Supporting Information

Structural Stability and Interface Optimization for Enhancing High-Voltage Electrochemical Performance of $LiNi_{0.83}Co_{0.11}Mn_{0.06}O_2$ Cathode Material

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Experimental Section

Material Preparation

A stoichiometric mixture of $LiNO_3$ (AR, ≥99.99%, Aladdin), $La(NO_3)_3 \cdot 6H_2O$ (AR, ≥99.9%, Aladdin), and H_3PO_4 (≥99%, Aladdin) was dissolved in 20 mL of ethanol, followed by adding tetraisobutyl titanate ($C_{16}H_{36}O_4Ti$, AR, ≥99.9%, Aladdin). The Li:La:Ti:P molar ratio was 1.3:0.3:1.7:3. After continuous stirring for 1 h, a homogeneous precursor solution of $Li_{1.3}La_{0.3}Ti_{1.7}(PO_4)_3$ was obtained.

The $Ni_{0.83}Co_{0.11}Mn_{0.06}(OH)_2$ precursor was synthesized *via* a coprecipitation method, as described in detail in previous reports [1, 2]. Subsequently, the obtained $Ni_{0.83}Co_{0.11}Mn_{0.06}(OH)_2$ precursor was thoroughly mixed with $LiOH \cdot H_2O$ (AR, Aladdin) by mechanical grinding for 0.5 h, with a molar ratio of Li/(Ni + Co + Mn) set to 1.05:1. The mixture was calcined under an O_2 atmosphere at 450 °C for 4 h, followed by a second calcination at 750 °C for 12 h to yield the $LiNi_{0.83}Co_{0.11}Mn_{0.06}O_2$ cathode material, denoted as LNCM.

For surface modification, the as-prepared LNCM powder was dispersed in ethanol by ultrasonic treatment and then mixed with a pre-prepared $Li_{1.3}La_{0.3}Ti_{1.7}(PO_4)_3$ precursor solution corresponding to a coating amount of 1.0 wt.%. After stirring at 25 °C for 6 h, the mixture was heated to 80 °C to evaporate the solvent, yielding a dried powder. The resulting powder was then calcined at 600 °C for 10 h under an argon atmosphere to form the $Li_{1.3}La_{0.3}Ti_{1.7}(PO_4)_3$-coated $LiNi_{0.83}Co_{0.11}Mn_{0.06}O_2$ composite, denoted as LNCM@LLTP. A schematic illustration of this process is shown in Fig. 1a.

Material Characterization

The crystal structures of the as-prepared samples were characterized by X-ray diffraction (XRD, PANalytical Empyrean 2) using Cu Kα radiation. Rietveld refinement was performed using the GSAS software package to obtain detailed structural parameters. Morphological features and elemental distributions were analyzed by scanning electron microscopy (SEM, JSM-7900F) equipped with energy-dispersive X-ray spectroscopy (EDS). Transmission electron microscopy (TEM, JEM-2100F) was employed to examine the microstructure and coating thickness. The surface chemical states of elements were investigated by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha).

Electrochemical Measurements

Electrochemical performance was assessed using CR2025-type coin cells. The cathode slurry was prepared by homogeneously mixing the active material, poly(vinylidene fluoride) (PVDF) binder, and Super P conductive carbon at a mass ratio of 8:1:1, using N-methyl-2-pyrrolidone (NMP) as the solvent. The slurry was uniformly coated onto a cleaned aluminum foil current collector and vacuum-dried at 120 °C for 12 h to remove residual solvent. The dried electrode was then punched into circular disks with a diameter of 12 mm.

Cell assembly was carried out in an argon-filled glovebox, employing Li metal foil as the counter and reference electrode, Celgard 2400 as the separator, and an electrolyte consisting of 1 M $LiPF_6$ dissolved in a mixed solvent of dimethyl carbonate (DMC), ethyl methyl carbonate, and ethylene carbonate (EC) (EMC) (1:1:1 v/v).

Galvanostatic charge–discharge cycling and rate performance tests were conducted

using a Land CT2001A battery testing system over a voltage window of 2.7–4.5 V (vs. Li^+/Li), with 1 C defined as 200 $mA \cdot g^{-1}$ Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed on a CHI600D electrochemical workstation. CV curves were recorded at a 0.1 $mV \cdot s^{-1}$ scan rate in the 2.7–4.5 V voltage range. EIS spectra were collected over a frequency range from 100 kHz to 10 mHz with an AC perturbation amplitude of 5 mV.

Table S1 Lattice parameters of all specimens.

Specimen	***a*** (Å)	***c***(Å)	***c***/***a***	Ni^{2+} in Li Layer(%)	R_p(%)	R_{wp}(%)
LNCM	2.87701	14.20624	4.938	5.89	3.30	4.38
LNCM@LLTP	2.87182	14.19673	4.940	2.25	3.04	3.86

Table S2 The electrochemical impedance fitting results and calculated D_{Li^+} values.

