

Supporting Information

A uniform and high-voltage stable LiTMPO₄ coating layer enabled high performance LiNi_{0.8}Co_{0.15}Mn_{0.05}O₂ towards boosting lithium storage

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1. Experimental

1.1 Material preparation

Spherical nickel rich $\text{Ni}_{0.8}\text{Mn}_{0.15}\text{Co}_{0.05}(\text{OH})_2$ precursors were prepared by a mixed hydroxide co-precipitation method using a continuously stirred tank reactor under N_2 atmosphere. The transition metal solution was prepared by using metal sulfate of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot 9\text{H}_2\text{O}$ with a molar ratio of 80:15:5 and concentration of 2 mol L^{-1} . The NH_4OH and NaOH solutions were prepared with concentration of 0.3 mol L^{-1} and 4 mol L^{-1} , respectively. Then, the TM solution, ammonia solution, and sodium hydroxide solution were slowly added into reaction vessel to produce co-precipitates. The pH value (11), stirring speed (500 revolutions per minute) and temperature ($50 \text{ }^\circ\text{C}$) were carefully controlled during the precipitation process. The total reaction time was set as 24 h.

LiTMPO_4 (mainly LiNiPO_4), coated $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$ cathodes was prepared as follows: 5g $\text{Ni}_{0.8}\text{Mn}_{0.15}\text{Co}_{0.05}(\text{OH})_2$ precursor was poured into 20 ml (0.01 mol L^{-1}) phytic acid aqueous solution ($\text{C}_6\text{H}_{18}\text{O}_{24}\text{P}_6$), and followed by stir intensely at $60 \text{ }^\circ\text{C}$. After that, the precipitates were washed and dried. The collected powders mixed with appropriate amount of $\text{LiOH} \cdot \text{H}_2\text{O}$ (excess of 3 %) and heat-treated at $500 \text{ }^\circ\text{C}$ for 3 h and $780 \text{ }^\circ\text{C}$ for 16 h under O_2 atmosphere to form $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$. The common and modified cathode were denoted as NMC and NMC@LTMP, The NMC@LTMP1, NMC@LTMP2 and NMC@LTMP3 represents that the mixing time of precursor and phytic acid solution is 30, 90 and 150 min, respectively. The pure phase coating material LiNiPO_4 was synthesized by mixing $\text{Ni}(\text{OH})_2$ and excess phytic acid solution, then heat-treated at $650 \text{ }^\circ\text{C}$ for 8 h under Ar atmosphere.

1.2 Characterization methods

The morphology and particle size were observed using scanning electron microscopy (SEM) measurements and the element distribution was confirmed by conducting energy dispersive spectrometer (EDS) tests. High resolution transmission electron microscope (HR-TEM) was gotten to verify the element distribution and specific crystallographic planes. The structure was characterized by X-ray diffraction (XRD) testing. The Rietveld method was used to refine XRD date. The surface property was characterized by X-ray photoelectron spectroscopy (XPS). The composition and transition metal ion (Ni, Co and Mn) concentration were verified by conducting inductively coupled plasma (ICP) measurements. To confirm the presence of transition metal in the electrolyte after extensive cycling. The cycled cathode was harvested and disassembled in the argon-filled glovebox. All components of the cell were washed in 10 mL EC/DEC solvent for 3 d, then, 2 mL of the solution was diluted in 2 ml HNO_3 (65-68 %) and heated at $80 \text{ }^\circ\text{C}$ to evaporate the solvent. The white crystals obtained were

collected and dissolved in 50 mL deionized water to measure transition metal content. The thermal stability of charged cathodes was evaluated by differential scanning calorimeter (DSC). The cathodes were first charged to 4.5 V at 0.2 C and then held at 4.5 V for an additional 1 h. The cathode materials were next collected from disassembled cells, rinsed with DMC to remove residual electrolytes and dried at 60 °C under vacuum for 2 h. Charged cathode powders (~ 5 mg) were placed in a hermetic aluminum pan and the temperature was increased from the ambient condition to 300 °C at a constant heating rate of 10 °C min⁻¹.

