

Supplementary Material

Engineering commercial polycrystalline precursor to single crystal Ni-rich cathode with outstanding long-cycle performance

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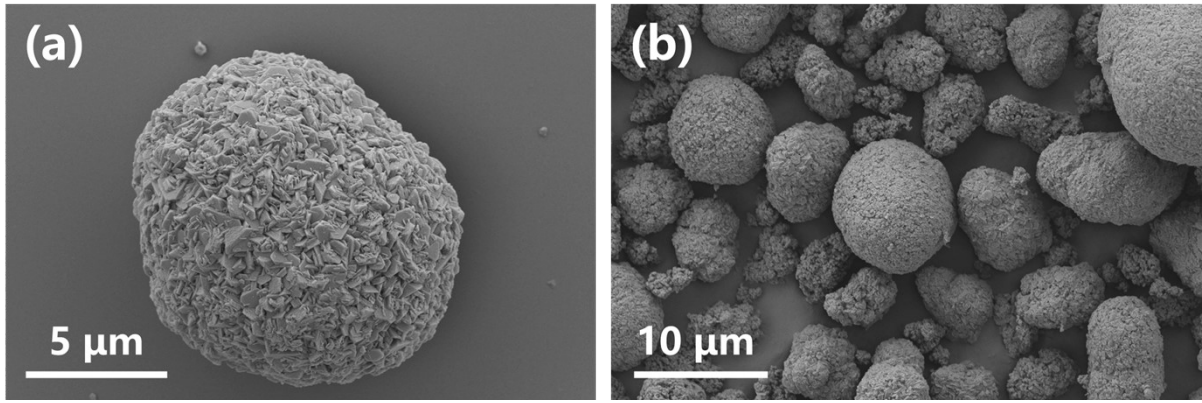


Fig. S1. Commercial polycrystalline NCM cathode precursors used in the synthesis process.

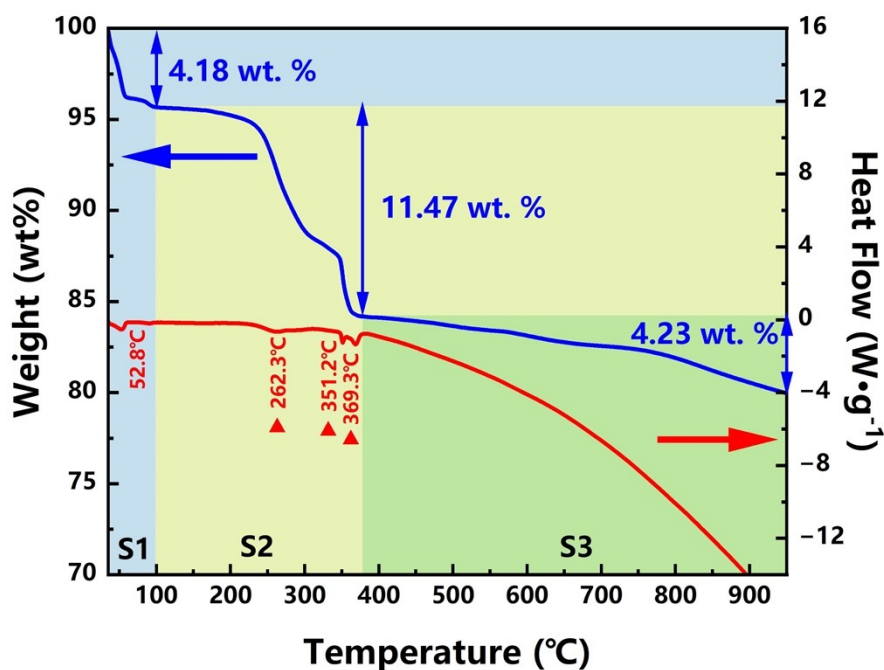


Fig. S2. TGA-DSC analysis of reactant.

