

## Cobalt/aluminum co-substitution in $\text{LiNi}_{0.9}\text{Mn}_{0.1}\text{O}_2$ layered cathode for improving kinetics

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### Experimental sections

**Preparation of  $\text{LiNi}_{0.84}\text{Mn}_{0.10}\text{Co}_{0.03}\text{Al}_{0.03}\text{O}_2$  (CA-NM).** The cathode material of  $\text{LiNi}_{0.84}\text{Mn}_{0.10}\text{Co}_{0.03}\text{Al}_{0.03}\text{O}_2$  was synthesized by a coprecipitation process. Typically, the mixed solution of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{NaAlO}_2$  with a molar ratio of Ni:Mn:Co:Al = 8.4:1.0:0.3:0.3 was pumped into a continuously stirred reactor through a peristaltic pump under inertial  $\text{N}_2$  atmosphere. Meanwhile, the NaOH solution and the  $\text{NH}_4\text{OH}$  solution were continuously pumped into the reactor. After reaction, the  $\text{Ni}_{0.84}\text{Mn}_{0.10}\text{Co}_{0.03}\text{Al}_{0.03}(\text{OH})_2$  precursor was obtained via filtering, washing, and drying. Then, we put the precursor mixed with  $\text{Li}(\text{OH})_2 \cdot \text{H}_2\text{O}$  in a molar ratio of 1:1.03, and calcined at 800 °C for 15 h in  $\text{O}_2$  atmosphere to obtain CA-NM material. Additionally, the  $\text{LiNi}_{0.9}\text{Mn}_{0.1}\text{O}_2$  (NM) was prepared at the same condition as CA-NM except for the constitution.

**Material characterization.** The crystal structure was identified by X-ray diffraction (XRD: Empyrean2, PANalytical). Scanning electron microscopy (SEM: MIRA4 LMH, TESCAN), transmission electron microscopy (TEM: Tecnai G2F20, FEI) and electron-probe micro-analysis

(EPMA: JXA-8530F PLUS, JEOL) were utilized to detect the morphology, microstructure and element distribution, respectively. X-ray photoelectron spectroscopy (XPS: Nexsa, ThermoFisher) was used to explore the chemical state on the particle surface.

**Electrochemical measurement and battery testing.** CR2032 coin cells were used to perform the electrochemical properties. To obtain cathode, the as-prepared materials were mixed with poly(vinylidene fluoride) and carbon black with a mass ratio of 8:1:1, and dissolved in N-methyl-1,2-pyrrolidone solvent. Then, the slurry was dispersed on Al foil. After drying, it was cut into wafers with a diameter of 12 mm. Using lithium foil as counter electrodes, 1 M LiPF<sub>6</sub> in ethyl carbonate (EC)/dimethyl carbonate (DMC) /ethyl methyl carbonate (EMC) (1:1:1, in vol%) as electrolyte and celgard 2400 as separator were assembled in an argon-filled glove box. The galvanostatic charge and discharge tests were performed at a LAND CT2001A system. The galvanostatic intermittent titration technique (GITT) was performed at 0.1 C, and the equation for calculation of Li<sup>+</sup> diffusion coefficient can be expressed as:

$$D_{\text{Li}^+} = \frac{4}{\pi\tau} \left( \frac{m_B V_M}{M_B S} \right)^2 \left( \frac{\Delta E_s}{\Delta E_\tau} \right)^2$$

where  $\tau$  is the constant current pulse time,  $m$  is the mass of cathode material,  $V$  is the molar volume of cathode material,  $M$  is the molar mass of cathode material,  $S$  is the electrode area,  $\Delta E_s$  is the change of the steady state voltage,  $\Delta E_\tau$  is the voltage change during a constant current pulse. Moreover, cyclic voltammetry (CV) with a sweep rate of 0.1 mV s<sup>-1</sup> and electrochemical impedance spectra (EIS) with the frequency range of 100 KHz to 10 mHz were evaluated on a Bio-Logic EC-LAB SP-300 electrochemical instrument.

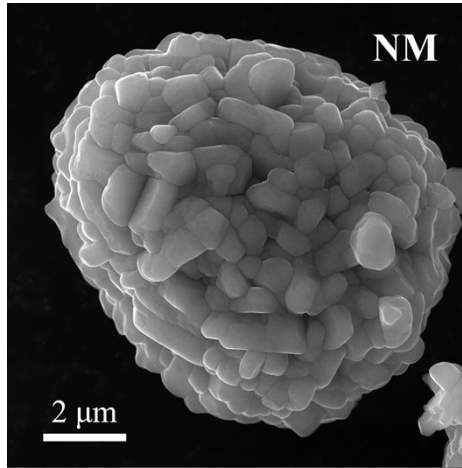


Fig. S1 SEM image of NM cathode.