1.3 Electrochemical test

The electrochemical performance of prepared cathode powder was tested using half cells with a lithium foil as negative electrode. The preparation of electrode is as follows: 80 wt% active materials, 10 wt% acetylene black and 10 wt% polyvinylidene fluoride were blended using N-methyl pyrrolidone (NMP) as a solvent. Then the mixture was coated on an aluminum foil using a scraper. The electrode sheet was dried at a vacuum drying oven at 80 °C for 24 h. Then the electrode sheet was cut into small disks with about 2 cm². The loading level of all negative electrodes was ~5 mg cm⁻². The preparation of cathode materials for full-cell fabrication was the same as that of half-cells. The pouch type full-cells with a 1.15:1 N/P capacity ratio with dimensions of 8 cm × 7 cm were assembled using pouch-cell production machine, and the same electrolyte was used. The charge-discharge tests were operated on cell test instruments (LAND CT-2001A). The impedance tests of cells were carried out on the Chenhua electrochemical workstation. The frequencies ranges from 100 kHz to 0.01 Hz and the fluctuation voltage is 5 mV.

2. Supplementary Figures

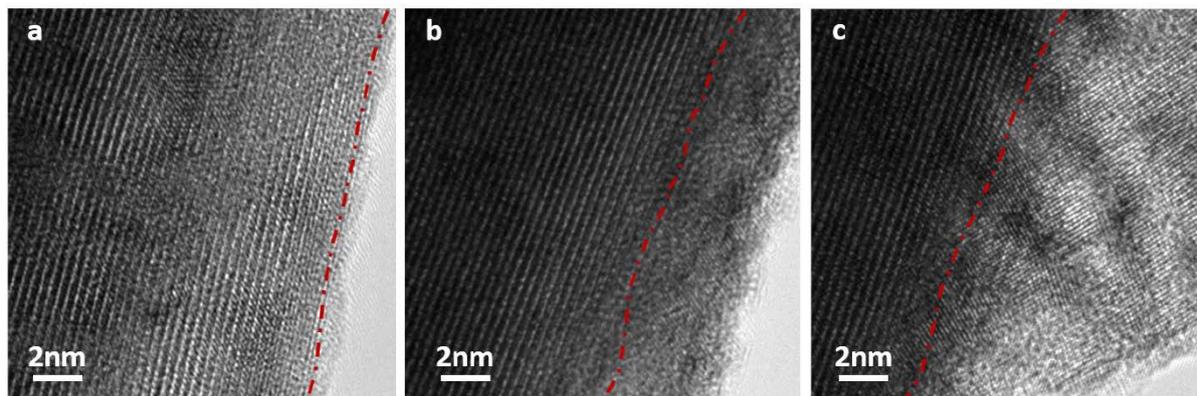


Fig. S1 HR-TEM images of (a) NMC@LTMP1, (b) NMC@LTMP2 and (c) NMC@LTMP3.

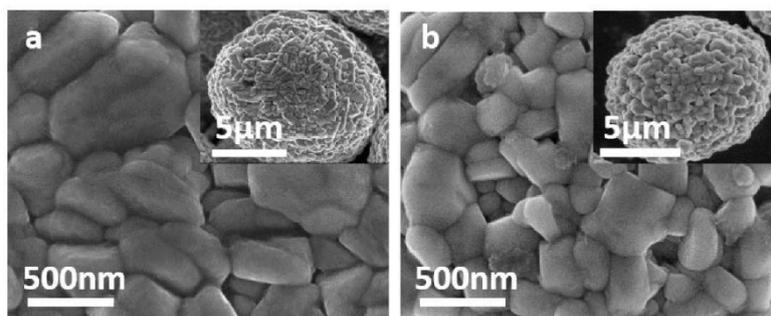


Fig. S2 SEM images of (a) NMC@LTMP2 and (b) pristine NMC. Insets: lower-magnification SEM images showing the morphology of the NMC secondary particles.

