the cathode; (d, h) LRMO cathodes.

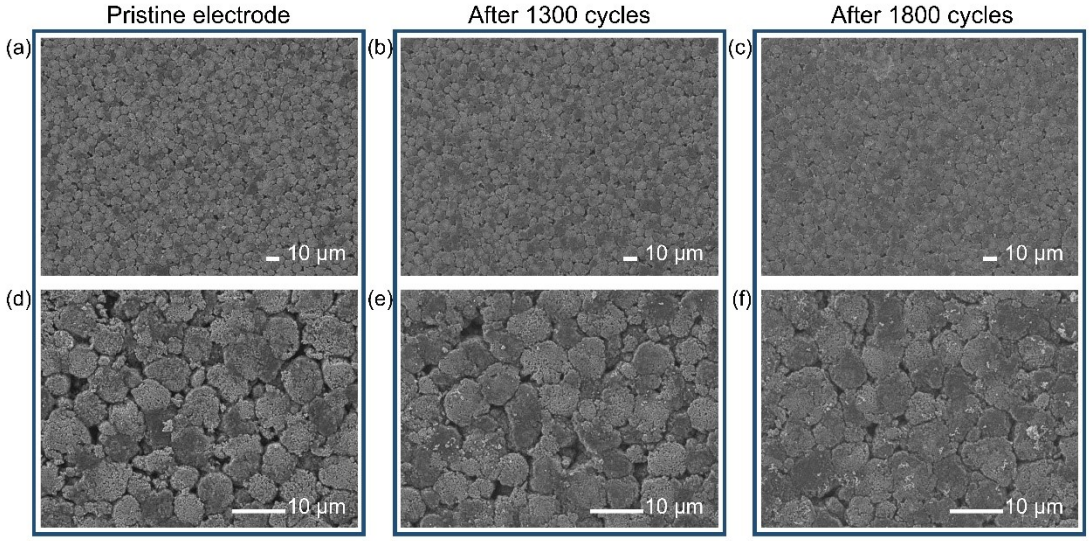

Figure S4 The SEM images of cathodes retrieved from the fully discharged pouch cells after different cycles.

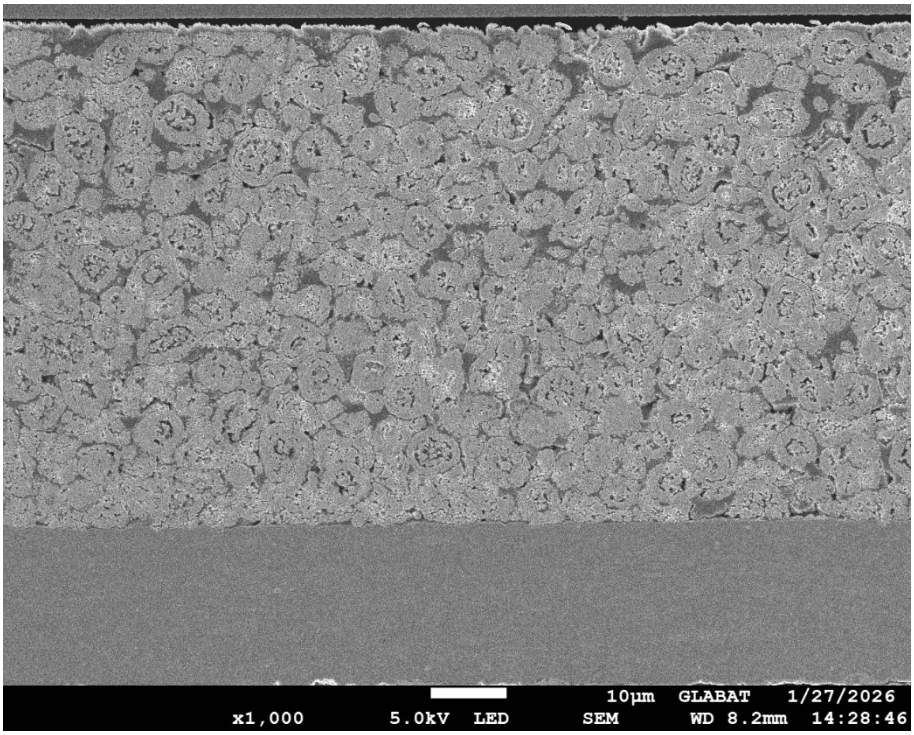

Figure S5 The cross-sectional SEM image of cathode retrieved from the fully discharged pouch cells after 1800 cycles.

