Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting information

Constructing a surface spinel layer to stabilize the oxygen frame of Li-rich layered oxides

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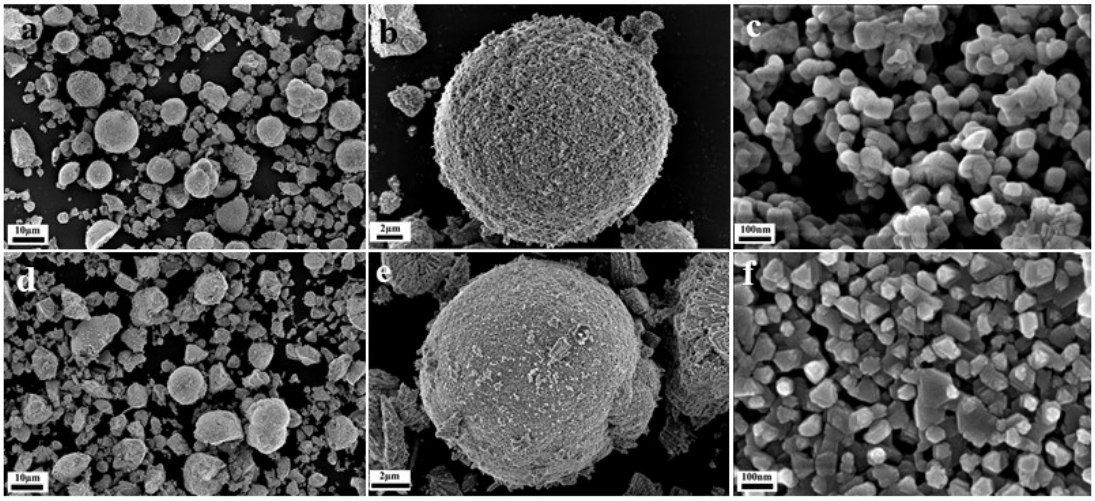

Figure S1. Scanning electron microscope images of various CA-treatment: **a)** 50g/L CA-treatment and **b)** 210g/L CA-treatment.

