

Supporting Information

Investigation of the structure and performance of
 $\text{Li}[\text{Li}_{0.13}\text{Ni}_{0.305}\text{Mn}_{0.565}]\text{O}_2$ Li-rich cathode materials derived from a
eco-friendly and simple coated techniques

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Experimental Section

Preparation of the precursor of Li rich cathode material $\text{Li}[\text{Li}_{0.13}\text{Ni}_{0.305}\text{Mn}_{0.565}]\text{O}_2$.

The precursor was prepared by co-precipitation method. 2 M $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ mixed solution was continually pumped into a stirring tank reactor (50 L); then 4 M NaOH solution and 0.2 M NH_4OH solution were pumped into the reactor, separately. The reaction temperature was controlled at 55 °C and the value of pH was 10.75.

Preparation of Li rich cathode material $\text{Li}[\text{Li}_{0.13}\text{Ni}_{0.305}\text{Mn}_{0.565}]\text{O}_2$.

$\text{Li}[\text{Li}_{0.13}\text{Ni}_{0.305}\text{Mn}_{0.565}]\text{O}_2$ were synthesized via solid state reaction of Li_2CO_3 and precursor. The precursor was prepared by co-precipitation method (in the Supporting Information). The precursor and Li_2CO_3 was mixed well by ball milling. Afterwards, the mixture was calcined at 920 °C for 10 h under air atmosphere to obtain $\text{Li}[\text{Li}_{0.13}\text{Ni}_{0.305}\text{Mn}_{0.565}]\text{O}_2$.

Fabrication of Al_2O_3 -Coated Li rich cathode material by DPC.

First the different quantities of Al_2O_3 (0 g, 5g, 10 g, 15 g) were prepared. Then the LLNM (1000 g) and the different amount Al_2O_3 were mixed into mixing pelletizer and stirred for 10 minutes, respectively. Afterwards, these mixed samples were calcined at 350°C for 2 h under air atmosphere and labeled as LLNM-A0, LLNM-A5, LLNM-A10 and LLNM-A15.

Materials Characterization

Crystal structure of the synthesized powders was characterized by X-ray diffraction (XRD, AXS D8 Advance, Bruker) with Cu $K\alpha$ radiation. Particle morphology was

conducted with a scanning electron microscope (SEM, SU-8010F, HITACHI) equipped with an energy dispersive spectroscope (EDS). Microstructural properties were obtained using high-resolution transmission electron microscopy (HR-TEM, Tecnai G2 F20, FEI). X-ray photoelectron spectroscopy analysis (XPS) was determined by a Kratos Axis Ultra spectrometer with a monochromatic Al K α radiation ($h\nu = 1486.6$ eV). LLNM Li-rich cathode materials with Al₂O₃ coating were prepared through DPC (NSEG-450).

Electrochemical Measurements

For electrochemical evaluation, the Al₂O₃ coating LLNM working electrode was manufactured: the active material acetylene black and polyvinylidene fluoride (PVDF) binder were mixed into N-methyl-2-pyrrolidone (NMP) at a weight ratio of 8:1:1. Whatman Glass Fiber was used as the separator, and Lithium metal was employed as the counter and reference electrode. 1M LiPF₆ dissolved in the ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume) solution was employed as the electrolyte. Galvanostatic charge-discharge experiment data was collected using LAND Cell test system (CT2001A, Wuhan). The batteries were cycled at 0.1 C rate in the first three cycles and then cycled at 1 C rate; AC impedance measurements were performed by an electrochemical workstation (CHI660E, Shanghai). A perturbation of 5 mV was applied and the frequency range applied is from 0.1 Hz to 100 KHz.