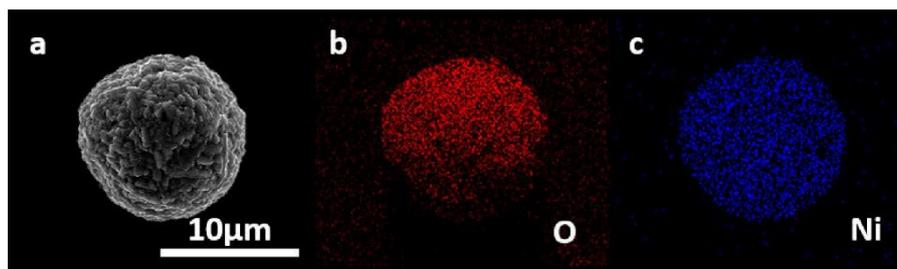


Fig. S3 (a) SEM images and (b and c) EDS mappings of pristine NMC.

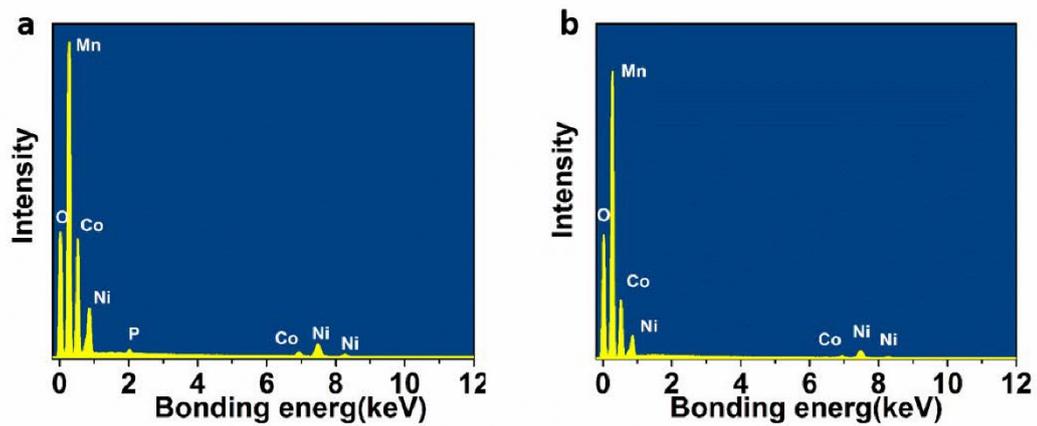


Fig. S4 The EDS spectra of (a) NMC@LTMP2 and (b) pristine NMC.

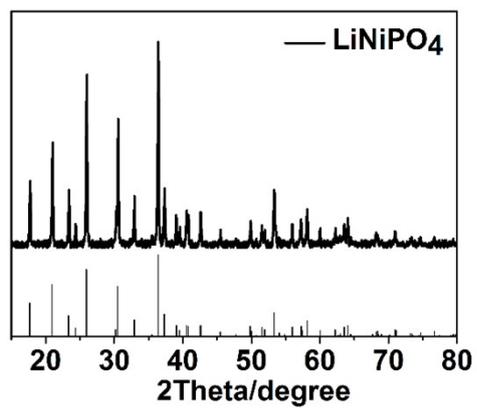


Fig. S5 XRD patterns of bare LiNiPO₄ material.