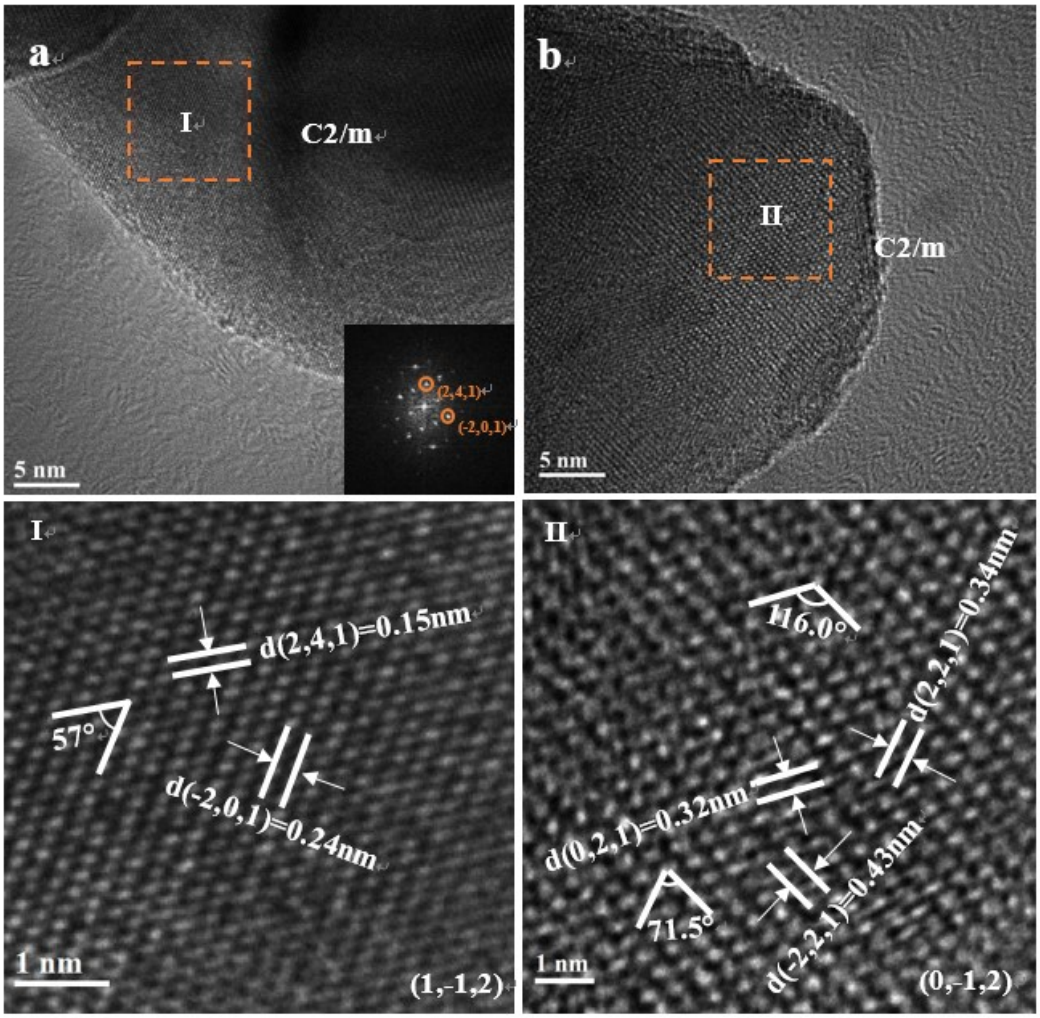

Figure S2. Transmission electron microscope images of the as-prepared PRI materials.

Figure S2 shows a selected domain of the transmission electron microscope images for the as-prepared PRI materials, which belong to the monoclinic structure of Li_2MnO_3 with spcing group of C2/m. Figure S2a shows a zone axis along (1,-1,2), which d-spacings was 0.15 and 0.24nm belongs to the (2,4,1) and (-2,0,1) planes, respectively, for the angle of 57º, and the slight and sharp FFT pattern was conducted. Another area of the PRI materials showed the (0,-1,2) zone axis along the (0,2,1), (2,2,1) and (-2,2,1) planes, for d-spacing of 0.32nm, 0.34nm and 0.43nm, respectively, and the included angle was 71.5º and 116.0º.