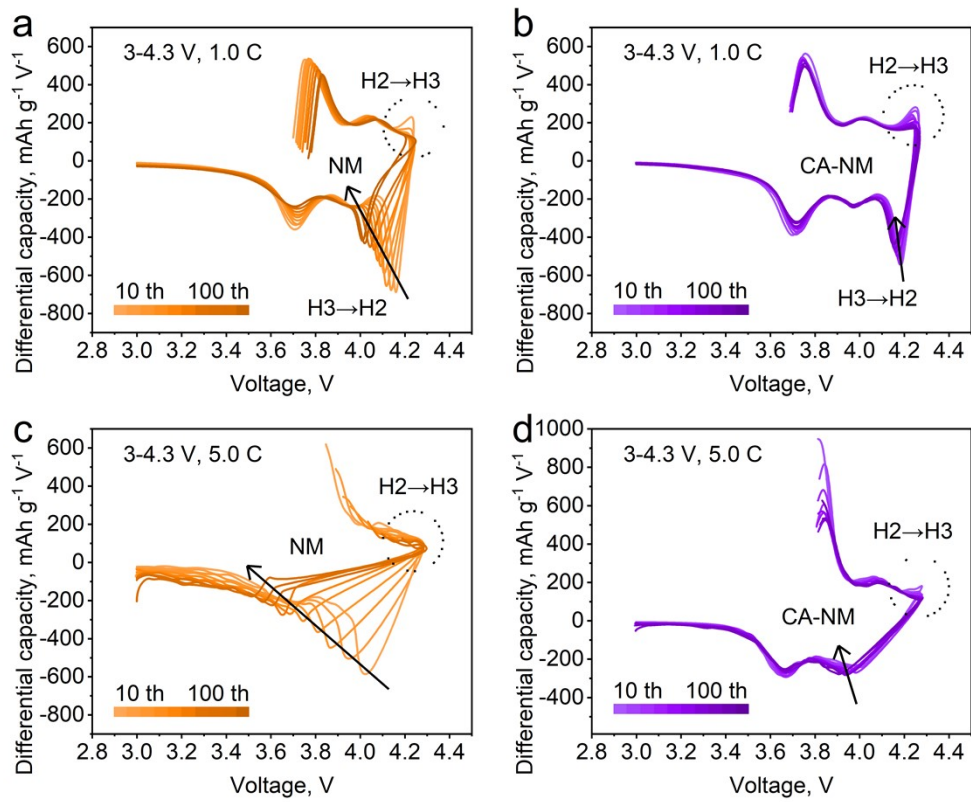


Fig. S2 The  $dQ/dV$  curves for different cycles of (a, c) NM and (b, d) CA-NM at 1.0 C and 5.0 C.

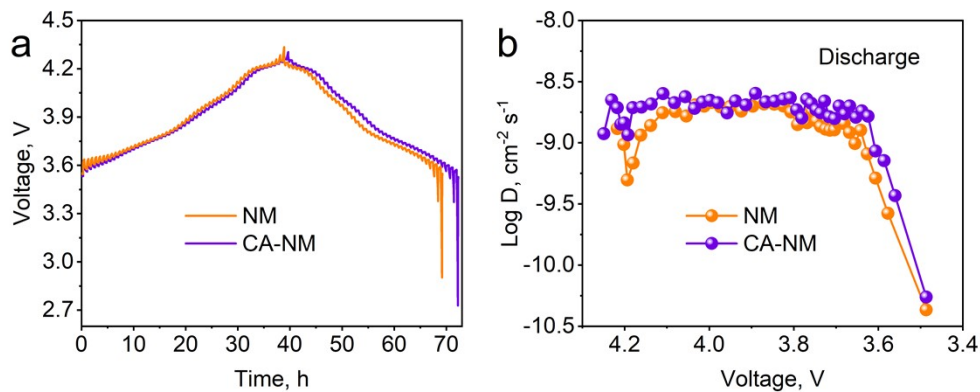


Fig. S3 (a) GITT test and (b) corresponding the calculated lithium ions diffusion coefficient at discharge stage.