Thermogravimetric analysis (TGA) is employed to determine the phase change, thermal decomposition of reactant by which the portion of weight change as a function of temperature can be obtained. As depicted in Fig. S2, in the initial stage (S1), a sudden weight reduction of about 4.18 wt. % (blue curve) corresponds to the evaporation of free water. The second stage (S2) shows a weight reduction of 11.47 wt. % from 100 °C to 375 °C, corresponding to the decomposition of reactants and melting of molten salts. The third stage (S3) decreases in weight by 4.23 wt. % and forms a stable plateau at around 600 °C while negligible weight loss can be observed until temperature reach up to 950 °C. We found out that the DSC curves indicate that the actual heat absorption process in second stage (S2) only occurs at 262.3 °C, 351.2 °C, and 369.3 °C which is lower than the eutectic temperature of LiOH-Li₂SO₄ system at 407 °C from phase diagram database. Therefore, it is assumed that the presence of transition metal hydroxide may lower the melting point of the system and promote the homogeneous dispersion of the reactants. The above results indicate that the stable product is generated after 750 °C before the molten salt agent is completely melted, and processes such as evaporation of the molten salt agent occur subsequently. Combined with the reports in literature, 950 °C was finally chosen as the optimum reaction temperature of the system.

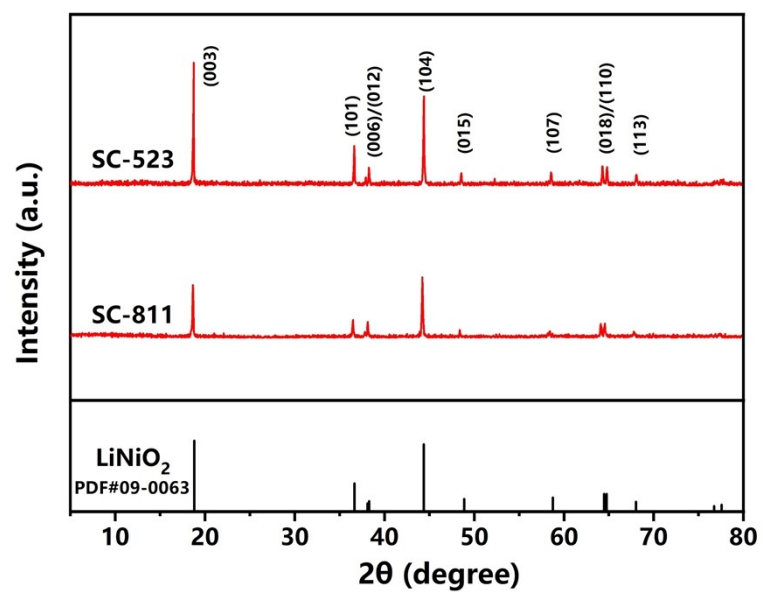


Fig. S3. XRD patterns of SC-523 and SC-811 cathode materials.

