

Supporting Information

Selective Formation of $\text{Li}_4\text{Mn}_5\text{O}_{12}$ Surface Spinel Phase in Sulfur-doped Li-excess Layered Cathode Materials for Improved Cycle Life

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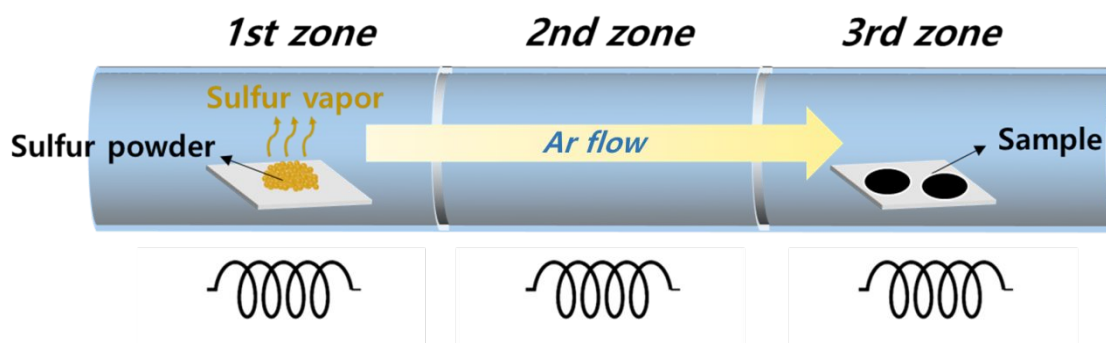


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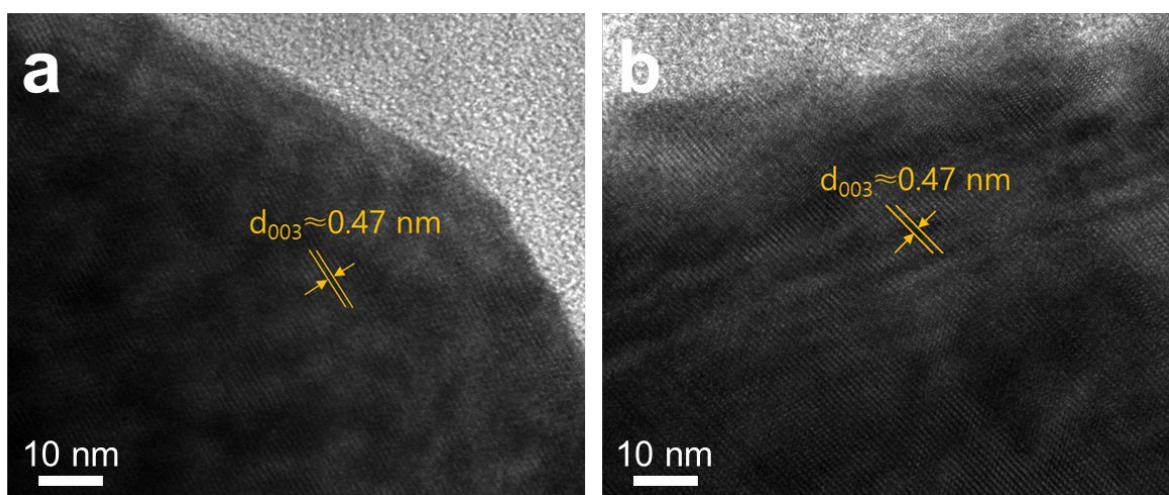


Figure S2. HRTEM images of the (a) LLC and (b) S-LLC samples.

Table S1. Different ratios of active materials of LLC and sulfur to optimize the amount of sulfur.