Specimen	R_s(Ω)	R_{ct}(Ω)	D_{Li^+}($cm^2 \cdot s^{-1}$)
LNCM	10.07	105.4	2.686×10^{-13}
LNCM@LLTP	3.025	33.90	6.665×10^{-13}

[1] G. Mao, Y. Yang, W. Jiao, W. Yu, X. Yuan, Q. Tian, L. Zeng, L. Jiang, H. Tong and X. Guo, *Journal of Materials Science*, 2022, **57**, 19892-19901.

[2] G. Mao, W. Yu, Q. Zhou, L. Li, Y. Huang, Y. Yao, D. Chu, H. Tong and X. Guo, *Applied Surface Science*, 2020, **531**, 147245.

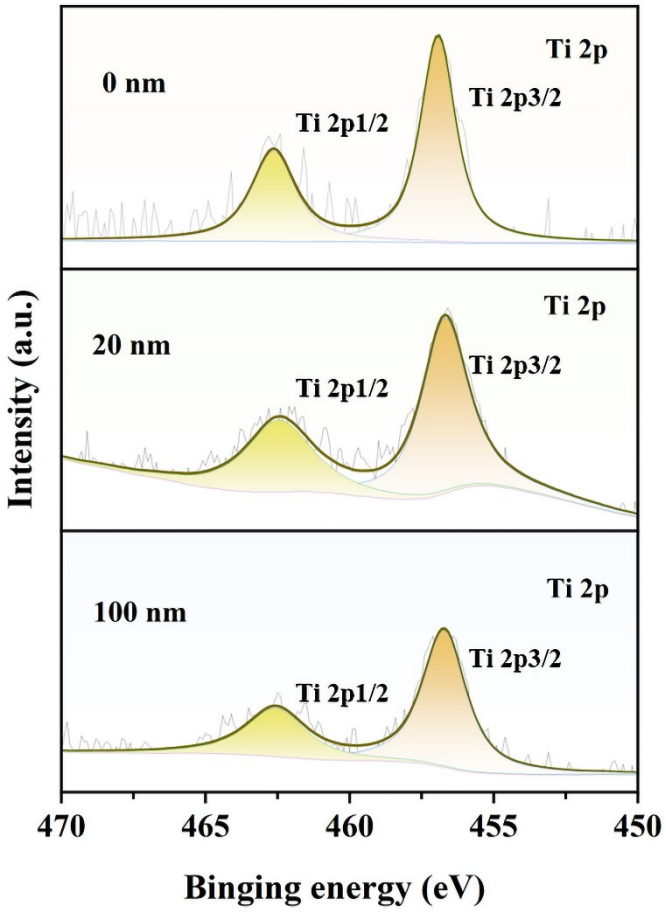

Fig. S1 Ti 2p XPS spectra of LLTP@LNCM at different Ar^+ etching depths (0 nm, 20 nm, and 100 nm).

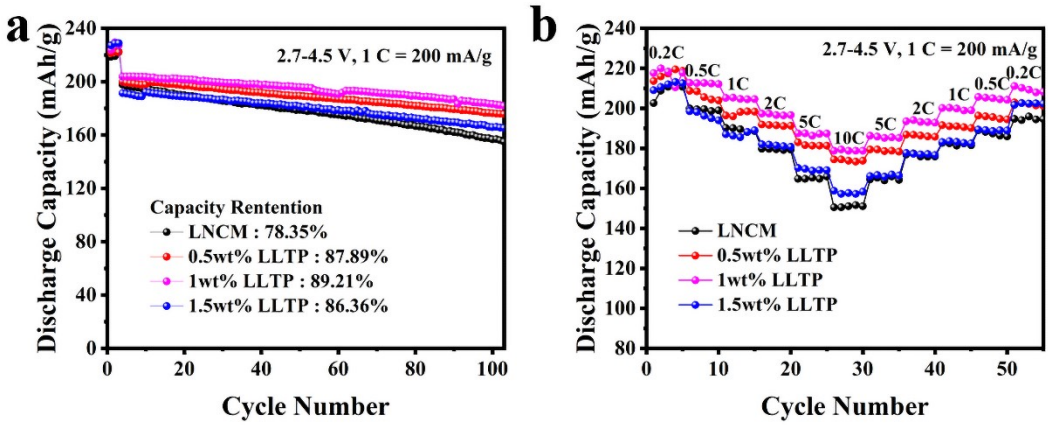

Fig. S2 Electrochemical performance of LNCM and LLTP@LNCM with different coating amounts (0.5 wt.%, 1.0 wt.%, and 1.5 wt.%): (a) Cycling performance at 1 C between 2.7–4.5 V, with capacity retention values labeled; (b) Rate capability at various current densities (0.2 C to 10 C).