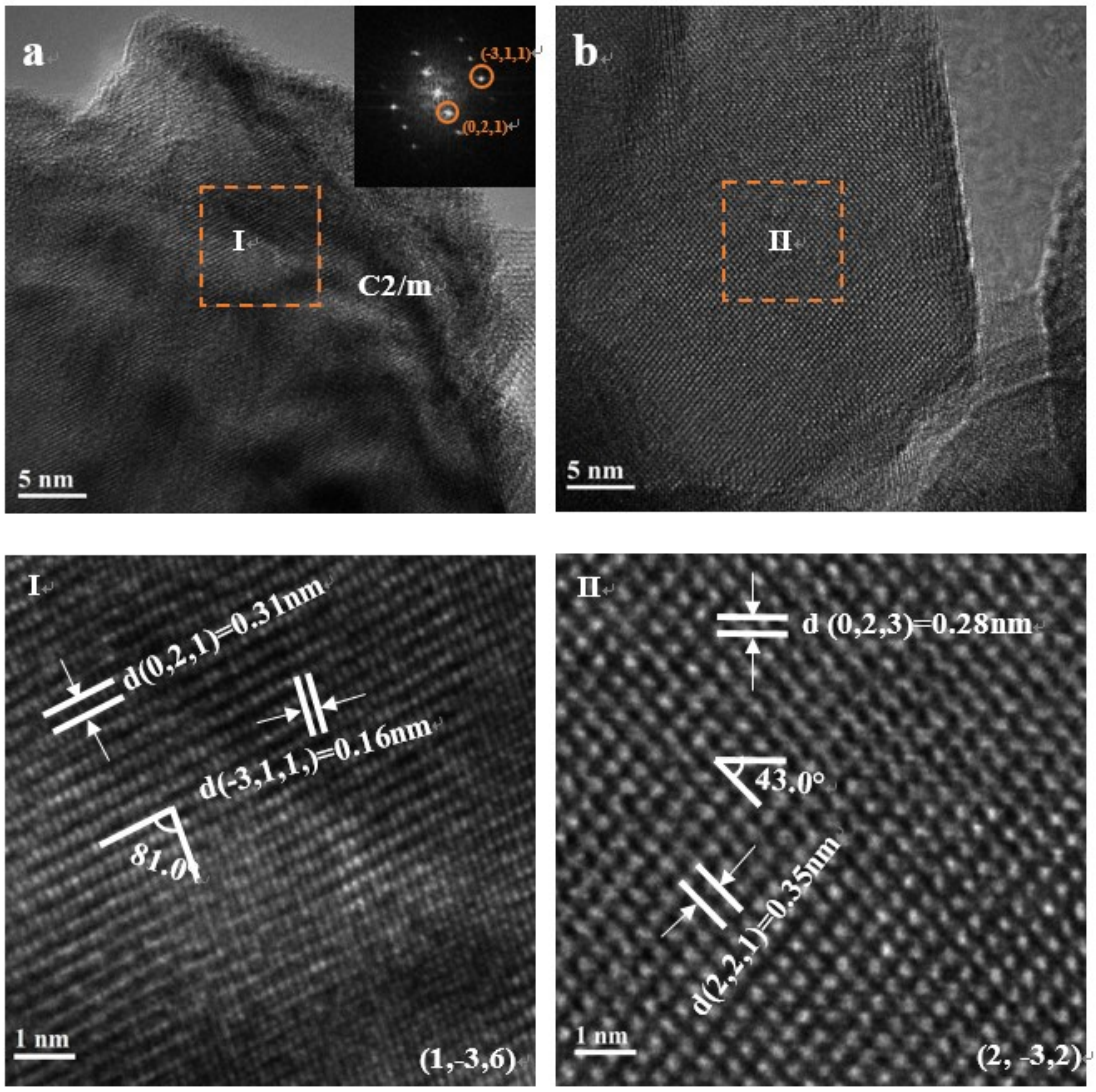

Figure S3. Transmission electron microscope images of the as-prepared CA-LR materials.

In addition, **Figure S3a** showed the diffuse streak pattern and the corresponding FFT pattern of the CA-LR materials, indexed to the Li_2MnO_3 phase (C2/m spacing group) along the (1,-3,6) zone axis, and d-spacing of 0.16 and 0.31nm, with the included angle of 81.0º. It was worthy to note that diffuse streak was indistinct, which was due to the treatment of citric acid to pre-activate the Li_2MnO_3 phase. Another region in Figure S3b showed the well-defined lattice stripe along (2,-3,2) zone axis, for d-spacing of 0.35 and 0.28nm, with the angle of 43.0º.