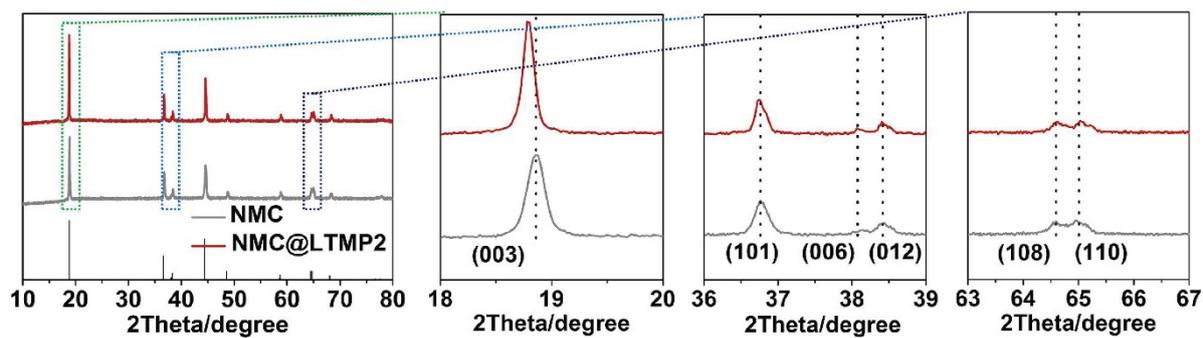


Fig. S6 XRD patterns of pristine NMC and NMC@LTMP2, and the magnification region of (003), (101)/(006)/(012) and (108)/(110) peak.

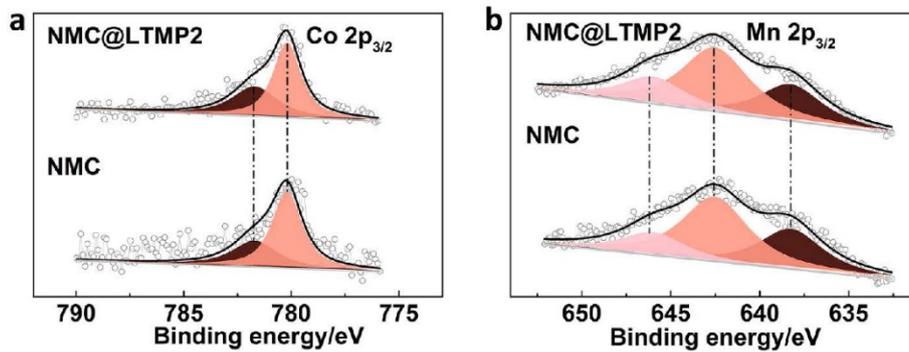


Fig. S7 The (a) Co 2p and (b) Mn 2p XPS spectrum of NMC@LTMP2 and pristine NMC.

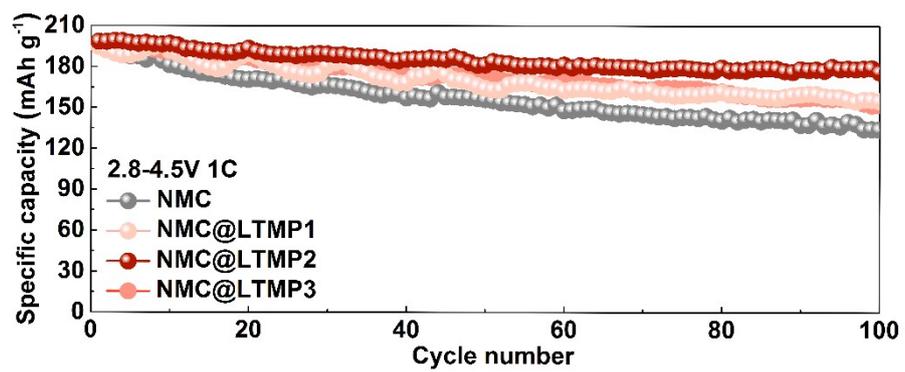


Fig. S8 Cycling performance of pristine NMC and different NMC@LTMP samples at 1 C (1 C defined as 200 mA g⁻¹)

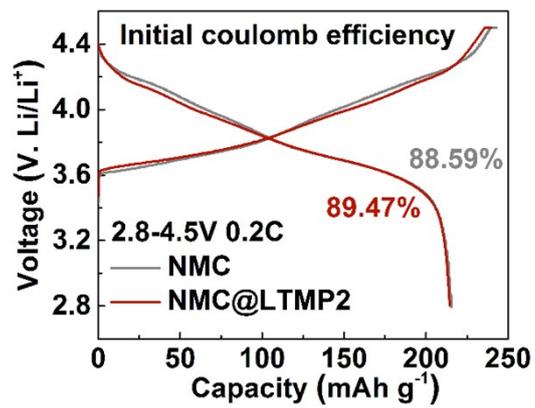


Fig. S9 The first charge-discharge curves at 0.2 C of pristine NMC and NMC@LTMP2.

