Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information for

Boosting the voltage/capacity stability of O2-type Li-rich layered cathodes by tailoring transition metal distribution for Li-ion batteries

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1. Experimental

1.1 Synthesis of precursors

The graded precursor with the tailored TM distribution was prepared by a modified co-precipitation reaction in Figure S1. The stoichiometric $NiSO_4 \cdot 6H_2O$ (157.68 g), $CoSO_4 \cdot 7H_2O$ (56.2 g), and $MnSO_4 \cdot H_2O$ (202.8 g) (Ni−Co−Mn=3/1/6) were added into deionized (DI) water (tank 2) and form aqueous solution (2L). The stoichiometric $NiSO_4 \cdot 6H_2O$ (52.56 g), $CoSO_4 \cdot 7H_2O$ (56.2 g), and $MnSO_4 \cdot H_2O$ (152.1 g) (Ni−Co−Mn=1/1/8) were added into deionized (DI) water (tank 1) and form aqueous solution (2L). At the beginning of co-precipitation, the Ni-rich solution (tank 2) was injected into Ni-poor solution (tank 1) at 100 mL h^{-1}. Meanwhile, the solution (tank 1) with ceaselessly tailored TM content was injected into the reactor at 200 mL h^{-1}. The aqueous alkali containing 2M Na_2CO_3 and 0.2M ammonia was employed to automatically controll the contant pH value (8.1). After about 20 h, both solutions were completely consumed, and the aimed precursors with tailored TM distribution were prepared. The bulk $[Ni_{0.2}Co_{0.1}Mn_{0.7}]CO_3$ precursors were also synthesized.

1.2 Synthesis of O2-type LLOs

The above precursors with stoichiometric Li_2CO_3 and Na_2CO_3 (Na/TM=5/6 and Li/TM=1/5) were calcined at 800 °C (10 h) to prepare the graded and bulk P2-type $Na_{5/6}Li_{1/5}[Ni_{0.2}Co_{0.1}Mn_{0.7}]_{4/5}O_2$. The formed P2-type oxides was calcined (300 °C, 2 h) to cause the Na/Li cation exchange in the binary molten salt ($LiNO_3$/LiCl of 88:12 w./w.%). After the ion exchange, the mixture was washed and dried in a vacuum. Finally, the graded and bulk O2-type LLOs were achieved.

1.3 Materials characterization

The morphology was measured by scanning electron microscope (SEM, VEGA3). The material phase was studied by X-ray diffraction (XRD, SmartLab, Rigaku). The microstructure was studied by

transmission electron microscopy (TEM, FEI titan themis 200). The content of Mn^{2+} dissolution and molar ratio of TM was measured by inductively coupled plasmas (ICP-OES, Agilent 5100). The elemental valence state was studied by X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250).

1.4 Electrochemical measurements

The manufacturing process of electrode can refer to our previous reports.[1,2] The material loading of the cathode is 2.5−3.0 mg cm^{-2}. The performance of graded and bulk O2-type LLOs was measured by 2032-type coin cells. Lithium foil with a diameter of 14 mm was used as the anode electrode. The electrolyte consisted of 1M $LiPF_6$ dissolved in the solvents of DMC and EC (0.7/0.3 by volume). The electrochemistry and cyclic voltammetry (CV) were tested by LAND instrument (CT−2001A, Wuhan Land) and electrochemical workstation (CHI660e, Shanghai Chenhua), respectively. The potential range of 2.0−4.8 V (vs. Li/Li^+) was selected while the current density of 1C was 300 mA g^{-1}. Galvanostatic intermittent titration technique (GITT) was conducted at 0.3C for 600s along with a relaxation time of 3600s. All electrochemical analysis were investigated at 25 °C.