Active material : Sulfur (mg)	
S-LLC1	1 : 500
S-LLC2	1 : 1000
S-LLC3	1 : 2000

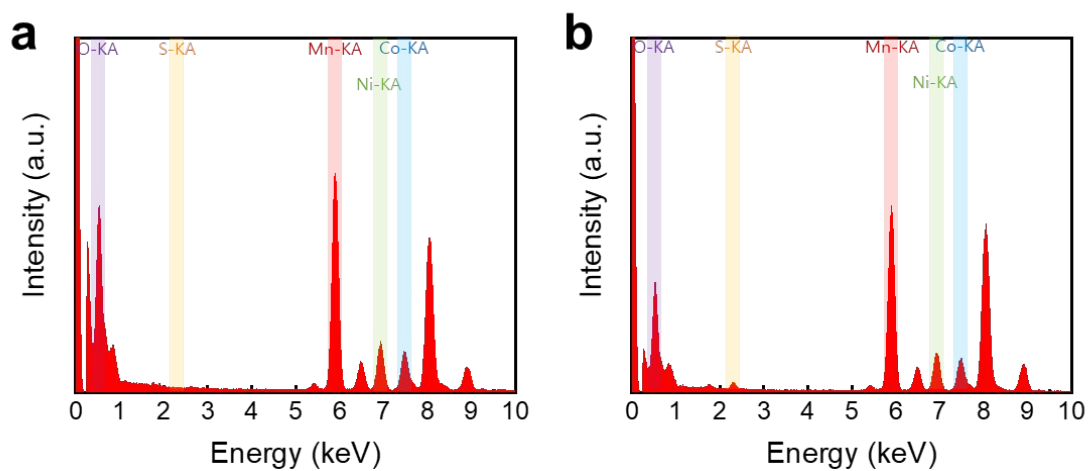


Figure S3. TEM-EDS spectra of (a) LLC and (b) S-LLC

Table S2. The TEM-EDS results (wt%) of LLC and S-LLC.

Element	Mn	Ni	Co	O	S
LLC	52.90	12.84	13.08	21.15	0.03
S-LLC	52.81	13.85	13.26	19.01	1.87

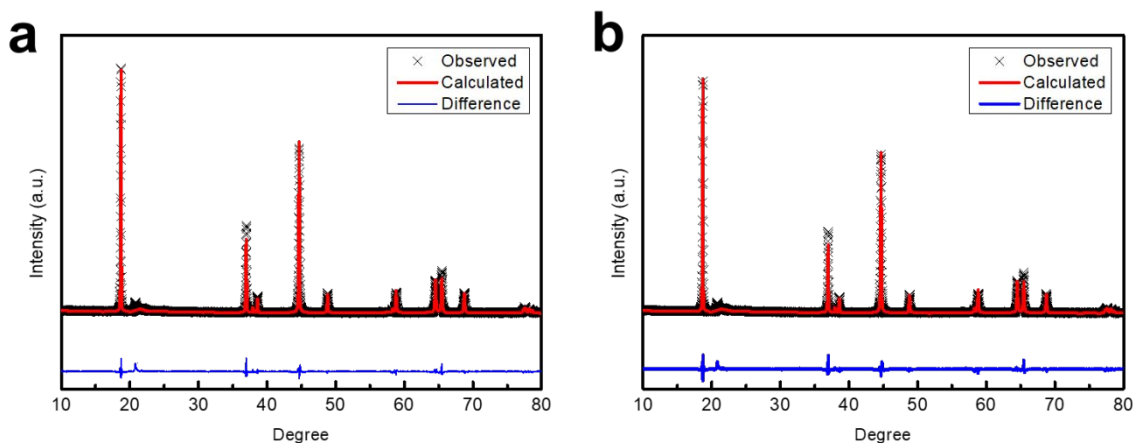


Figure S4. The Rietveld refinement of the XRD patterns of (a) LLC and (b) S-LLC.

Table S3. Refined lattice parameters of LLC and S-LLC.