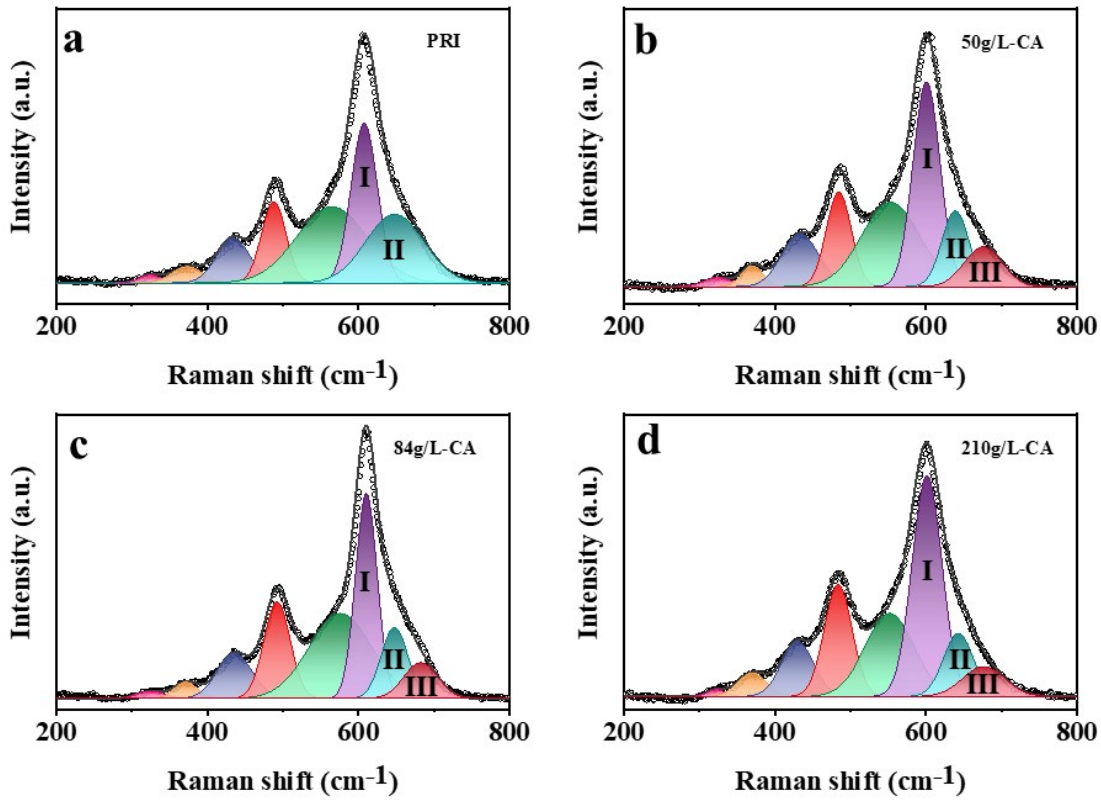

Figure S4. Raman spectra before cycling. **a)** PRI, **b)** 50g/L-CA, **c)** 84g/L-CA and **d)** 210g/L-CA samples.

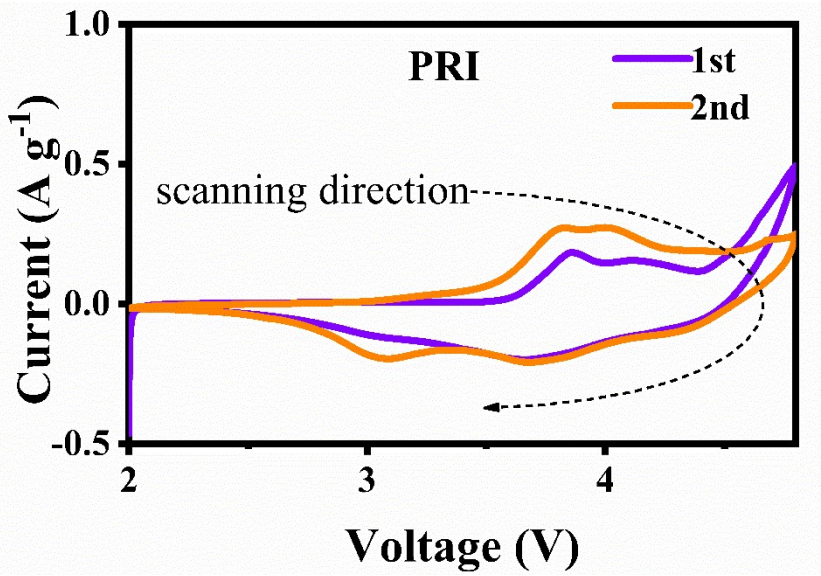

Figure S5. Cycle voltammetry curves of the as-prepared pristine material at the scan rate of 0.1 mV s^{-1} starting from the oxidation process under the 1st and 2nd cycle.

