## Supplementary Information

## $\ensuremath{\mathsf{Nano-LiNbO_3}}\xspace$ coating layer and diffusion-induced surface control

## towards high-performance 5-V spinel cathodes for rechargeable

## batteries

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**Fig. S1** Field-emission SEM images of (a) pristine  $LiNi_{0.5}Mn_{1.5}O_4$ , (b) 1 wt.%, (c) 3 wt.% and (d) 5 wt.%  $LiNbO_3$ -coated  $LiNi_{0.5}Mn_{1.5}O_4$ .



Fig. S2 XRD patterns of the 10 wt.% LiNbO<sub>3</sub>-coated LNMO and LiNbO<sub>3</sub>.



Fig. S3 XPS full-scan spectra of pristine LNMO and various amounts of LiNbO<sub>3</sub>-coated LNMO.



**Fig. S4** Rietveld refined XRD patterns of pristine LNMO and various amount of LiNbO<sub>3</sub>-coated LNMO. The black and red lines represent the experimental and calculated data, respectively. The blue line is the difference curve. The Bragg peak positions of each phase are indicated by the short vertical dark green lines.



**Fig. S5** Initial charge-discharge voltage profiles at 0.1 C of pristine LNMO and various amount of  $LiNbO_3$ -coated LNMO in the potential range of 3.5–4.9 V (vs.  $Li/Li^+$ ).



**Fig. S6** Discharge capacity contributions of  $Ni^{4+}/^{2+}$  and  $Mn^{4+}/^{3+}$  calculated from the initial charge-discharge voltage profiles in Fig. S5.



**Fig. S7** Charge-discharge voltage profiles with Coulombic efficiency (%) of pristine LNMO and various amount of LiNbO<sub>3</sub>-coated LNMO for 3 cycles at 0.1 C.

**Table S1** Electronic conductivities for the pristine LNMO and various amount of  $LiNbO_3$ -coatedLNMO.

Sample	Conductivity (S cm <sup>-1</sup> )
Pristine LNMO	2.09 × 10 <sup>-7</sup>
1 wt.% LiNbO3-LNMO	1.35 × 10 <sup>-6</sup>
3 wt.% LiNbO <sub>3</sub> -LNMO	1.27 × 10 <sup>-6</sup>
5 wt.% LiNbO₃-LNMO	9.79 × 10 <sup>-7</sup>



Fig. S8 XPS depth profiles of before and after 100 cycled electrodes at  $60^{\circ}$ C for (a,b) pristine

 $LiNi_{0.5}Mn_{1.5}O_4$  and (c,d) 1 wt.%  $LiNbO_3\text{-}coated\ LiNi_{0.5}Mn_{1.5}O_4.$ 

 Table S2 The result of inductively coupled plasma optical emission spectrometry (ICP-OES) of

Cathode	Deposited Mn on Li metal anode (ppm)
	Mn
Pristine LNMO	183.7
1 wt.% LiNbO3-LNMO	90.17
3 wt.% LiNbO <sub>3</sub> -LNMO	86.37
5 wt.% LiNbO <sub>3</sub> -LNMO	46.68

Li metal anodes after 100 cycled at 60°C.