References

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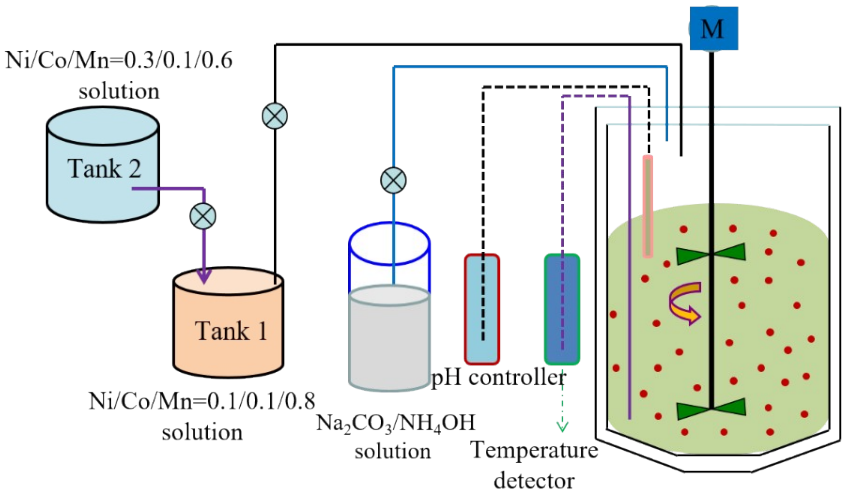

Figure S1 Scheme of synthesis of compositionally graded precursors *via* a carbonate co-precipitation route.

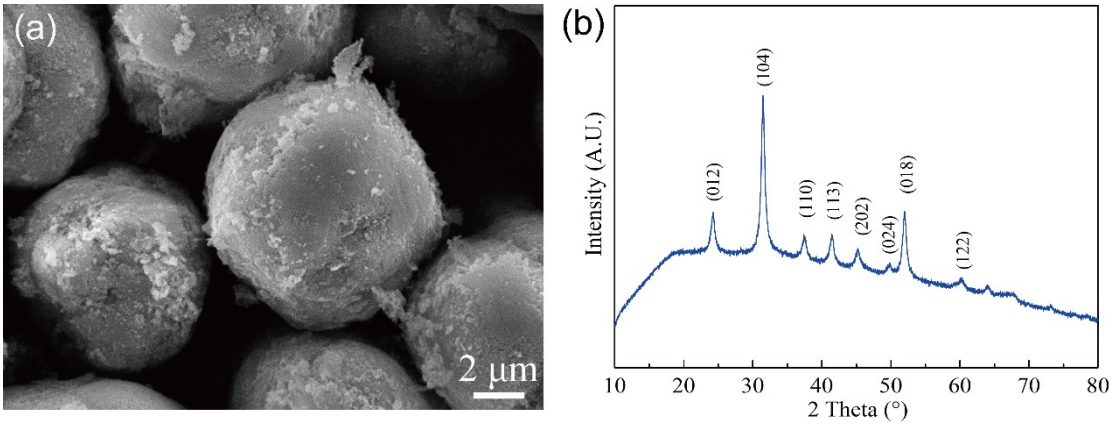

Figure S2 (a) SEM image and (b) XRD pattern of the as-prepared compositionally graded precursors by co-precipitation reactions.