Materials	a (Å)	c (Å)	c/a ratio	Refined parameter	
				R _p	R _{wp}
LLC	2.8492	14.2317	4.9949	4.84	5.85
S-LLC	2.8480	14.2309	4.9968	4.42	5.40

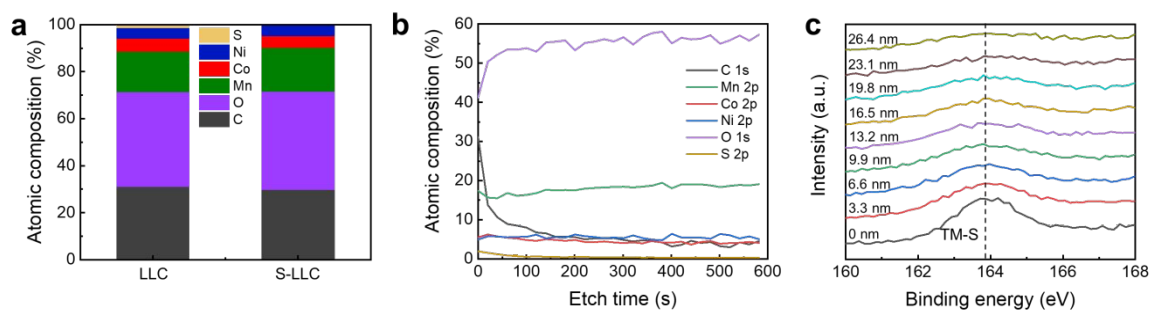


Figure S5. (a) Chemical composition of LLC and S-LLC obtained from the XPS spectra.

XPS depth profile of (b) total elements and (c) S 2p region in S-LLC. The small amount of S signal is detected in the surface region of S-LLC, it indicates the S²⁻ anion is mainly doped at the surface of LLC.

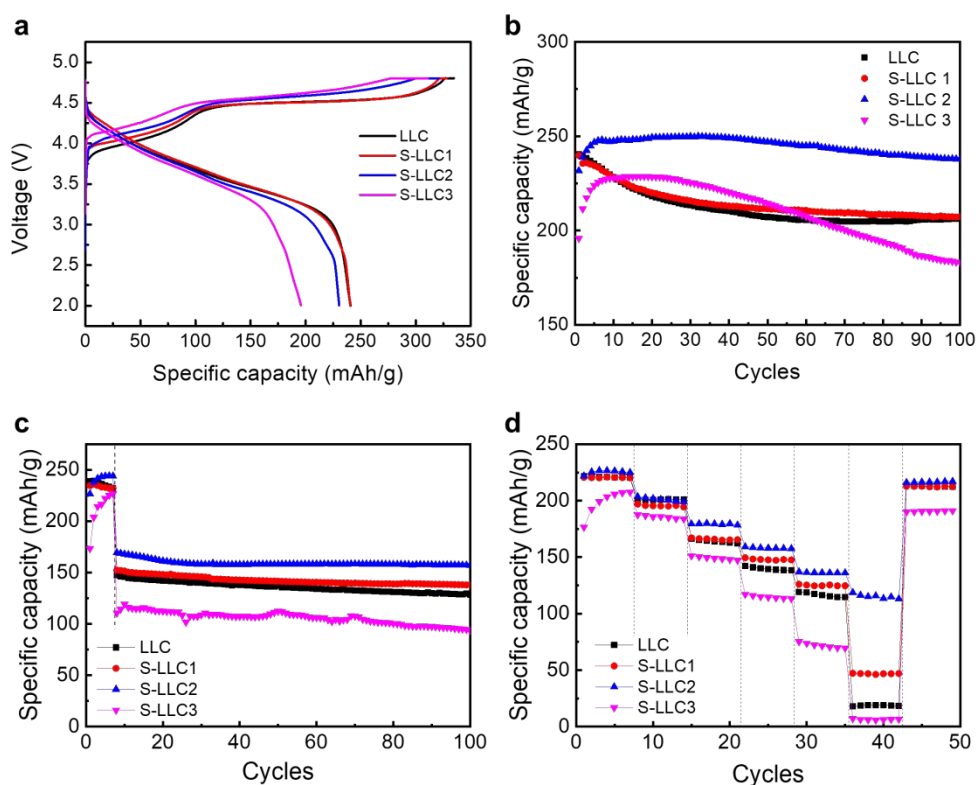


Figure S6. (a) Charge-discharge curves at 1st cycle and electrochemical performances of the LLC and various sulfurized LLC with different sulfur ratio at the (b) 0.1 C rate. (c) Cycling performance at the 1 C rate and (d) rate capability outcomes of the LLC and sulfurized LLCs.