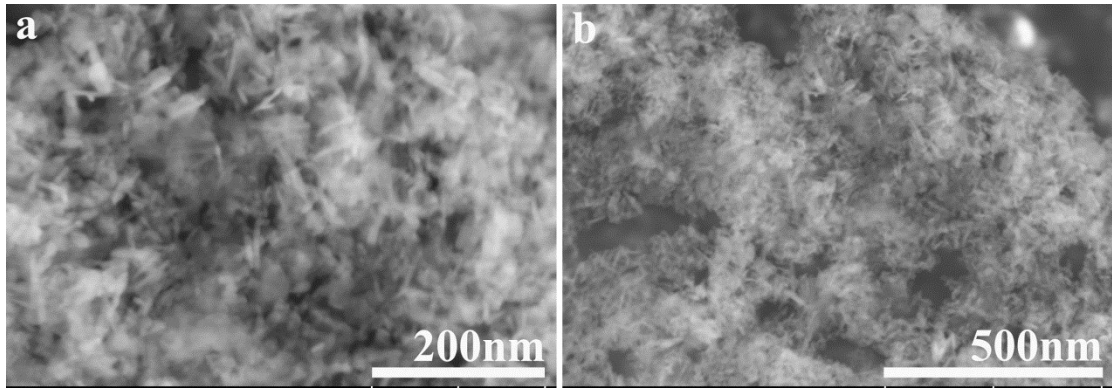


Figure S1. FESEM images of Al₂O₃

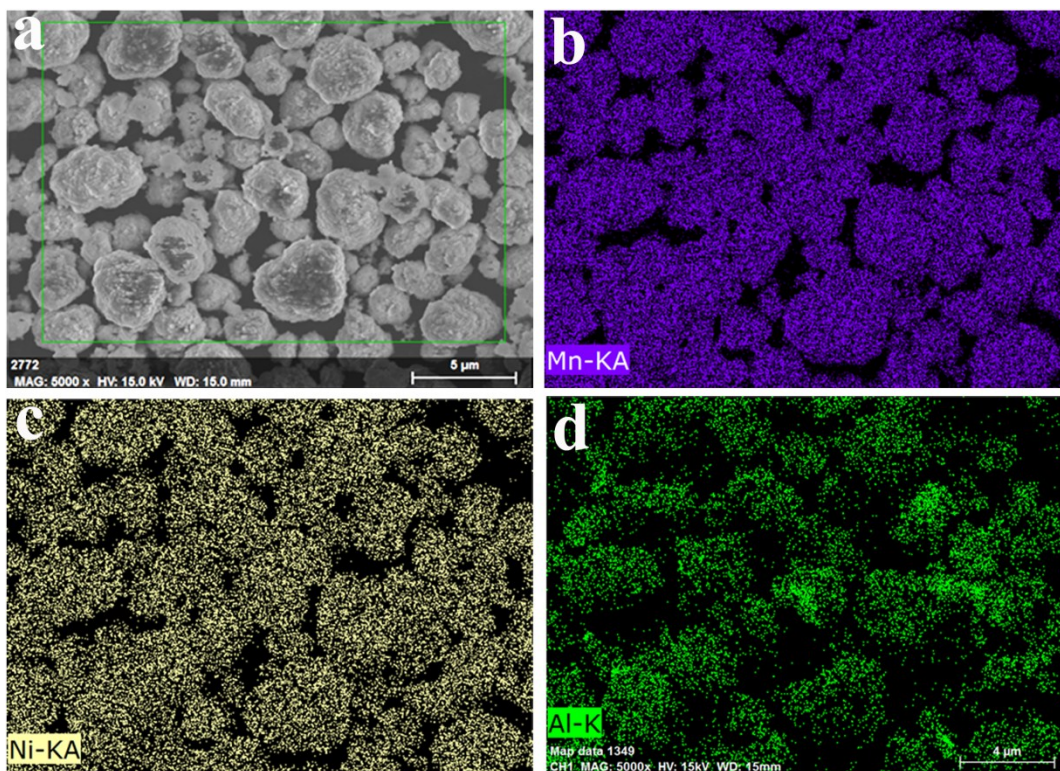


Figure S2. SEM and element mappings of LLNM-A10 (a-d).