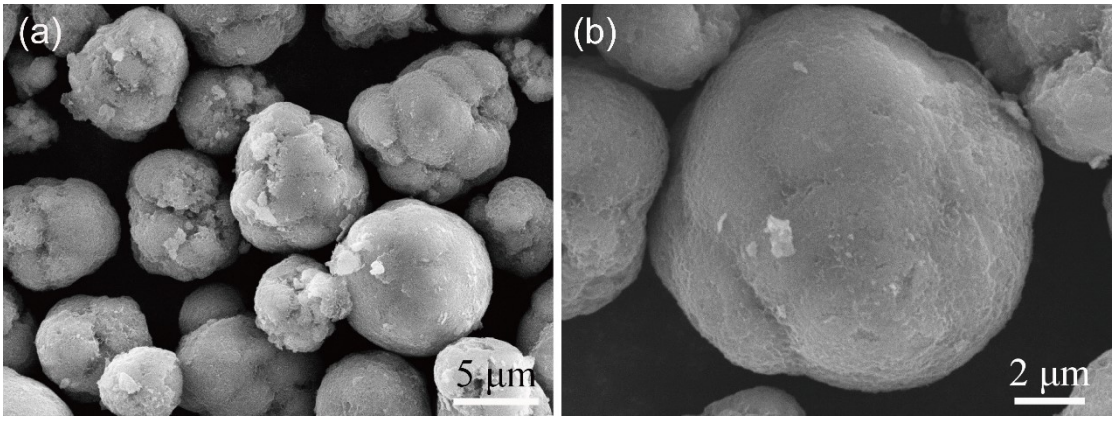

Figure S3 (a,b) SEM images of the as-prepared bulk precursors by co-precipitation reactions.

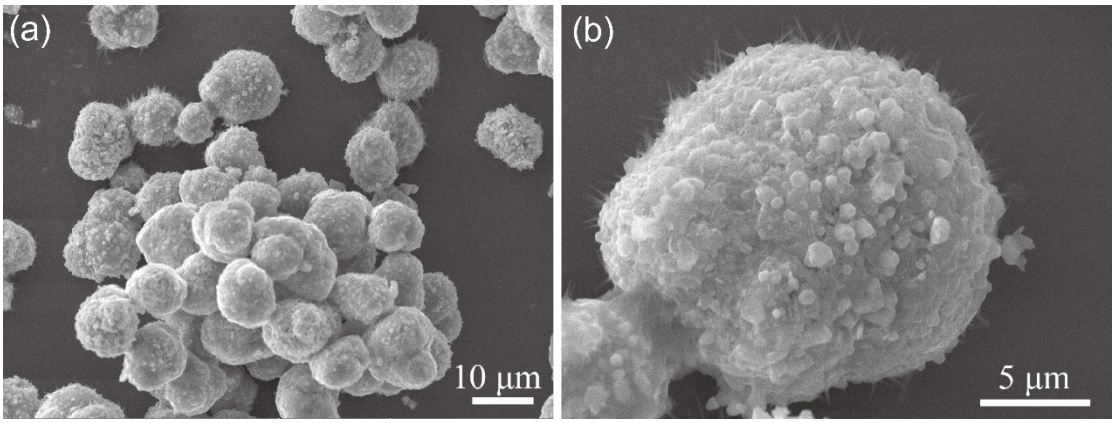

Figure S4 (a,b) SEM images of the bulk P2-type oxide $Na_{5/6}Li_{1/5}[Ni_{0.2}Co_{0.1}Mn_{0.7}]O_2$ calcined the mixture of precursors with stoichiometric Li_2CO_3 and Na_2CO_3 at 800 °C.

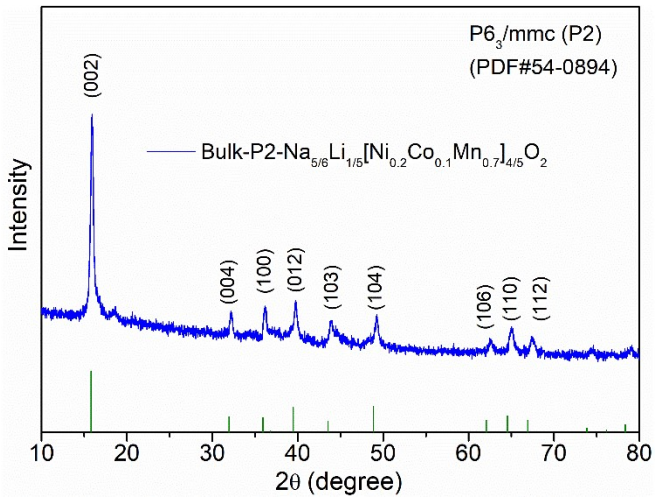

Figure S5 XRD of the bulk P2-type oxide $Na_{5/6}Li_{1/5}[Ni_{0.2}Co_{0.1}Mn_{0.7}]O_2$ calcined the mixture of precursors with stoichiometric Li_2CO_3 and Na_2CO_3 at 800 °C.