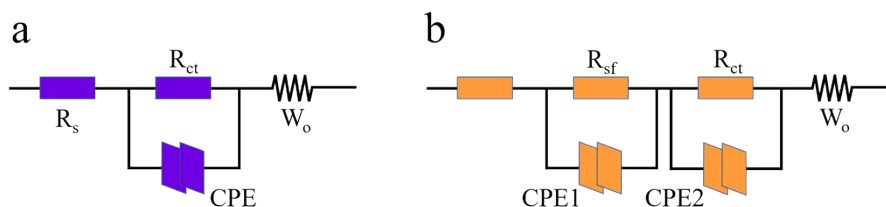


Fig. S4 The equivalent circuit models for fitting EIS data (a) before and (b) after cycle.

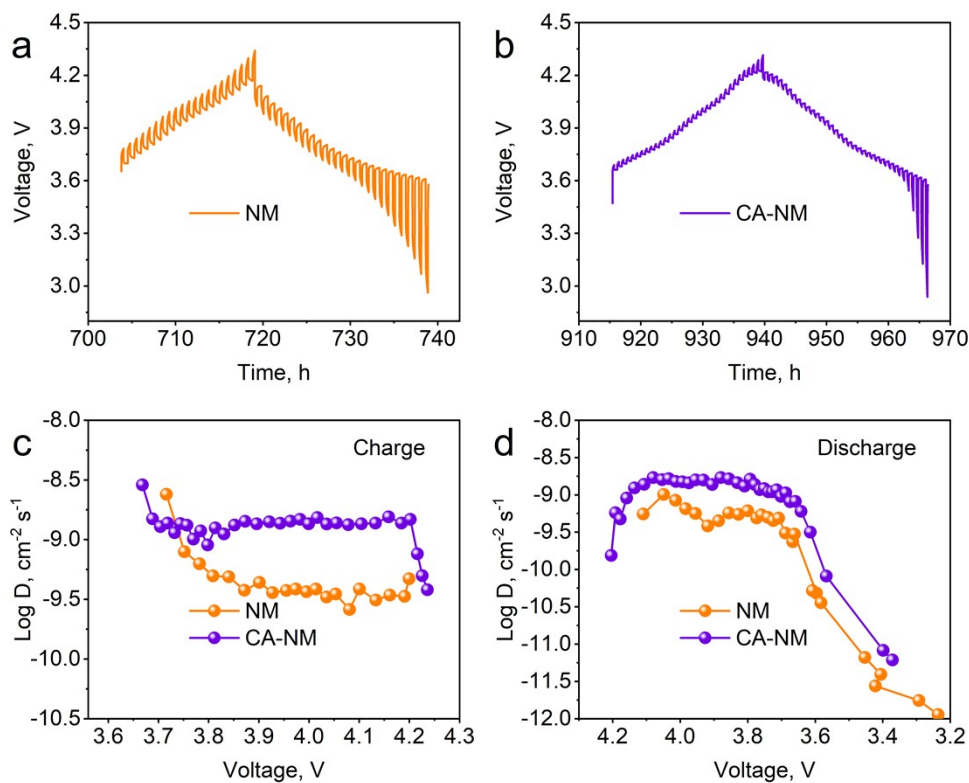


Fig. S5 GITT curves of (a) NM and (b) CA-NM, and corresponding the calculated  $D_{Li^+}$  at (c) charge

and (d) discharge stage.

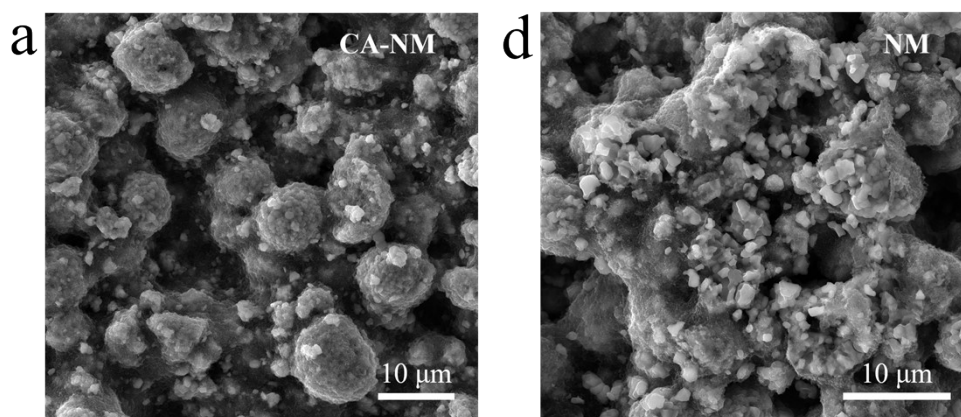


Fig. S6 SEM images of (a) CA-NM and (b) NM after 200 cycles

Table S1 EIS fitted results after 200 cycles

Sample	$R_{sf}$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )
NM	27.7	753.7
CA-NM	16.52	196.8