Table S4. The SEM-EDS results (wt%) of sulfurized LLC with different sulfur ratio.

Element	Mn	Ni	Co	O	S
S-LLC1	53.84	12.45	12.95	20.64	0.12
S-LLC2	53.41	12.35	12.48	19.56	2.20
S-LLC3	53.12	12.07	12.22	18.27	4.32

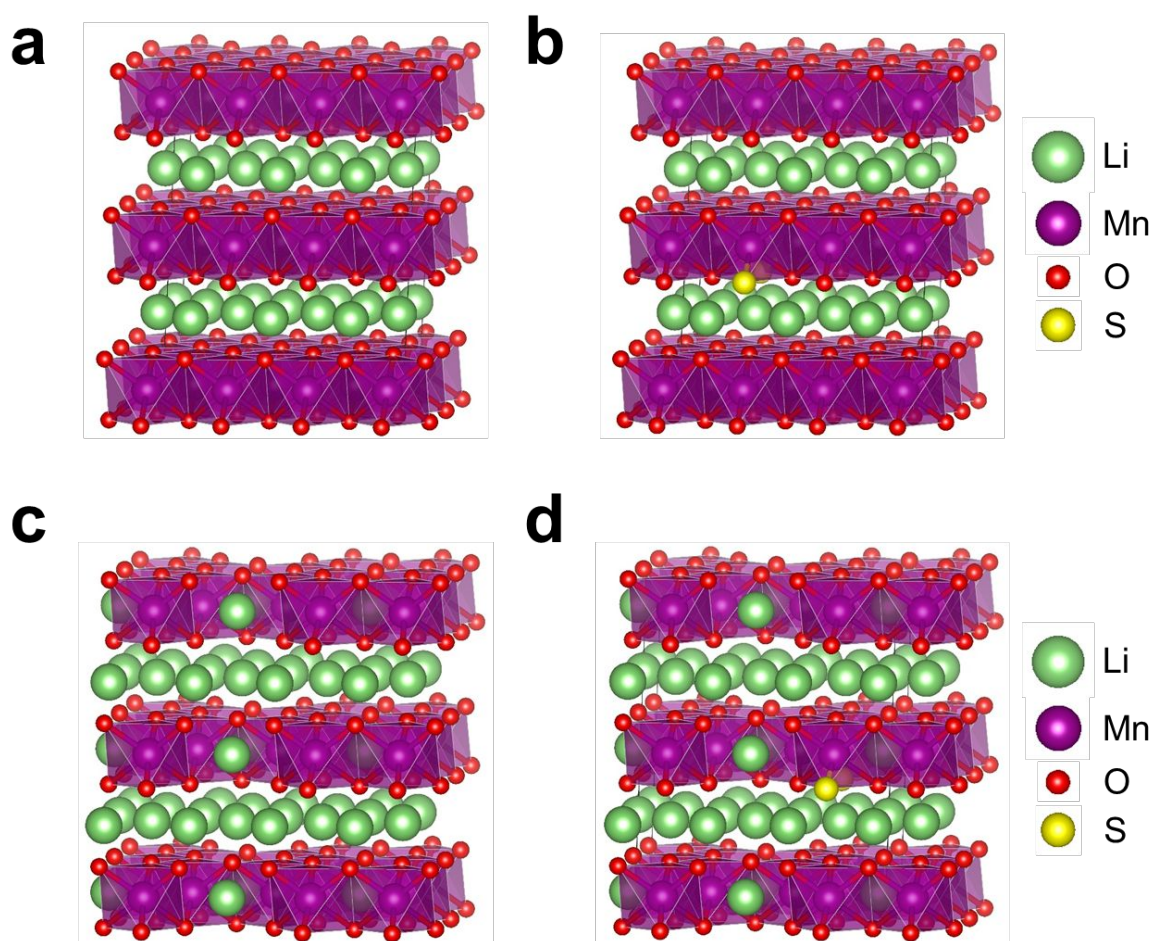


Figure S7. Optimized layered structures of fully lithiated (a) pristine LiMnO_2 , (b) S-doped LiMnO_2 , (c) pristine Li_2MnO_3 , and (d) S-doped Li_2MnO_3 .