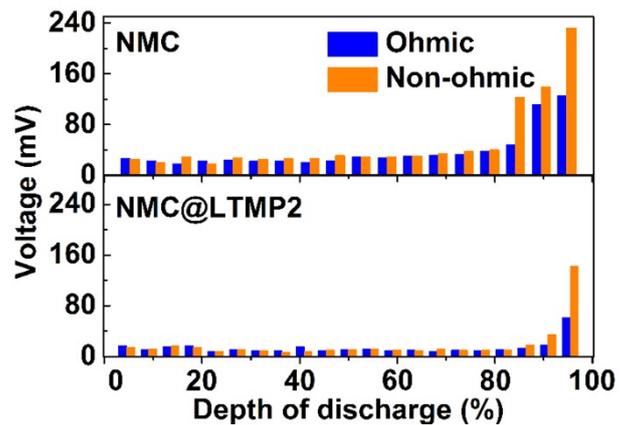


Fig. S10 The ohmic and non-ohmic voltage losses over different GITT steps of NMC@LTMP2 and pristine NMC.

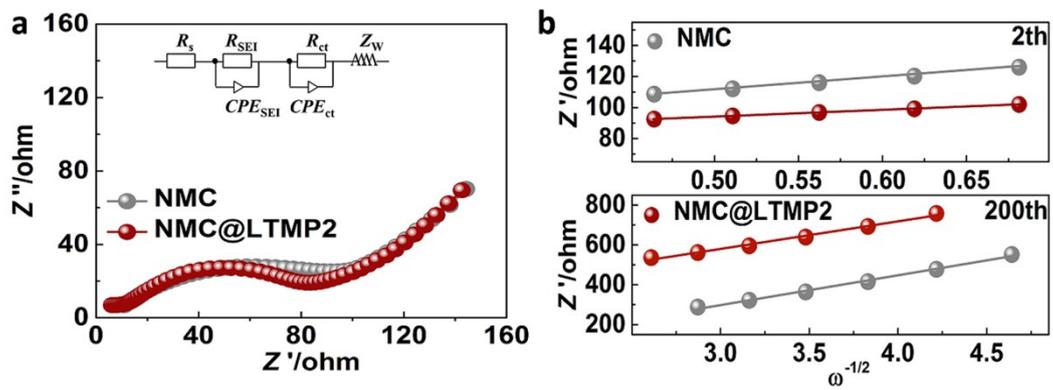


Fig. S11 (a) The EIS measurements of NMC@LTMP2 and pristine NMC after 2th cycles. (b) The relationships between Z'_{re} and $\omega^{-1/2}$ based on the 2th and 200th cycles.

3. Supplementary Tables

Table S1 Element composition of the bulk particles for as-prepared materials by ICP.

Sample	Ni	Co	Mn	P
NMC@LTMP2	0.8132	0.1490	0.0378	0.0023
NMC	0.8120	0.1499	0.0381	--

Table S2 The refinement data for NMC@LTMP2 and pristine NMC.

Sample	Site (Li)	Site (Ni)	Site (O)	a (Å)	c (Å)	χ^2	R_p	R_{wp}
NMC@LTMP2	3b	3a	6c	2.872(2)	14.188(2)	2.14	0.027	0.035
NMC	3b	3a	6c	2.866(1)	14.168(2)	1.79	0.026	0.032

Table S3 The values of R_s , R_{CEI} , R_{ct} , and D_{Li^+} for cycled electrodes.

Sample	Cycle	$D_{\text{Li}^+}/(\text{cm}^2 \text{ s}^{-1})$	R_s / Ω	R_{CEI} / Ω	R_{ct} / Ω
NMC@LTMP2	2th	8.62×10^{-12}	6.02	37.46	75.98
	200th	1.13×10^{-13}	4.50	39.90	78.60
NMC	2th	2.69×10^{-12}	6.18	44.05	81.99
	200th	1.32×10^{-14}	3.75	124.25	154.00