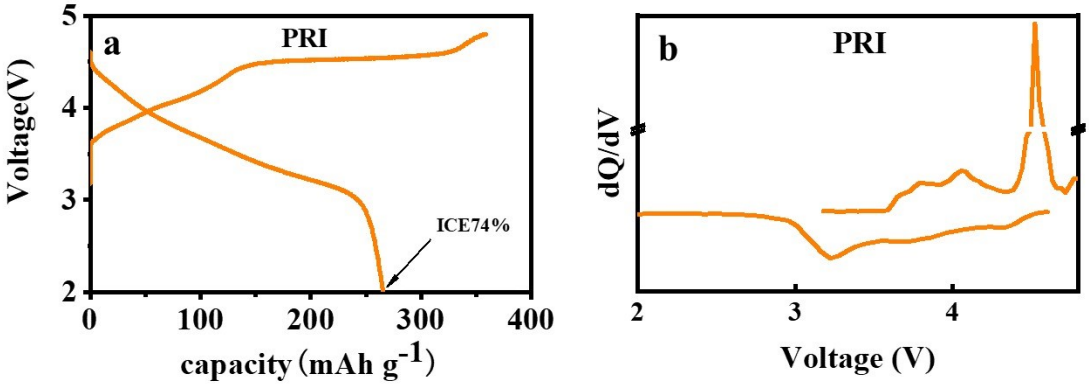

Figure S6. a) Initial galvanostatic cycling profile of the as-prepared pristine material at the current density of 0.1C. **b)** Iinitial dQ/dV image of the PRI at the current density of 0.1 C.

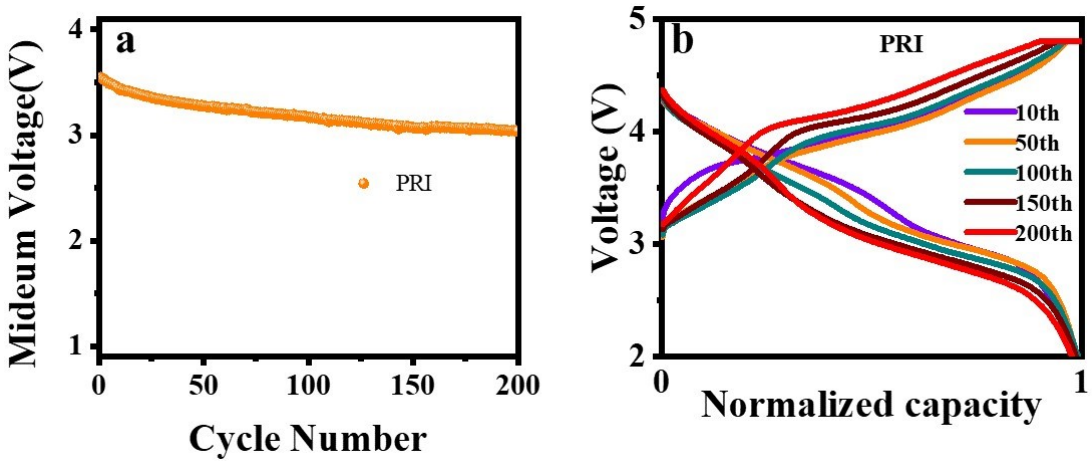

Figure S7. a) Medium voltage versus cycle number plot PRI samples at 1C. **b)** Normalized charge-discharge curves of the PRI sample in the 10^{th}, 50^{th}, 100^{th}, 150^{th} and 200^{th} cycles at 1 C

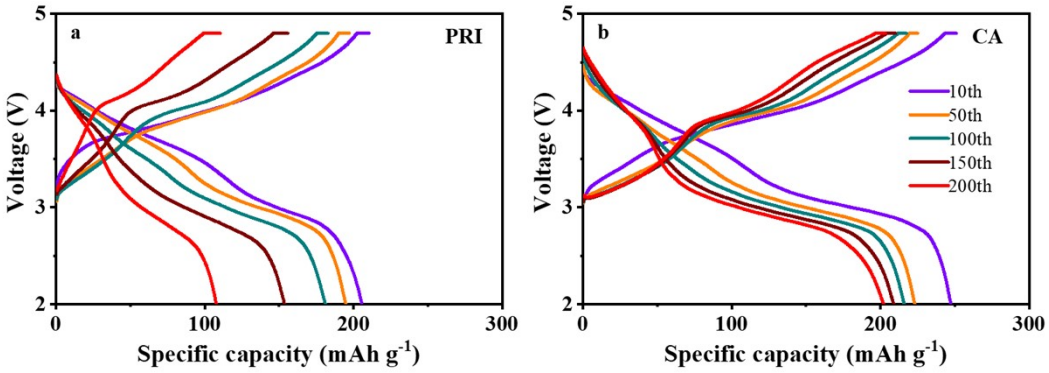

Figure S8. Charge-discharge curves of **a)** PRI and **b)** CA-LR materials at 1 C between 2.0 and 4.8 V.