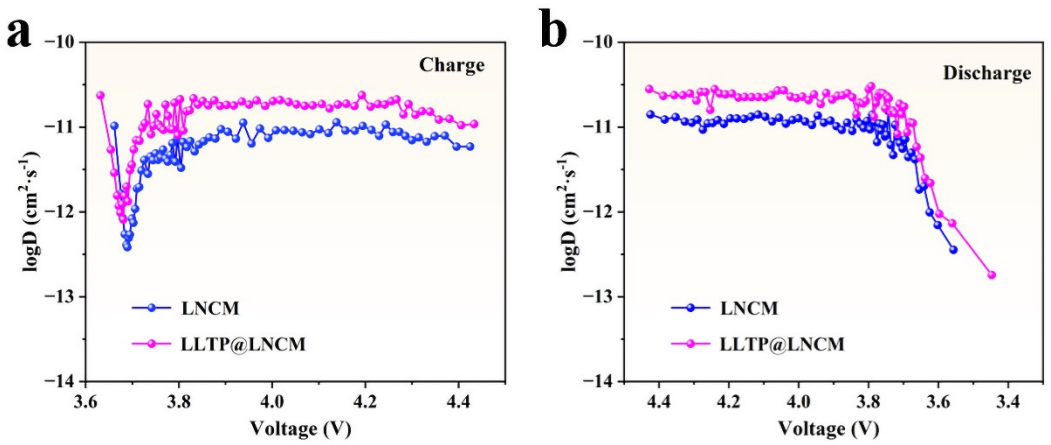

Fig. S3 Li^+ diffusion coefficients as a function of voltage for LNCM and LLTP@LNCM during (a) charge and (b) discharge processes.

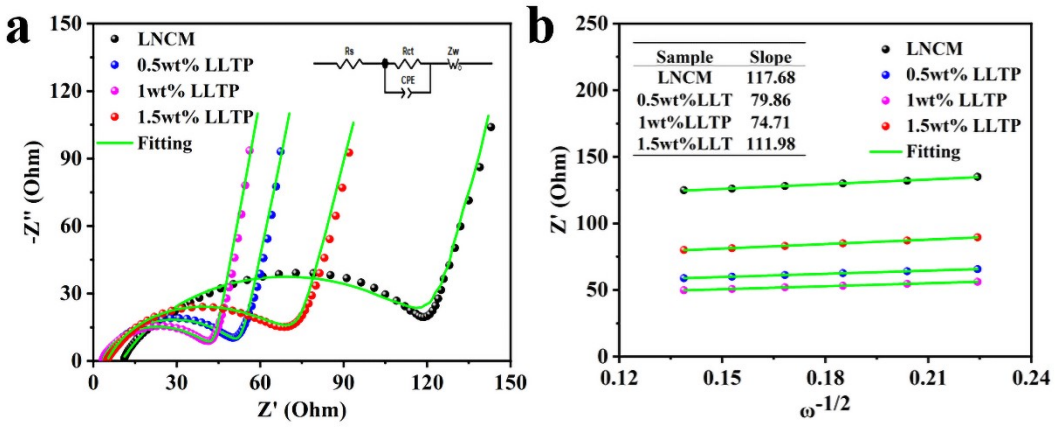

Fig. S4 EIS of LNCM and LLTP@LNCM with different coating amounts: (a) Nyquist plots with equivalent circuit fitting; (b) Linear fitting of Z′ vs. $\omega^{-1/2}$ to extract the Warburg factor (slope), which correlates with Li^+ diffusion kinetics.

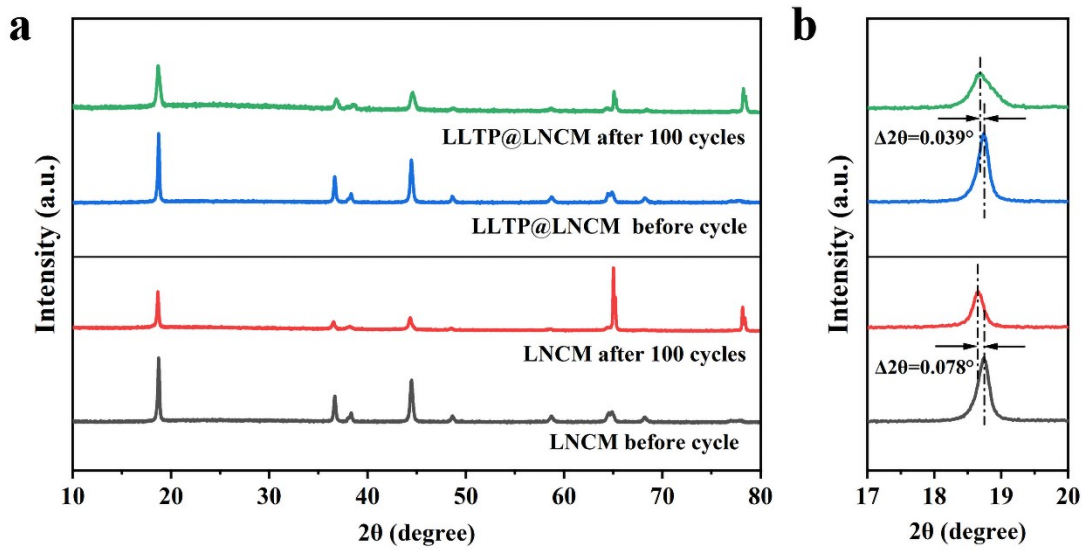

Fig. S5 Structural stability of LNCM and LLTP@LNCM before and after 100 cycles: (a) Full XRD patterns; (b) Magnified view of the (003) peak, showing the 2θ shift (Δ2θ) induced by cycling.