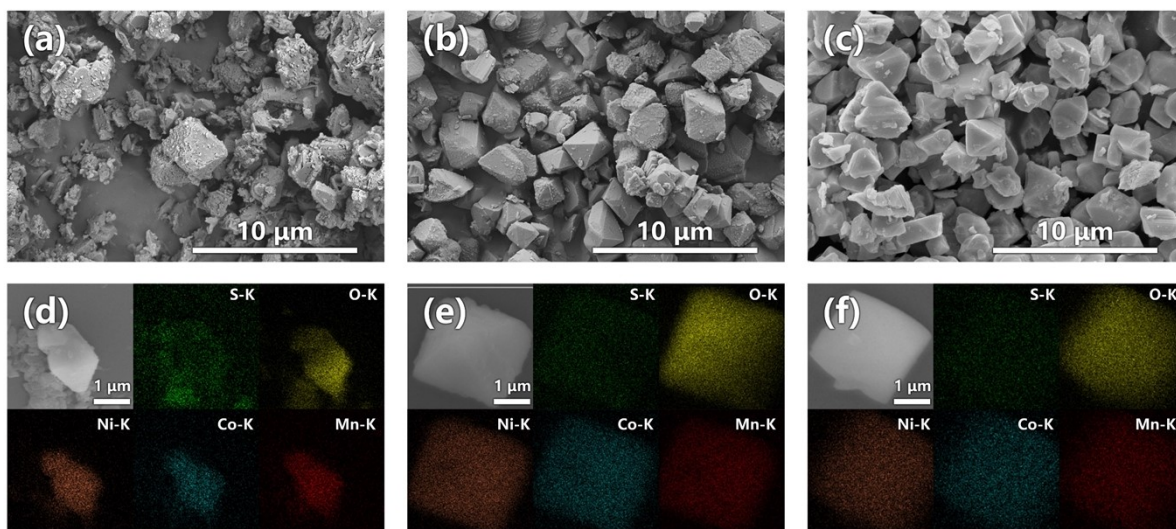


Fig. S4. SEM images of a) SC-1, b) SC-2, c) SC-3, element mapping of d) SC-1, e) SC-2, f) SC-3, respectively.

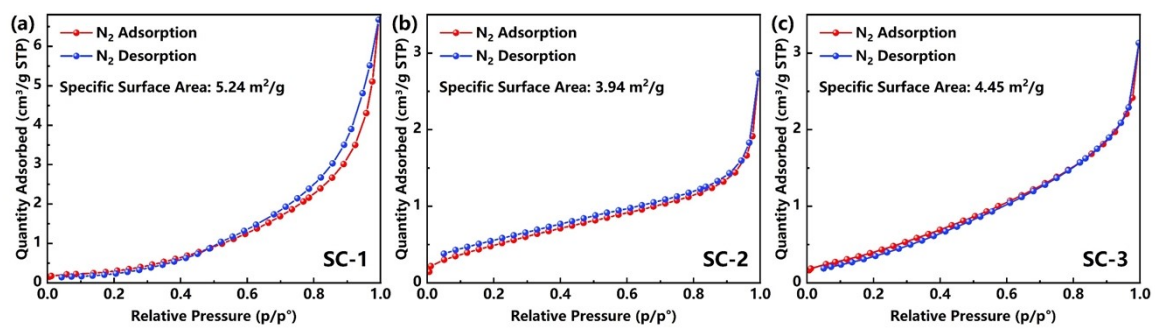


Fig. S5. N_2 adsorption/desorption isotherms of SC-1, SC-2 and SC-3, respectively.

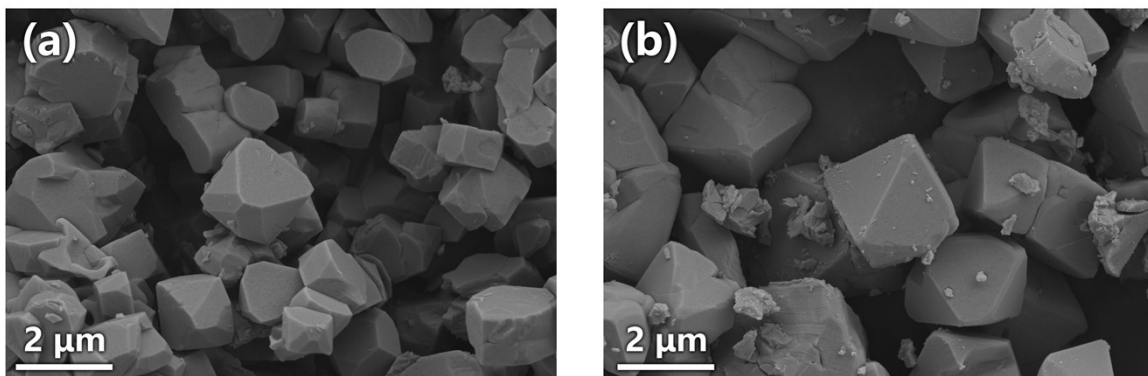


Fig. S6. SEM images of a) SC-523 and b) SC-811 cathode materials.