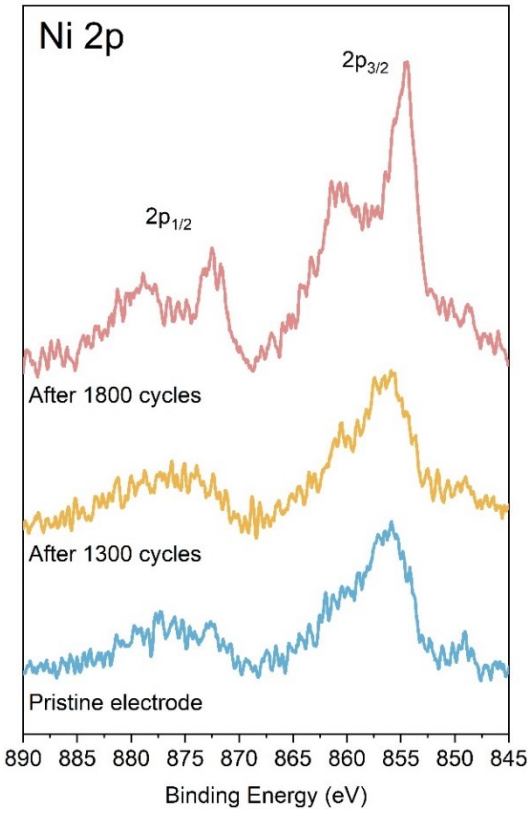

Figure S6 High-resolution Ni 2p XPS spectra of cathodes extracted from the fully discharged pouch cells after different cycles.

Table S1 The surface elemental composition of the cathodes with different cycles by XPS measurements (Atomic, %)

	Pristine electrode	After 1300 cycles	After 1800 cycles
B1s	0.67	2.61	4.57
C1s	67.36	54.20	51.38
F1s	13.33	7.63	7.70
Li1s	2.20	2.51	2.47
Mn2p	0.98	0.40	0.61
Mn3s	0.00	0.91	1.26
N1s	2.00	3.45	2.07
Ni2p	1.65	0.82	0.90
O1s	11.57	25.59	26.82
P2p	0.14	1.23	1.69
S2p	0.11	0.66	0.54

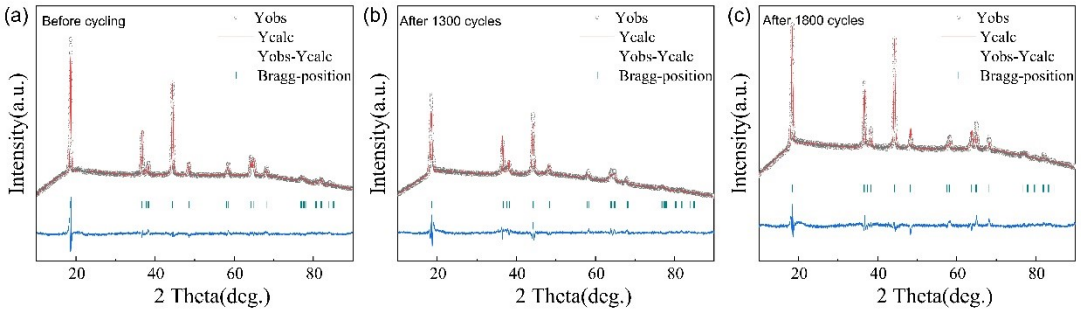

Figure S7 XRD patterns with Rietveld refinements of cathodes retrieved from the fully discharged pouch cells after different cycles. Black markers are experimental datapoints, the red line is refinement fit line and the blue line is the difference between experimental data and fit.

Table S2 Rietveld refinement results for cathodes retrieved from the fully discharged pouch cells after different cycles.

Sample	a/Å	c/Å	V/Å^3	Rp/%	Rwp/%
Before cycling	2.873671	14.288630	102.187	1.35	2.27
After 1300 cycles	2.876390	14.346576	102.796	1.55	2.40
After 1800 cycles	2.873369	14.430241	103.178	1.44	2.08