Figure S3. TEM element mappings of LLNM-A10 (a-e).

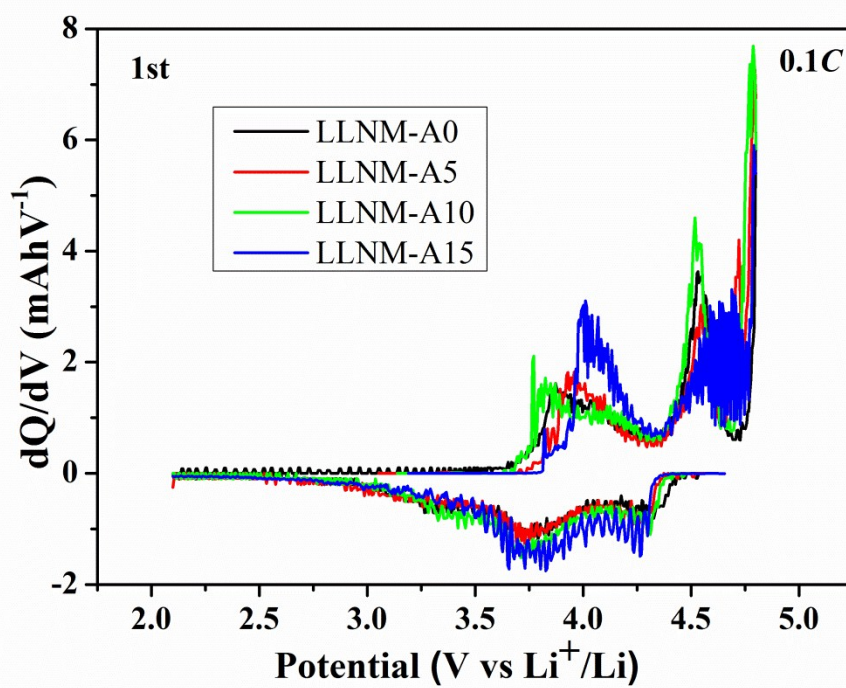


Figure S4. Differential capacity vs. voltage curves of the pristine and the coated LLNM cathode materials at 0.1 C for the first cycle.