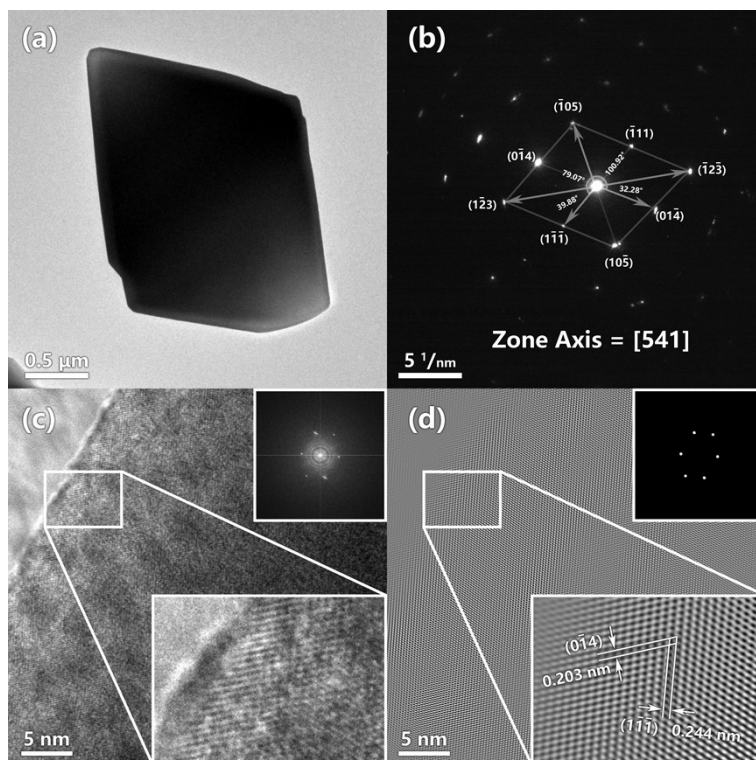


Fig. S7. TEM and SAED images of selected area of SC-3. a) TEM image b) SAED image c) HRTEM image, and d) processed HRTEM image of c) by filter.

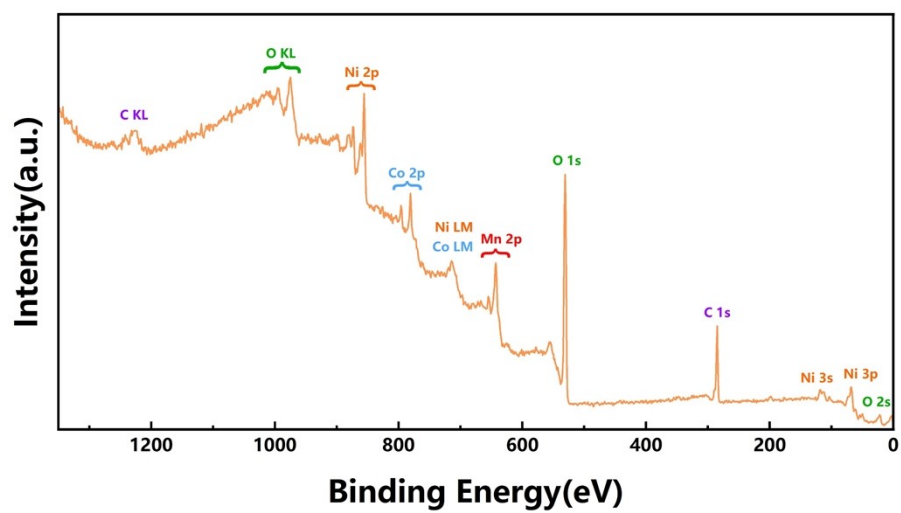


Fig. S8. XPS survey of SC-3.

Table S1. Binding energy (eV) and peak area (%) of Ni, Co and Mn elements obtained from XPS spectra.