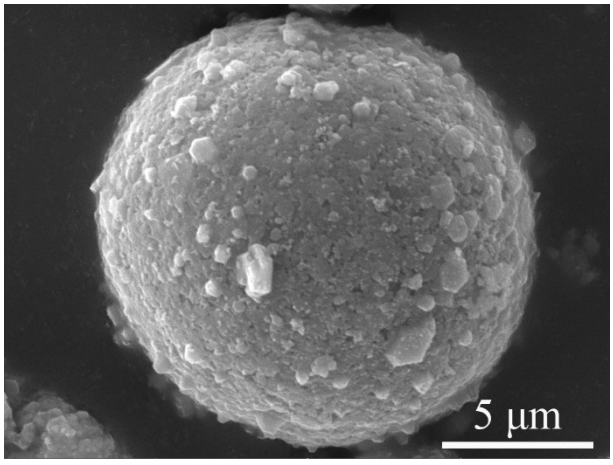

Figure S6 SEM image of the bulk O2-type oxide after Na/Li ion exchange.

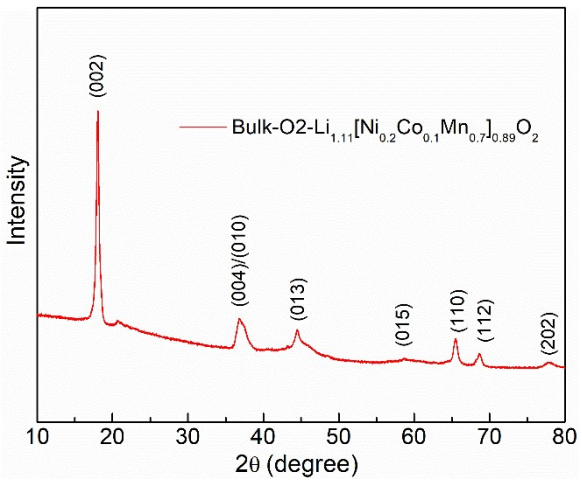

Figure S7 XRD of the bulk O2-type oxide after Na/Li ion exchange.

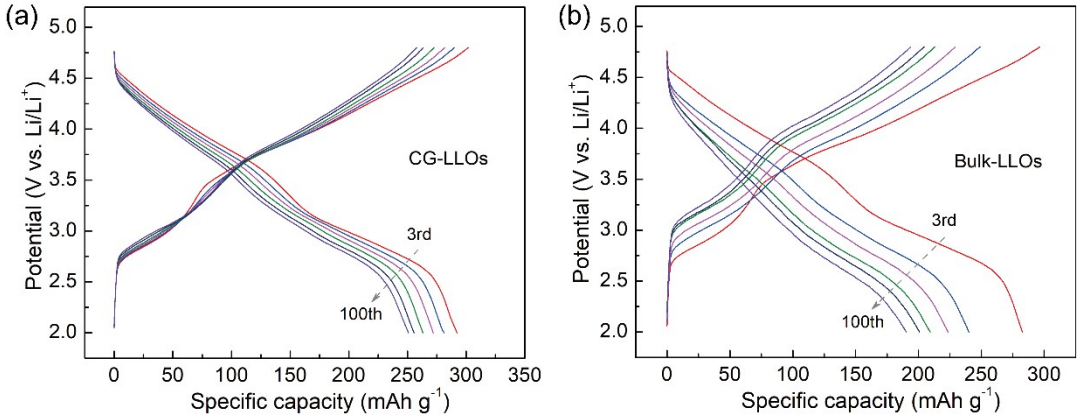

Figure S8 The continuous charge/discharge curves from 3rd to 100th cycles of (a) CG-LLOs and (b) bulk-LLOs.

