

Supplementary Information

Overcoming the Chemical Instability on Exposure to Air of Ni-rich Layered Oxide Cathodes by Coating with Spinel $\text{LiMn}_{1.9}\text{Al}_{0.1}\text{O}_4$

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Experimental section

Preparation of LNCM material. To prepare the hydroxide precursor $\text{Ni}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}(\text{OH})_2$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ were dissolved in a molar ratio of Ni : Co : Mn = 70 : 15 : 15 in distilled water at a combined concentration of 1 M. A 2.5 L continuously stirring tank reactor (CSTR) was used for the co-precipitation reaction, and an appropriate amount of saturated NH_4OH and KOH were added in order to reach the initial condition. Subsequently, the mixed-metal solution was fed separately into the CSTR along with 2 M KOH aqueous solution under N_2 atmosphere. During the reaction, the pH (= 11), the amount of NH_4OH added as a chelating agent, and the temperature (50 °C) were monitored and adjusted carefully. The total feed rate was regulated to assure an average residence time of 4 – 12 h in the reactor. The co-precipitated particles were filtered, washed, and dried at 120 °C under vacuum for 24 h to obtain the $\text{Ni}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}(\text{OH})_2$ precursor. The prepared precursor was then mixed with $\text{LiOH} \cdot \text{H}_2\text{O}$ at a molar ratio of 1: 1.03 and preheated at 500 °C for 5 h and then calcined at 800 °C for 15 h to obtain the Ni-rich layered oxide $\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ (denoted as the LNCM).

Coating process. The as-prepared LNCM sample was mixed with the coating precursor consisting of a desired amount of $\text{Li}(\text{CH}_3\text{COO}) \cdot 2\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO}) \cdot 4\text{H}_2\text{O}$, and $\text{Al}(\text{OH})(\text{C}_2\text{H}_3\text{O}_2)_2$ in ethanol solvent. After stirring for 30 min, the coating solution was dried at 120 °C for 10 h in air. The obtained material was then fired at 700 °C for 5 h.

Electrochemical tests. The electrochemical performances of the different samples were assessed with a coin-type (2032R) half-cell with a lithium-metal anode. The electrolyte consisted of 1 M LiPF_6 in ethylene carbonate (EC) / dimethyl carbonate (DMC) (1 : 1 vol. %). The

cathode electrode consisted of Super P carbon black, polyvinylidene fluoride (PVDF) binder, and active material, in a weight ratio of 1 : 1 : 8 with the active material loaded at 4.0 – 4.5 mg cm⁻².

Table S1. Quantitative comparison of the LiOH and Li₂CO₃ amounts before and after exposing LNCM to air

	Li ₂ CO ₃ (wt. %)	LiOH (wt. %)
Fresh LNCM	0.89	0.25
LNCM after exposing to air for 3 months	1.82	0.44

The amounts of Li₂CO₃ and LiOH were determined quantitatively by a potentiometric titrator (888 Titrand, Metrohm). For the analysis, the powders were washed with deionized water and the solution was filtered to remove the active material. The filtrate was then titrated with the potentiometric titrator to measure the amounts of LiOH and Li₂CO₃. As seen in Table S1, the amounts of Li₂CO₃ and LiOH have increased on exposing to air.