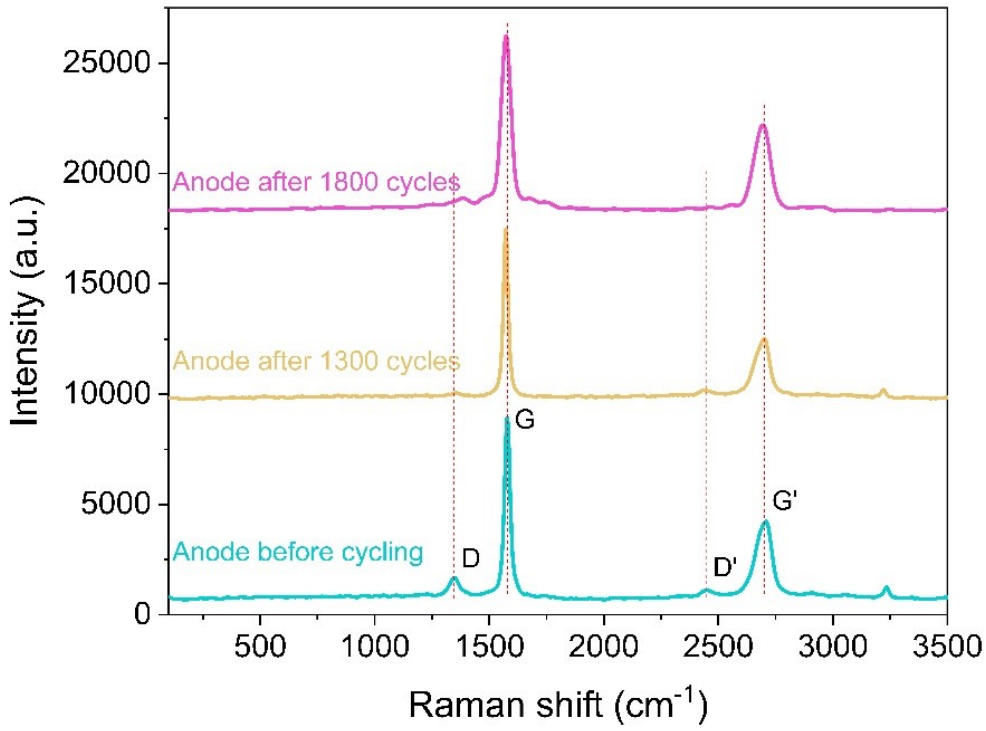

Figure S8 Raman spectra of graphite anodes after different cycles.

Raman spectroscopy was conducted to investigate the change of graphite structure during cycling, as shown in Fig. S7. The intensity of the G band for graphite after heavily cycling indicates a well-ordered structure with a defined crystal size. While the width of the G band broadens, pointing to an increase in the disorder of graphite. The increased disorder of graphite leads to the reduction of reversible capacity, but this structural change is usually not the main reason for the deterioration of battery performance.

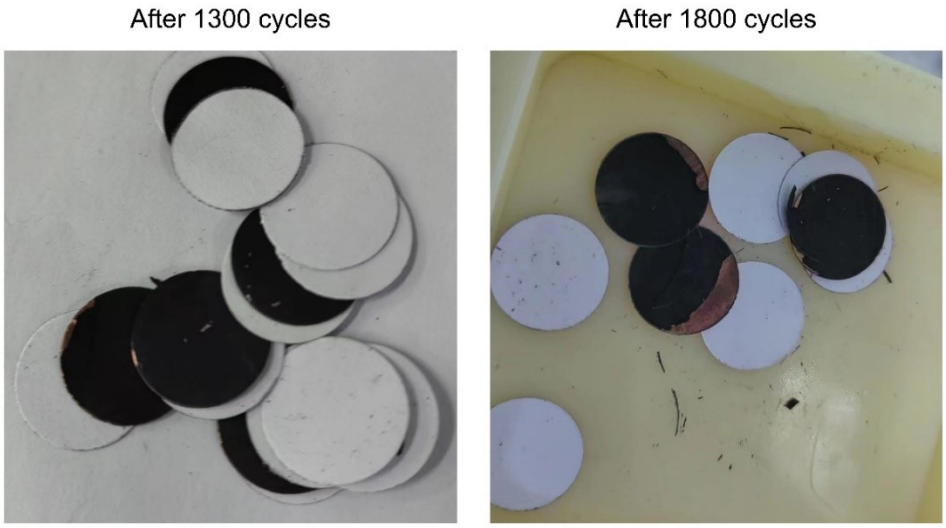

Figure S9 The small pieces of extracted anode after different cycles used to manufacture coin cell.

Table S3 The relative percentages (Atomic, %) of key functional groups obtained by peak fitting of C 1s, O 1s, F 1s, P2p and Li1s XPS spectra on the surface of anodes with different cycles

	Name	After 1300 cycles	After 1800 cycles
C1s	Super-P		5.09
	C-C, C-H	36.47	22.57
	C-O	4.81	6.83
	O-C=O	2.74	2.29
	O(C=O)O	0.66	0.53
O1s	Li_2O	1.30	0.39
	Li-O	2.48	1.96
	C=O	8.56	11.67
	C-O	5.81	6.96
F1s	MFx	11.92	10.92
	$Li_xPO_yF_z$	0.68	2.39
P2p	LixPOyFz	1.55	1.94
Li1s	Li		4.58
	$ROCO_2Li$, Li_2CO_3	14.49	9.87
	LiF	5.10	6.56

Table S4 Trace metal contents anodes with different cycles determined by ICP-AES.

	Content (%)		
	Li	Ni	Mn
After 1300 cycles	3.13	0.01	0.01
After 1800 cycles	4.21	0.05	0.06