Supplementary Information

Sr and Co Co-doping Stabilizes Ultrahigh-Nickel Single-Crystal Cathodes for High-Performance Lithium-Ion Batteries

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Materials synthesis

For the synthesis of LiNi_{0.94}Co_{0.04}Mn_{0.02}O₂ (SNCM), the precursor of Ni_{0.94}Co_{0.04}Mn_{0.02}(OH)₂ (purchased from Zhejiang Huayou Cobalt Co., Ltd., Zhejiang, China) was mixed with appropriate amounts of LiOH·H₂O (aladdin, 99%) (Li:M molar ratio = 1.05:1) by ball milling for 30 minutes. The mixture was calcined at 550 °C for 3 h and then heated at 800 °C for 12 h in pure oxygen environment (O₂ purity≥99.999%). The heating rate was set to be 3 °C min⁻¹. SNCM-Sr material is prepared by adding 0.3 wt.% SrO during mixing, and the other preparation processes are the same as SNCM. SNCM-Sr and 0.4 wt.% Co₃O₄ were taken into a mixing bottle, then mixed evenly on the rolling mixer for 2 h. The uniformly powder is calcined at 500 °C for 5 h in pure oxygen environment to obtain SNCM-Sr-Co.

Materials Characterization

The morphology and elemental distribution of the cathode particles were analyzed using field emission scanning electron microscopy (GeminiSEM 300, ZEISS), equipped with energy dispersive X-ray spectroscopy (EDS) (Smart EDX of SE2). In order to obtain the element distribution of the single crystal particle phase, the electrode was sliced using an ion beam cutting system (Leica EM TIC3X). Microstructural analysis was conducted using transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) at 200 kV (JEOL JEM 2100F). Before measuring the elemental phase distribution, single crystal particles were cut open using a focused ion beam (FIB, Crossbeam 350, Zeiss). Powder X-ray diffraction (XRD) analysis was conducted using a Bruker D8 Advance X-ray diffractometer with a scan rate of 1° min⁻¹, employing a Cu-sealed tube ($\lambda = 0.15418$ nm) at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Fisher Scientific ESCALAB 250Xi instrument, maintaining a base pressure of approximately 1 × 10⁻⁹ mbar. The XPS was excited using AI K α X-ray radiation (hv = 1486.68 eV) with a spot size of 500 µm.

Electrochemical Measurements

The cathode slurries were prepared by mixing 90 wt.% active material, 5 wt.% Super P and 5 wt.% polyvinylidene fluoride in N-methyl-2-pyrrolidinone. After mixing, the slurry was coated onto carbon-coated aluminum foil with a mass loading of approximately 3 mg cm⁻² and dried at 120 °C under vacuum overnight to remove the solvent. The electrodes were punched into disks with a

diameter of 12 mm and assembled into CR2032 coin cells. Lithium foil, Celgard 2400, and 1 M LiPF₆ in ethylene carbonate (EC)/ethyl-methyl carbonate (EMC) (3:7; v:v) with 2 wt.% vinylene carbonate (VC) were used as the counter/reference electrode, separator, and electrolyte, respectively. Galvanostatic charge/discharge cycling was conducted using a Xinwei CT-4008Q battery testing system, with a voltage range of 2.8 to 4.3 V (vs. Li/Li⁺) at 25 °C. The full cell, consisting of commercial graphite as the anode and SNCM-Sr-Co as the cathode, was assembled in a coin cell with a selected N/P ratio of 1.1. Electrochemical impedance spectroscopy (EIS) measurements were carried out with a Bio-Logic VSP-3e electrochemical workstation (chassis with 8 slots) at an amplitude voltage of 5 mV and a frequency range of 1 mHz to 100 kHz. The lithium ion diffusion coefficient (D_{Li+}) based on EIS test can be calculated from the following equation¹:

$$D_{Li^{+}} = \frac{R^2 T^2}{2A^2 n^4 F^4 C^{02} \sigma^2} \#$$

where *R* is the gas constant, *T* is the room temperature, *A* is the surface area of the electrode, *n* is the electron transfer number, *F* is the Faraday constant, C^0 is the concentration of Li⁺, and σ is the Warburg factor. The galvanostatic intermittent titration technique (GITT) was performed at a constant current of 0.1C for 10 min, followed by a 1-hour rest period. The D_{Li^+} derived from the GITT measurements can be calculated using the following equation²:

$$D_{Li^{+}} = \frac{4}{\pi\tau} \left(\frac{n_m V_s}{S}\right)^2 \left(\frac{\Delta E_s}{\Delta E_{\tau}}\right)^2 \left(\tau \ll \frac{L^2}{D_{Li^{+}}}\right)$$

where τ is the duration of the pulse, n_m is the molar mass of the active material, V_m is the molar volume of the active material, S is the cell interfacial area, ΔE_s and ΔE_τ represent the voltage changes caused by the pulse and constant current, respectively, and L is the diffusion length of Li⁺.



Fig. S1 (a, b) SEM images of the $Ni_{0.94}Co_{0.04}Mn_{0.02}(OH)_2$ precursor.



Fig. S2 XRD pattern of the $Ni_{0.94}Co_{0.04}Mn_{0.02}(OH)_2$ precursor.



Fig. S3 The TEM images of (a) SNCM and (b) SNCM-Sr and the corresponding marked regions and FFT diagrams.



Fig. S4 XRD Rietveld refinements of (a) SNCM and (b) SNCM-Sr.



Fig. S5 The magnified view of the diffraction peaks corresponding to the (003) crystal plane of SNCM, SNCM-Sr, and SNCM-Sr-Co.



Fig. S6 The EDS mappings of SNCM and SNCM-Sr.



Fig. S7 XPS spectra of Ni 2p, Mn 2p, C 1s and O1s for (a-d) SNCM, (e-h) SNCM-Sr, and (i-l) SNCM-Sr-Co.



Fig. S8 Charge–discharge curves of (a) SNCM, (b) SNCM-Sr, and (c) SNCM-Sr-Co at different rates.



Fig. S9 (a) Cycling performance of full cell with SNCM-Sr-Co as cathode and graphite as anode at 0.5C, following activation at 0.05C in the first cycle, within a voltage range of 2.75–4.2 V. (b) First charge-discharge profile of the graphite ||SNCM-Sr-Co full cell at 0.05C.



Fig. S10 Linear fitting plot of Warburg impedance coefficients (σ).



Fig. S11 CV curves at different scan rates for (a) SNCM and (b) SNCM-Sr.

Material	I (003)/ I (104)	a/b(Å)	C(Å)	Li/Ni mixing	χ²
SNCM	2.312399	2.875491	14.186508	2.76%	5.13%
SNCM-Sr	2.374742	2.875964	14.190366	2.03%	4.28%
SNCM-Sr-Co	2.630796	2.874971	14.188315	1.2%	7.423%

 Table S1.
 The Rietveld-refined XRD results of SNCM, SNCM-Sr, and SNCM-Sr-Co.

Table S2. EIS data obtained by fitting Nyquist plots using the equivalent circuit in Fig 3e.

Material	<i>R</i> _s (Ω)	<i>R</i> _{ct} (Ω)
SNCM	3.0	337.4
SNCM-Sr	10.9	127
SNCM-Sr-Co	6.35	122.8

Reference:

1. Y. Liang, Z. Wang, Z. Xu, S. Li, H. Luo, C. Xu and X. Cui, Applied Surface Science, 2024, 651, 159234.

2. F. Li, Z. Liu, C. Liao, X. Xu, M. Zhu and J. Liu, ACS Energy Letters, 2023, 8, 4903-4914.