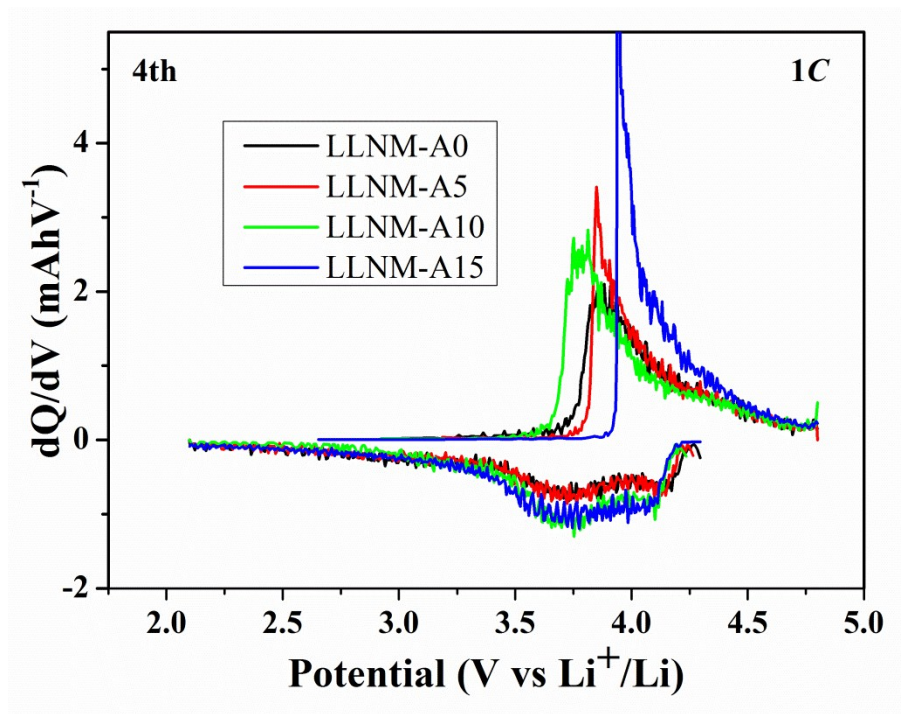


Figure S5. Differential capacity vs. voltage curves of the pristine and the coated LLNM cathode materials at 1 C for the 4th cycle.

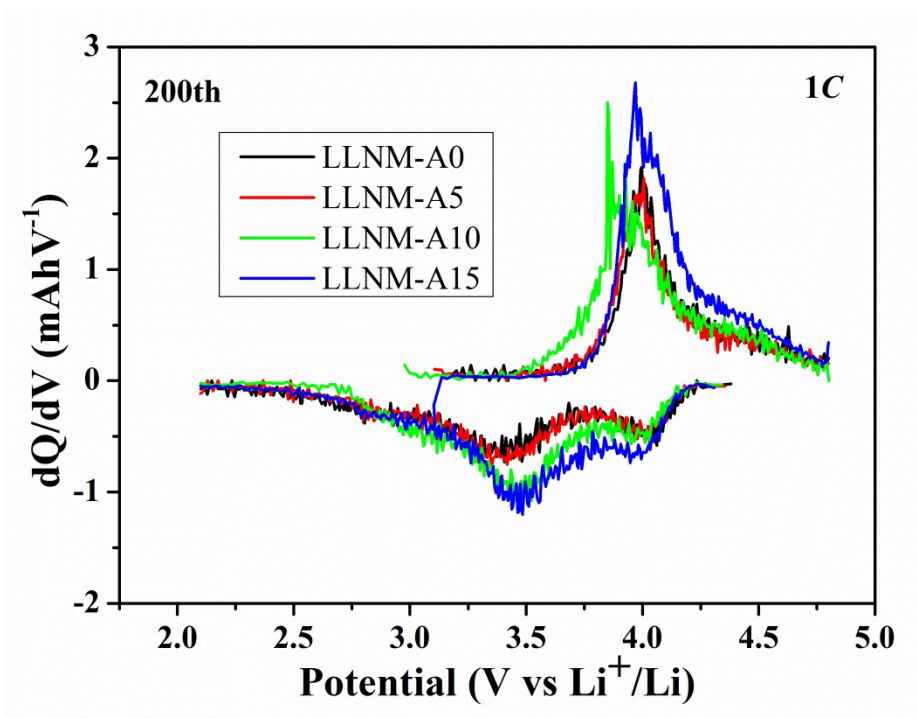


Figure S6. Differential capacity vs. voltage curves of the pristine and the coated LLNM cathode materials at 1 C for the 200th cycle.