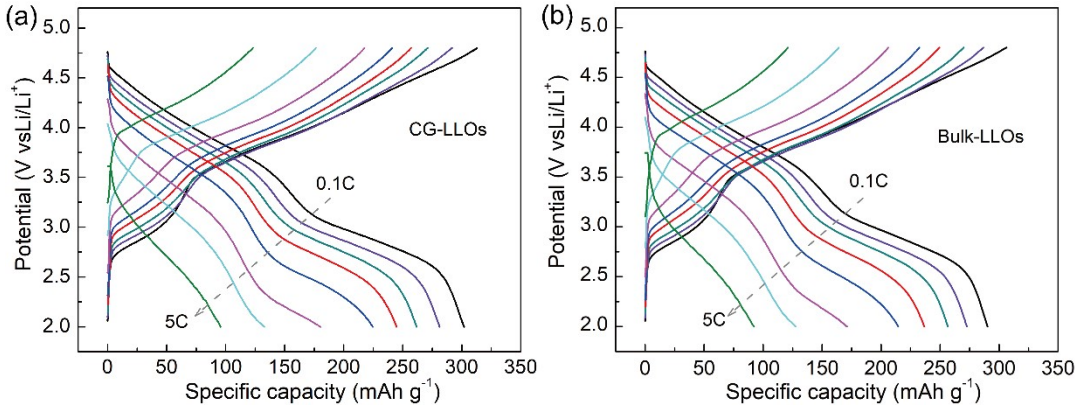

Figure S9 The charge/discharge profiles at varied rates for (a) CG-LLOs and (b) bulk-LLOs.