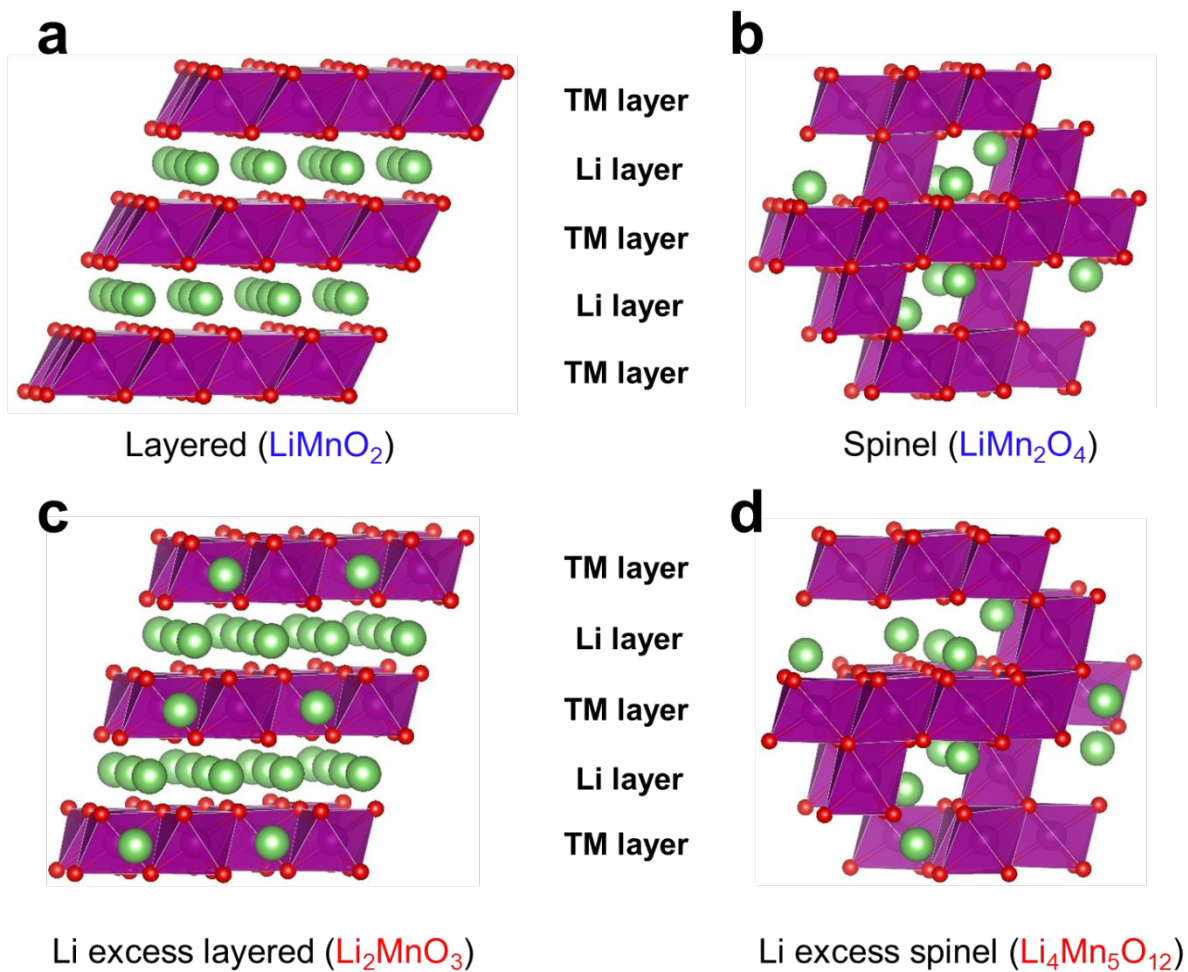


Figure S8. Optimized atomic structures of (a) layered LiMnO_2 , (b) spinel LiMn_2O_4 , (c) Li-excess layered Li_2MnO_3 , and (d) Li-excess spinel $\text{Li}_4\text{Mn}_5\text{O}_{12}$.