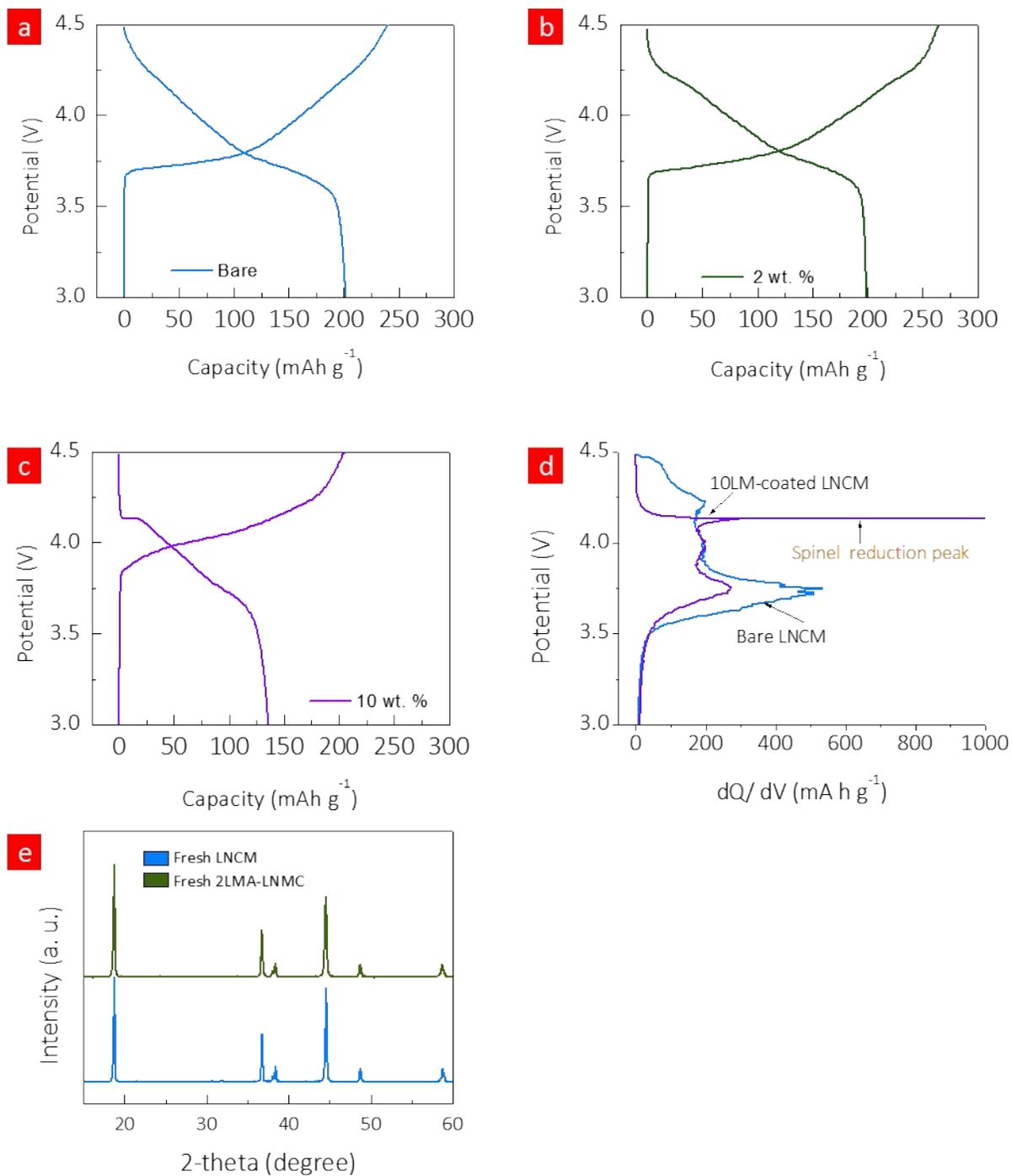


Fig. S1 Voltage profiles of the initial cycle of (a) the bare LNCM, (b) 2 wt. % LiMn_{1.9}Al_{0.1}O₄-coated LNCM, and (c) 10 wt. % LiMn_{1.9}Al_{0.1}O₄-coated LNCM. (d) Differential capacities of bare

LNCM and 10 wt. % $\text{LiMn}_{1.9}\text{Al}_{0.1}\text{O}_4$ -coated LNCM. (e) X-ray diffraction (XRD) data of fresh LNCM and 2LMA-LMMC sample.

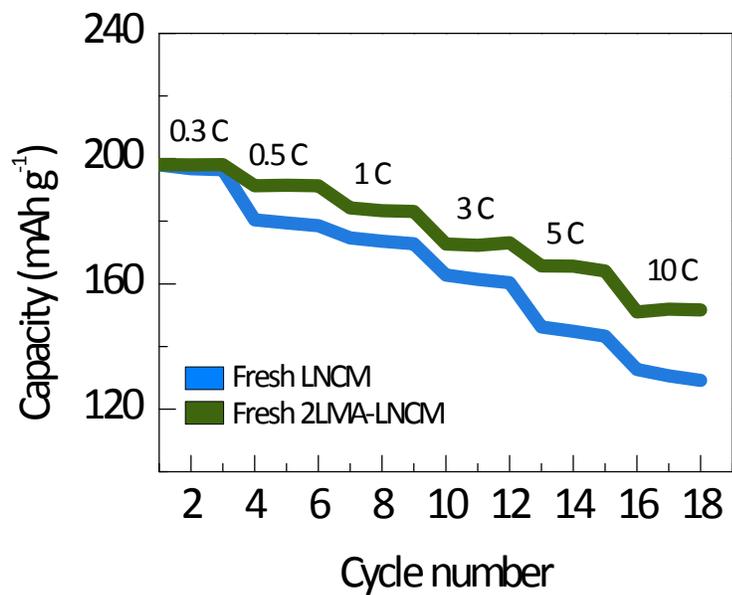


Fig. S2 Rate capabilities of fresh LNCM and 2LMA-LNCM samples with various C rate from 0.3C to 10C rate.