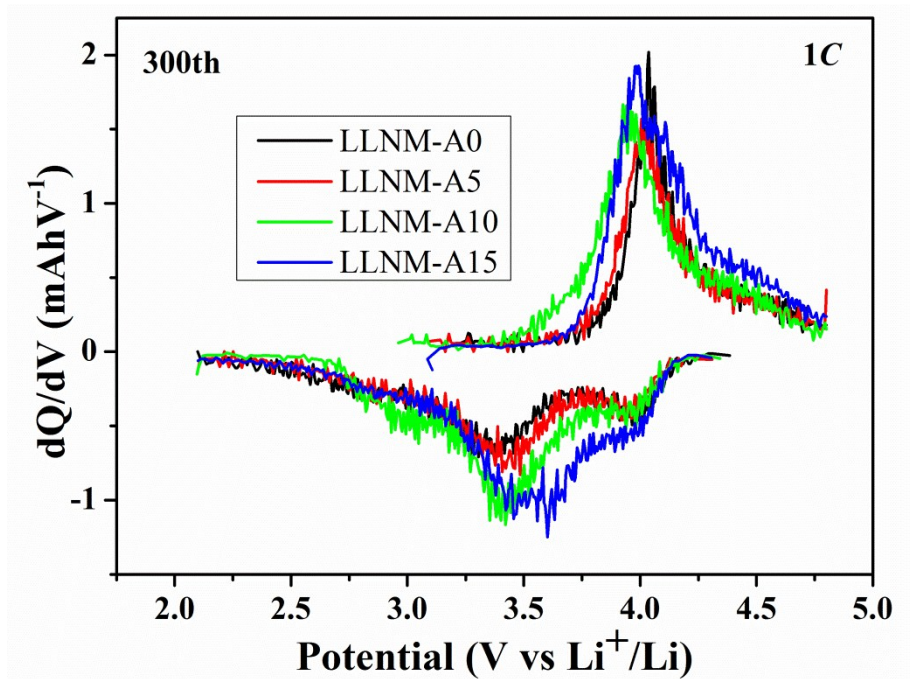


Figure S7. Differential capacity vs. voltage curves of the pristine and the coated LLNM cathode materials at 1 C for the 300th cycle.

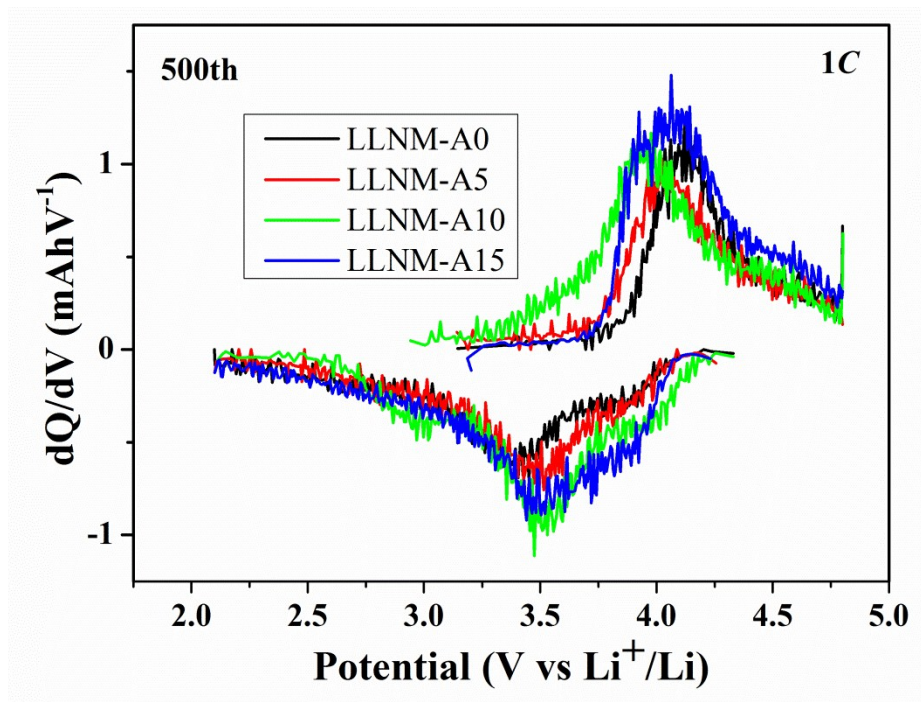


Figure S8. Differential capacity vs. voltage curves of the pristine and the coated LLNM cathode materials at 1 C for the 500th cycle.