Item	Unit	2p 3/2 Peak					3s Peak
		Ni ²⁺	Ni ³⁺	Co ²⁺	Co ³⁺	Mn	Δ Mn
Binding Energy	eV	855.0	856.1	780.8	780.1	642.6	4.6
Peak Area	%	32.7	67.3	52.7	47.3	-	-

Table S2. Comparison of single crystal NCM cathode under different synthesis strategies at room temperature (25 °C).

Electrode material	Preparation strategy	Specific Capacity (mAh·g ⁻¹)	Rate	Cycles	Capacity Retention	Ref.
				150	97.3%	
				200	92.2%	
				300	86.3%	
LiNi _{0.6} Co _{0.2} Mn _{0.2} O ₂	Molten salt method	168.4	1.0 C	400	81.1%	This work
				600	74.2%	
				800	70.0%	
				1000	52.9%	
LiNi _{0.8} Co _{0.1} Mn _{0.1} O ₂	High temperature method (HT)	~170.0	1.0 C	150	91.1%	[56]
LiNi _{0.8} Co _{0.1} Mn _{0.1} O ₂	HT	170.0	0.5 C	150	90.0%	[37]
LiNi _{0.88} Co _{0.09} Mn _{0.03} O ₂	HT	202.3	0.5 C	200	86.5%	[57]
LiNi _{0.6} Co _{0.2} Mn _{0.2} O ₂	HT	~160.0	0.5 C	200	84.8%	[55]
LiNi _{0.76} Mn _{0.14} Co _{0.1} O ₂	Molten salt method	193.4	0.1 C	200	81.6%	[36]
LiNi _{0.6} Co _{0.2} Mn _{0.2} O ₂	HT	~190.0	1.0 C	200	58.8%	[35]
LiNi _{0.8} Co _{0.1} Mn _{0.1} O ₂	HT	190.0	1.0 C	300	84.1%	[58]
LiNi _{0.76} Mn _{0.14} Co _{0.1} O ₂	HT	185.0	0.3 C	400	78.5%	[18]

Reference for theoretical calculation

Gibbs-Wulff Theorem:

The crystal morphology was constructed based on Gibbs-Wulff Theorem:

$$\frac{\sigma_1}{\nu_1} = \frac{\sigma_2}{\nu_2} = \frac{\sigma_3}{\nu_3} = \dots = \frac{\sigma_1}{r_1} = \frac{\sigma_2}{r_2} = \frac{\sigma_3}{r_3} = \dots$$

Reasons for selecting LiNiO₂ cells for the calculations:

- (1) The LiNiO₂ and NCM cells belong to the same *R-3m* space group, and the NCM cathode can be regarded as the doping product of LiNiO₂, with only the atomic distribution of the transition metal layer being different, and the physical phase characteristics and electrochemical properties of NCM622 are quite similar to those of LiNiO₂ due to its high nickel content.
- (2) The LiNiO₂ transition metal layer has only one kind of transition metal atoms, which well solves the problem of low symmetry, non-chemometric ratios and arithmetic power limitation in the case of non-homogeneous distribution of multiple elements.

About exposed surface Li-mix:

Similar to Li-Ni mixing, when Ni atoms are exposed to the surface, *d*-orbitals with high energy will lead to a large increase in surface energy, when Li atoms exchange positions with Ni atoms could reduce the energy of the system. This property will lead to a large change in the surface atomic distribution, and the surface energy can be reduced. This phenomenon is named as Li-mix.

Effect of process parameters on product:

In Fig. 7a, the crystal formation process is closely related to the process parameters (Fig. 1a). The suitable synthetic formulations and higher calcination temperature allowed the growth of single crystal particles of moderate size, and the rapid natural cooling process with a slightly lower annealing temperature avoided the change of crystal morphology. Under the above synthesis conditions, the low surface energy of the specific crystalline facets drives the crystals to form single crystal particles with octahedral morphology, and only the facet families (003) and (012) constitute the surface. This explains why the above process parameters allow the formation of octahedral-shaped single crystals.

