Supplementary Information

Atomic layer deposition of a thin TiO₂ layer on nickel-rich cathode NCM83 for improved cycling stability

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Fig. S1 Schematic illustration of the coating process of TiO₂ layer on NCM83 using the ALD method.



Fig. S2 FTIR spectrum of NCM83.



Fig. S3 FESEM image of NCM83.



Fig. S4 XRD patterns of NCM83, NCM83-P, NCM83-Ti20, NCM83-Ti60 and NCM83-100.



Fig. S5 XRD Rietveld refinement patterns of NCM83, NCM83-Ti20 and NCM83-Ti100.



Fig. S6 FESEM images of NCM83-Ti20 (a) and NCM83-Ti100 (b).



Fig. S7 TEM images of NCM83-Ti20 (a) and NCM83-Ti100 (b).



Fig. S8 Ti 2p XPS fitting spectrum of NCM83-Ti60 after 10 s of etching.



Fig. S9 EDS images of randomly selected multiple NCM83-TiO2 secondary particles.



Fig. S10 FESEM images and corresponding EDS elemental mappings for samples (a) NCM83-Ti20, (b) NCM83-Ti60, and (c) NCM83-Ti100.



Fig. S11 Raman spectra of NCM83-P and NCM83-Ti60.







Fig. S13 GCD profiles of (a) NCM83-P and (b) NCM83-Ti60 for different cycles at 1C.



Fig. S14 Radar chart comparing the cycling performance of NCM83-Ti60 with other ALD-modified NCM cathode materials reported in the literature.



Fig. S15 GITT curves and Li-ion diffusion coefficient of NCM83-P before cycling.



Fig. S16 GITT curves and Li-ion diffusion coefficient of NCM83-Ti60 before cycling.



Fig. S17 FTIR spectra of NCM83-P and NCM83-Ti60 after 100 cycles at 1C.



Fig. S18 HRTEM image of NCM83-P after 100 cycles at 1C, along with the corresponding FFT (fast Fourier transform images of selected regions).



Fig. S19 HRTEM image of NCM83-Ti60 after 100 cycles at 1C, and the corresponding FFT (fast Fourier transform) images of selected regions.



Fig. S20 In situ XRD patterns of NCM83-P.



Fig. S21 In situ XRD patterns of NCM83-Ti60.



Fig. S22 Rietveld-refined XRD patterns of NCM83-P electrode before and after 100 cycles at 1C.



Fig. S23 Rietveld-refined XRD patterns of NCM83-Ti60 electrode before and after 100 cycles at 1C.

Sample	a (Å)	<i>c</i> (Å)	V (ų)	Ni ²⁺ in Li layer (%)	R _p %	R _{wp} %
NCM83	2.88	14.25	102.50	2.24	1.69	0.97
NCM83-P	2.88	14.24	102.40	2.18	1.74	0.99
NCM83-Ti20	2.88	14.24	102.43	2.11	1.73	0.99
NCM83-Ti60	2.88	14.23	102.24	2.20	1.53	0.91
NCM83-Ti100	2.88	14.25	102.49	2.35	1.54	0.92

Table S1. Rietveld refinement results of XRD patterns for NCM83, NCM83-P, NCM83-Ti20, NCM83-Ti60,and NCM83-Ti100.

 Table S2. EIS fitting data for NCM83-P, NCM83-Ti20, NCM83-Ti60, and NCM83-Ti100.

Sample	$R_{\rm ct}$ (Ω)	Error (%)
NCM83-P (before cycling)	186.2	7.1
NCM83-Ti20 (before cycling)	210.5	5.6
NCM83-Ti60 (before cycling)	246.8	7.7
NCM83-Ti100 (before cycling)	300.4	5.3
NCM83-P (after 100 cycles)	764.4	6.5
NCM83-Ti60 (after 100 cycles)	320.6	7.8

Table S3. Summary of peak positions and relative areas obtained from the C1*s* XPS spectra shown in Figs. 4a and 4b for samples NCM83-P and NCM83-Ti60 after 100 cycles within the voltage range between 2.7 and 4.3 V.

Cracios	$\mathbf{Post}_{\mathbf{r}} = \mathbf{Post}_{\mathbf{r}} $	Percentage (%)		
species	Peak position (ev) -	NCM83-P	NCM83-Ti60	
C–C/C-H	284.8	53.9	62.0	
C–O	286.3	21.1	18.2	
C=O	288.0	3.7	14.6	
(CO ₃) ^{2–}	290.0	21.3	5.2	

Spacias	Dook position (a)()	Percentage (%)		
species		NCM83-P	NCM83-Ti60	
Lattice O	529.8	11.6	13.3	
(CO ₃) ^{2–}	532.3	28.2	24.3	
C=O	533.2	31.5	32.5	
С-О	534.2	28.7	29.9	

Table S4. Summary of peak positions and relative areas obtained from the O1s XPS spectra shown in Figs. 4a and 4b for samples NCM83-P and NCM83-Ti60 after 100 cycles within the voltage range between 2.7 and 4.3 V.

Table S5. Summary of peak positions and relative areas obtained from the F1*s* XPS spectra shown in Figs. 4a and 4b for samples NCM83-P and NCM83-Ti60 after 100 cycles within the voltage range between 2.7 and 4.3 V.

Creation	$\mathbf{Posk} = \mathbf{position} (\mathbf{o})(0) = \mathbf{posk}$	Percentage (%)			
species	Peak position (ev) =	NCM83-P	NCM83-Ti60		
LiF/MF _x	684.5	17.6	59.2		
Li _x PO _y F _z	687.1	82.4	40.8		

Table S6. Summary of peak positions and relative areas obtained from the Ni 2*p* XPS spectra in Figs. 4a and 4b for samples NCM83-P and NCM83-Ti60 after 100 cycles within the voltage range of 2.7 V-4.3 V.

Species	Dook position (a)/)	Percentage (%)			
species		NCM83-P	NCM83-Ti60		
Ni ²⁺ 2p _{3/2}	855.6	15.4	11.5		
Ni ³⁺ 2p _{3/2}	858.8	21.7	26.9		
Ni ²⁺ 2p _{1/2}	873.4	7.2	5.4		
Ni ³⁺ 2p _{1/2}	877.2	10.1	12.5		
Satellite	862.8	25.1	22.6		
	881.3	20.5	21.1		

Sample		م (Å)	<i>c</i> (Å)	<i>V</i> (ų)	Ni ²⁺ in Li	R _p %	R _{wp} %
		<i>u</i> (A)			layer (%)		
NCM83-P	before cycling	2.88	14.25	102.60	2.01	1.69	1.07
	100 cycles	2.89	14.27	103.21	7.78	1.49	1.04
NCM83-Ti60	before cycling	2.88	14.23	102.38	2.01	1.79	1.09
	100 cycles	2.88	14.24	102.76	2.35	1.49	1.05

Table S7. Rietveld refinement results of XRD patterns for NCM83-P and NCM83-Ti100 electrodes beforecycling and after 100 cycles.