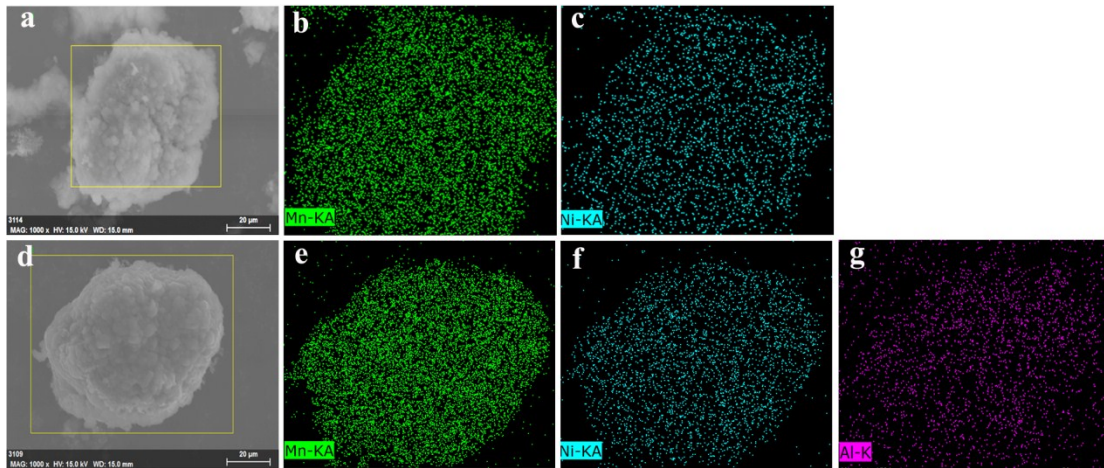


Fig. S9. SEM and element mappings of coating samples of LLNM-A0 (a, b, c) and LLNM-A10 (d, e, f, h, g) after 500 cycles.

Table S1. Comparison of the cycling performance among Al₂O₃ coated Li-rich cathode materials

Coated methode	reversible capacity (mAhg ⁻¹)	cycle number	Voltage (V)	rate (mA g ⁻¹)	ref.
Chemical solution	228	60	2.0-4.8	0.1C (1C = 250)	1
Freeze Drying	~157	150	3.0-4.3	1C (1C = 200)	2
Sol-gel	170	100	2.0-4.8	1C (1C = 200)	3
ALD	120	20	2.0-4.8	1C (1C = 240)	4
(This work)	170.7	100	2.1-4.8	1C (1C = 300)	-
	153.8	500	2.1-4.8	1C (1C = 300)	-

References

- [1] Wen, X. F.; Liang, K.; Tian, L. Y.; Shi, K. Y.; Zheng, J. S. Al₂O₃ coating on Li_{1.256}Ni_{0.198}Co_{0.082}Mn_{0.689}O_{2.25} with spinel–structure interface layer for superior performance lithium ion batteries. *Electrochi. Acta*, 2018, 260, 549–556.
- [2] Wang, J. P.; Du, C. Y.; Yan, C. Q.; He, X. S.; Song, B.; Yin, G. P.; Zuo, P. J.; Cheng, X. Q. Al₂O₃ Coated Concentration-Gradient Li[Ni_{0.73}Co_{0.12}Mn_{0.15}]O₂ Cathode Material by Freeze Drying for Long-Life Lithium Ion Batteries. *Electrochi. Acta*, 2015, 174, 1185–1191.
- [3] Zhang, W. X.; Liu, Y. T.; Wu, J. L.; Shao, H. X.; Yang, Y. F. Surface modification of Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O₂ cathode material with Al₂O₃/SiO₂ composite for lithium–ion batteries. *J. Electrochem. Soc.*, 2019, 166 (6), 863–872.
- [4] Dannehl, N.; Steinmuller, S. O.; Szabo, D. V.; Pein, M.; Sigel, F.; Esmezjan, L., Hasenkox, U.; Schwarz, B.; Indris, S.; Ehrenberg, H. High–resolution surface analysis on aluminum oxide–coated Li_{1.2} Mn_{0.55}Ni_{0.15}Co_{0.1}O₂ with improved capacity retention. *ACS Appl. Mater. Interfaces*, 2018, 10 (49), 43131–43143.