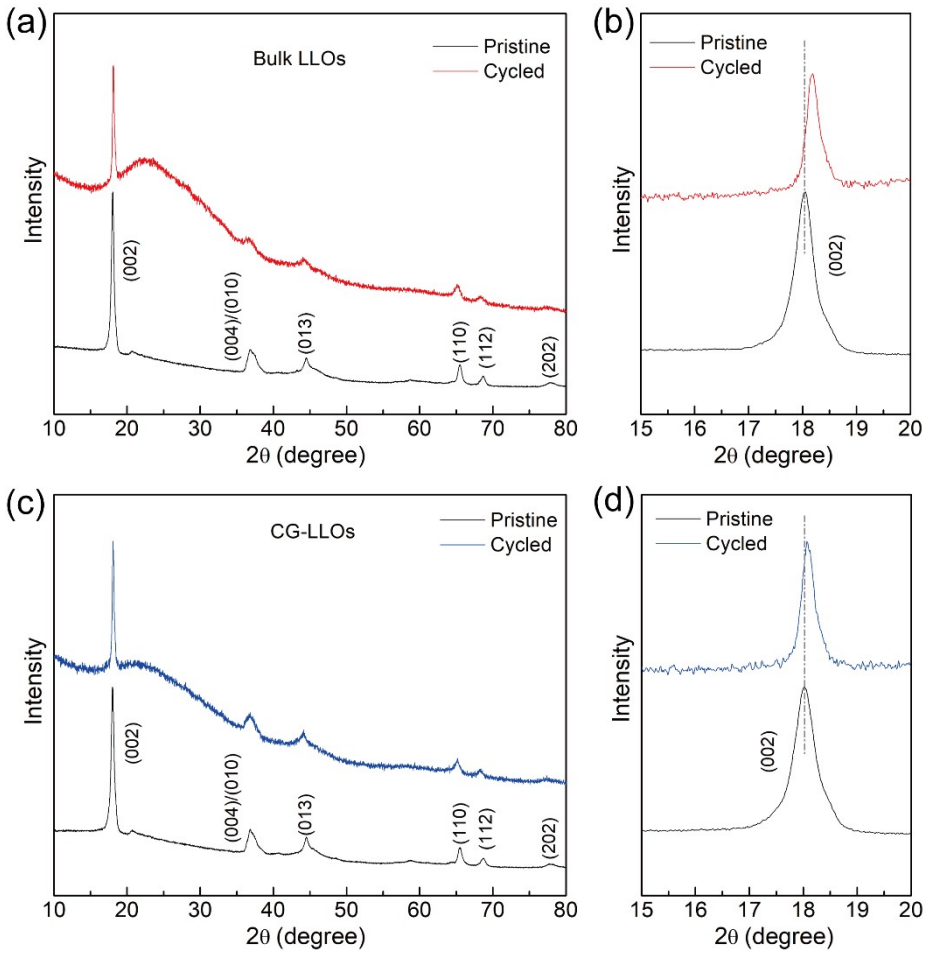

Figure S10 (a,c) XRD patterns of pristine and cycled CG-LLO and bulk-LLO electrodes, and (b,d) the enlarged region between 15 and 20 degree. The cycled electrodes measured at discharge state after 100 cycles.

Table S1 The comparison of the electrochemical performance between this work and these reported O2-type cathodes.

Structural formula	Modified method	Capacity (mAh g^{-1})	Cycling stability (%)	Ref
$Li_{1.12}[Ni_{0.18}Co_{0.09}Mn_{0.61}]O_2$	Graded structure	300 (0.1C)	86.7 (100 cycles@0.1C)	This work
$Na_{0.007}Li_{1.17}Ni_{0.27}Mn_{0.73}O_{2+x}$	-	278 (0.1C)	82.0 (100 cycles@1C)	1
$Na_{0.003}Li_{1.14}Ni_{0.26}Mn_{0.74}O_{2+x}$	-	224 (0.1C)	79.0 (100 cycles@1C)	1
$Li_{0.78}[Li_{0.24}Mn_{0.76}]O_2$	Nanowires	275 (0.1C)	81.1 (100 cycles@1C)	2
$Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_{2+\delta-x}F_x$	F doping	280 (0.1C)	94.4 (100 cycles@1C)	3
$Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$	All-fluorinated electrolyte	278 (2/3C)	83.3 (100 cycles@2/3C)	4
$Li_{0.9}[Li_{0.3}Mn_{0.7}]O_2$	O2/O3 biphasic	220 (0.1C)	90.5 (100 cycles@0.1C)	5
$Li_{1.091}Na_{0.01}Mn_{0.506}Co_{0.214}Ni_{0.122}O_2$	O2/O3 hybrid	279 (0.1C)	77.8 (100 cycles@0.5C)	6
$Li_{1.25}Co_{0.25}Mn_{0.50}O_2$	Single-layer Li_2MnO_3	400 (0.1C)	90 (50 cycles@0.2C)	7
$Li_{0.83}Li_{0.2}Ni_{0.08}Mn_{0.58}Co_{0.14}O_2$	-	258 (0.1C)	76.9 (50 cycles@0.1C)	8
$Li_{1.033}Ni_{0.2}[O_{0.1}Mn_{0.5}]O_2$	Native vacancies	228 (0.1C)	102.3 (50 cycles@0.1C)	9
$Li_{1.033}Ni_{0.2}Mn_{0.6}O_2$	-	186 (0.1C)	75.8 (50 cycles@0.1C)	9
$Li_x[Li_{1/4}Mn_{3/4}]O_2$	-	224 (0.1C)	74.3 (50 cycles@0.1C)	10

$Li_{0.83}(Li_{0.2}Ni_{0.2}Mn_{0.6})O_2$	-	235 (0.05C)	82.5 (40cycles@0.05C)	11

Table 2 The simulated results from EIS measurement of the bulk-LLOs and CG-LLOs at discharge state under varied cycles.

Samples	States	Simulated electrochemical parameters			
		R_s (Ω)	R_{sf} (Ω)	R_{ct} (Ω)	W_o (Ω)
Bulk-LLOs	1st	2.11	441.8	131.7	578
	100th	2.76	819.1	608.3	1678
CG-LLOs	1st	2.26	513.3	135.7	884
	100th	2.43	639.7	221.6	1036

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