Electronic Supplementary Information

Suppressing Structural Degradation of Ni-rich Cathode Materials towards Improved Cycling Stability Enabled by a Li₂MnO₃ Coating

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Figure S1. XRD pattern of the preheated NCM811-PH intermediate obtained by heating the NCM811 precursor at 750 °C for 5 h in the pure O_2 flow. The quantitative Rietveld refinement analysis indicates the formation of a Li-poor Li_{0.955}Ni_{0.8}Co_{0.1}Mn_{0.1}O_{2-δ} phase.



Figure S2. Structural transformation of MnO_2 particles through a one-step high-energy sonofragmentation: (a) TEM image and (b) HRTEM image of original MnO_2 nanorods, and (c) TEM image and (d) HRTEM image of the obtained mixture of ultrafine MnO_2 monocrystals and some amorphous matter after the high-energy sonication in the ethanol for 6 h.



Figure S3. (a) TEM image with (b) enlarged selected area of NCM8111-HP@MnO₂-3% particles.



Figure S4. TEM images of (a) the bare NCM811, (b) NCM811@LMO-1%, (c) NCM811@LMO-3% and (d) NCM811@LMO-5% particles.



Figure S5. EDS mappings of the NCM811@LMO-3% particle, showing uniform distribution of Ni, Co, Mn and O elements.



Figure S6. XRD patterns of (a) NCM811@LMO-1% and (b) NCM811@LMO-5%, coupled with Rietveld refinements, and (c) XRD pattern of NCM811@LMO-5% with an enlarged 2θ range of 20-23°, verifying the existence of Li₂MnO₃ coating component.



Figure S7. XRD patterns of as-prepared Li₂MnO₃ materials at gradually increased sintering temperatures between 650 and 800 °C.



Figure S8. SEM images of (a) the bare NCM811, (b) NCM811@LMO-1%, (c) NCM811@LMO-3% and (d) NCM811@LMO-5%, together with corresponding particle size distributions of (e) primary nanoparticles and (f) secondary micron-sized particles.



Figure S9. High-resolution Ni 2p XPS spectra of (a) the bare NCM811, (b) NCM811@LMO-1% and (c) NCM811@LMO-5% materials with recorded intensities.



Figure S10. Charge/discharge curves in different cycles up to 100 cycles at 0.1 C of (a) NCM811@LMO-1% and (b) NCM811@LMO-5% cathode materials.



Figure S11. CV curves of the bare NCM811 and NCM811@LMO-3% cathodes recorded at a scanning rate of 0.1 mV s⁻¹: (a) the first CV cycle of two cathodes, and second to forth CV cycles of (b) the bare NCM811 and (c) NCM811@LMO-3% cathode materials.



Figure S12. *In-situ* XRD patterns showing evolutions of 003, 101, 104 and 018/110 reflections recorded in the first cycle during charge/discharge of (a) the bare NCM811 and (b) NCM811@LMO-3% cathode materials.



Figure S13. *In-situ* XRD examinations during charge/discharge of (a) the bare NCM811 and (b) NCM811@LMO-3% in the second cycle, showing recorded charge/discharge curves and contour plots of 003, 101, 104 and 018/110 reflections.



Figure S14. *In-situ* XRD patterns showing evolutions of 003, 101, 104 and 018/110 reflections recorded in the second cycle during charge/discharge of (a) the bare NCM811 and (b) NCM811@LMO-3% cathode materials.



Figure S15. Two different equivalent circuits used to simulate EIS spectra of cycled NCM811 and NCM811@LMO-3% cathodes: (a) recorded at the initial state and after 1 cycle and (b) recorded after 500 cycles, according to EIS spectra as shown in Figure 5g and 5h.

Figure 5g and 5h plot measured EIS spectra of the bare NCM811 and NCM811@LMO-3% cathodes after 1 and 500 cycles at the fully-discharged state, respectively. The EIS spectra of these two fresh cathodes at their initial states before cycling were also measured for comparison. According to different EIS spectra, especially recorded at the 500th cycle, two different equivalent circuits are used for the simulation analyses as shown in Figure S15, and the fitting results are presented in Table S4.

Where, R_s stands for the resistance value of the electrolyte in the cells. The high frequency semicircle represents the interfacial film resistance (R_f); the semicircle of the middle frequency region relates to the charge transfer resistance (R_{ct}) of the electrode/electrolyte interface; finally, the low frequency slant represents Warburg (W) impedance, which is related to Li⁺ diffusion. Note that the bare NCM811 shows considerably enlarged R_{ct} value to 1105 Ω after 500 cycles, much higher than that of in the NCM811@LMO-3% cathode (317 Ω), implying the worse surface condition after prolonged cycles without the Li₂MnO₃ coating. However, both two cathodes give rise to increased R_{ct} values after the first cycle compared with their initial states (Table S4), which can be attributed to the irreversible structural changes during the initial delithiation process as indicated by dQ/dV profiles and *in-situ* XRD patterns (Figures 4d-f).



Figure S16. Enlarged voltage profiles for a single step of GITT curves at ~3.64 V during the charge of (a) the bare NCM811 and (b) NCM811@LMO-3% cathode material at 0.1 C as shown in Figure 7a-b.