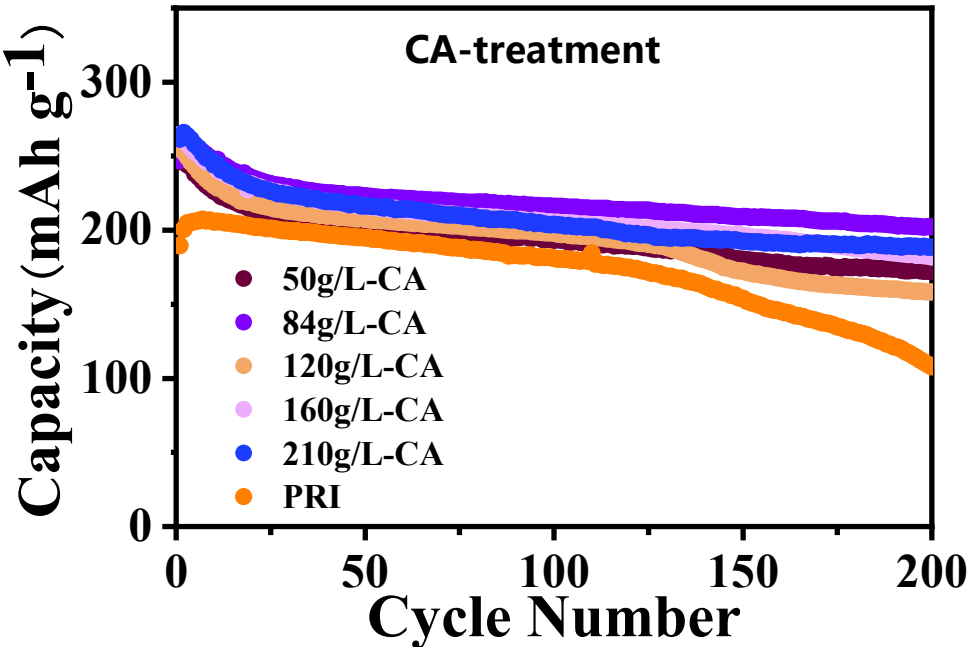

Figure S9. Cycling performance of the Li-rich material before and after citric acid treatment between 2.0 and 4.8 V with current density of 1 C.

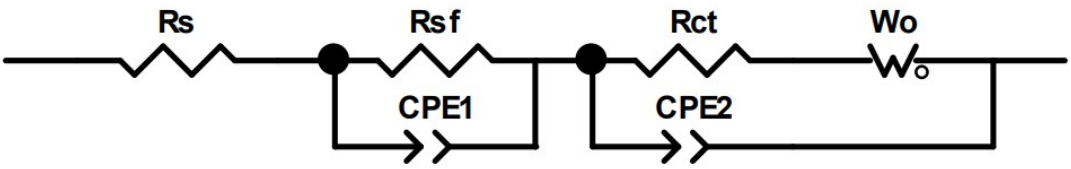

Figure S10. Equivalent electric circuit used to fit the experimental.