The calculation of the lithium ion diffusion coefficient (D_{Li}^+) from the recorded GITT curve is explained as follows: The cell was first charged from open circuit voltage (OCV) at a $\tau = 20$ min under a current pulse of 0.1 C, followed by a relaxation time of 60 min to allow the system to reach electrochemical equilibrium. This operation is repeated until the end of the voltage window. Figure 7a shows the GITT curves of the NCM811/Li half-cell in the 10th cycle. The D_{Li}^+ can be determined by applying Fick's second law of diffusion and was calculated by the following Eqn. (1)^{1,2}

$$\mathbf{D} = \frac{4}{\pi} \left(\frac{\mathbf{m}_{\mathrm{B}} \mathbf{V}_{\mathrm{M}}}{\mathbf{M}_{\mathrm{B}} \mathbf{A}} \right)^{2} \left(\frac{\triangle \mathbf{E}_{\mathrm{s}}}{\triangle \mathbf{E}_{\mathrm{\tau}}} \right)^{2} \tag{1}$$

where, m_B is the mass loading (g), V_M is the molar volume (cm³ mol⁻¹), M_B is the molecular weight (g mol⁻¹), A is the contact area of the electrode (cm²), and τ is the time when the current pulse is applied (s), ΔEs is the voltage difference between the steady-state potentials before and after the current pulse is applied, and $\Delta E\tau$ refers to the voltage difference between the cell potential at the start and the end of current pulse as shown in Figure S16.

References

- 1. W. Jayawardana, C. L. Carr, D. Zhao and E. H. Majzoub, *J. Electrochem. Soc.*, 2018, **165**, 2824-2832.
- P. Li, X. Zheng, H. Yu, G. Zhao, J. Shu, X. Xu, W. Sun and S. X. Dou, *Energy Storage Materials*, 2019, 16, 512-518.



Figure S17. Initial charge/discharge curves at 0.1 C of (a) the bare NCM811 and (b) NCM811@LMO-3% cathodes in different voltage ranges of 2.7-4.3/4.4/4.5/4.6 V vs. Li⁺/Li. (c) high-rate performance up to 2 C and (d) cycling performance at 0.1 C of NCM811 and NCM811@LMO-3% cathodes in a wide voltage range of 2.7-4.5 V vs. Li⁺/Li compared with that of the NCM811@LMO-3% cycled in 2.7-4.3 V. (e) CV curves in the first four cycles of NCM811@LMO-3% at a scanning rate of 0.1 mV s⁻¹ in a very wide voltage range of 2.7-4.8 V vs. Li⁺/Li. (f) Cycling performance of NCM811 and NCM811@LMO-3% at 1 C in different voltage ranges of 2.7-4.3/4.5 V vs. Li⁺/Li.

Samples	a (Å)	s.d.	c (Å)	s.d.	Volume (A ³)	s.d.	c/a ratio	Li ⁺ in 3b sites (%)	s.d.	Rwp (%)	R _P (%)
NCM811	2.8722	2.5*10 ⁻⁵	14.1944	2.4*10-4	101.41145	2.4*10-3	4.9420	0.9799	3.983*10 ⁻³	4.66	3.98
NCM811@ LMO-1%	2.8711	2.3*10 ⁻⁵	14.1934	2.2*10-4	101.40181	2.3*10 ⁻³	4.9434	0.9823	2.003*10-3	4.68	3.46
NCM811@ LMO-3%	2.8692	2.4*10 ⁻⁵	14.1929	2.3*10-4	101.38483	2.4*10-3	4.9466	0.9850	2.771*10 ⁻³	4.50	3.36
NCM811@ LMO-5%	2.8688	3.3*10 ⁻⁵	14.1903	3.6*10-4	101.36571	3.5*10 ⁻³	4.9464	0.9830	3.030*10-3	4.84	3.67

Table S1 Crystal parameters of different Li₂MnO₃-coated NCM811@LMO-x% materials in comparison with the bare MCN811 material, accordint to XRD patterns coupled with quantitative refinement analyses as shown in Figures 3b-c and S6a-b.

Table S2. Quantitative analyses of Ni²⁺ and Ni³⁺ contributions in the Ni $2p_{3/2}$ XPS peaks of the bare NCM811 and different NCM811@LMO-x% (x=1, 3, 5) materials on the basis of fitting patterns as shown in Figures 3d and S9a-b.

Samples	Ni ²⁺	Ni ³⁺
NCM811	47%	53%
NCM811@LMO-1%	45%	55%
NCM811@LMO-3%	40%	60%
NCM811@LMO-5%	33%	67%

Samples	LiOH (wt.%)	Li ₂ CO ₃ (wt.%)		
NCM811	0.366	0.541		
NCM811@LMO-3%	0.255	0.310		

Table S3. Contents of residual LiOH and Li_2CO_3 by-products within the bare NCM811 and NCM811@LMO-3% materials as shown in Figure 3e.

	NCM811			NCM811@LMO-3%			
Resistances (Ω)	Rs	R _{ct}	$R_{\rm f}$	Rs	R _{ct}	R _f	
At the initial state	5	30	×	5	25	X	
After 1 cycle	6	266	×	4	205	×	
After 500 cycles	2	1105	54	2	317	34	

Table S4. Simulated values based on EIS spectra recorded at fully-discharged 2.7 V of cycled NCM811 and NCM811@LMO-3% cathode materials compared with that at their initial states as shown in Figure 5g and 5h.