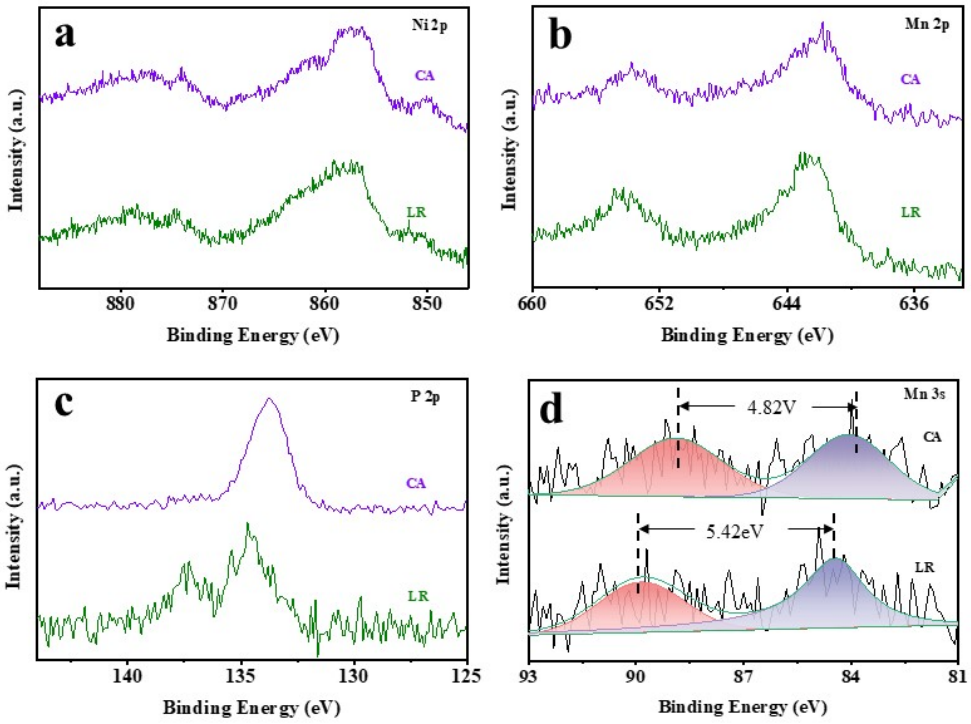

Figure S11. a) Ni 2p, b) Mn 2p, c) P 2p and d) Mn 3s X-ray photoelectron spectroscopy spectra after 200 cycles.

Table S1. Lattice parameters of the samples.

sample			PRI	CA-LR
Lattice parameter	R-3m phase	a(Å)	2.8594	2.8601
		c(Å)	14.2566	14.2649
		V(Å^3)	100.95	101.06
		c/a	4.9859	4.9876

Table S2. Occupancy of atoms in PRI and CA-LR sample as calculated by Rietveld refinement.

Sample	Atom	Site	x	y	z	Occupancy	Mental in Li 3a site
PRI	Li	3a	0	0	0	0.9573	4.27%
	Ni	3a	0	0	0	0.0427	
	Li	3b	0	0	0.5	0.0427	
	Ni	3b	0	0	0.5	0.4573	
	Mn	3b	0	0	0.5	0.5000	
	O	6c	0	0	0.242	1.0000	

Sample	Atom	Site	x	y	z	Occupancy	Mental in Li 3a site
CA-LR	Li	3a	0	0	0	0.9152	8.48%
	Ni	3a	0	0	0	0.0848	
	Li	3b	0	0	0.5	0.0848	
	Ni	3b	0	0	0.5	0.4152	
	Mn	3b	0	0	0.5	0.5000	
	O	6c	0	0	0.242	1.0000	

Table S3. Area ratios of peak I, II and III in Raman spectra of the three samples.

sample	Peak I (%)	Peak II (%)	Peak III (%)
PRI	51.4	48.6	0
50g/L-CA	61.0	22.5	16.5
84g/L-CA	58.9	25.0	16.1
210g/L-CA	67.7	19.4	12.9

Table S4. Parameters for electrochemical impedance spectroscopy in term of the fitted results.

sample	R_s（Ω）	R_{sf}（Ω）	R_{ct}（Ω）	R_{total}（Ω）
PRI	2.615	214.8	908.8	1126.2
PRI-4.8V	4.026	86.3	1805	1895.3
CA	1.683	138.2	7.269×10^{-2}	140.0
CA-4.8V	2.196	127.8	407.6	537.6

Table S5. Diffusion coefficient of Li^+ for PRI and CA-LR samples before and after charged to 4.8V.

	PRI	PRI-4.8V	CA	CA-4.8V
D（Li^+）	5.60×10^{-17}	2.19×10^{-16}	9.51×10^{-17}	4.00×10^{-15}