

## Supporting Information

### Effect of electrochemically active element species on the stability of the layered cathode-sulfide electrolyte interface

Yiming Sun, Senhao Li, Kai Yang, Yue Ma, Hongzhou Zhang, Dawei Song, Yi Wang\*,  
Chunliang Li, Defa Wang\*, Lianqi Zhang\*

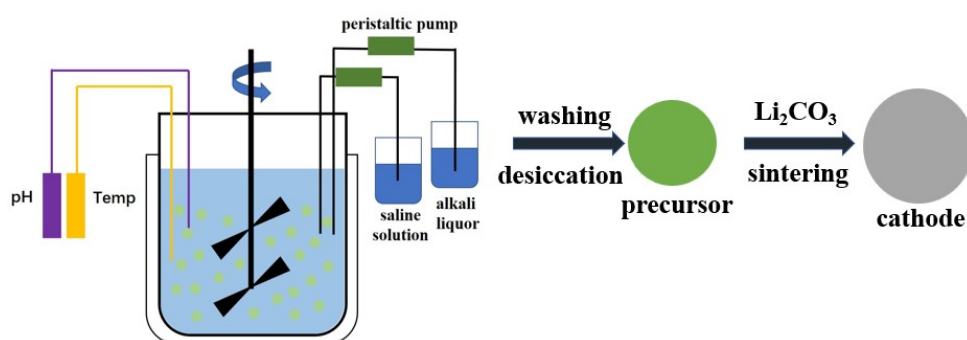


Fig. S1. Scheme of precursor and cathode material preparation.

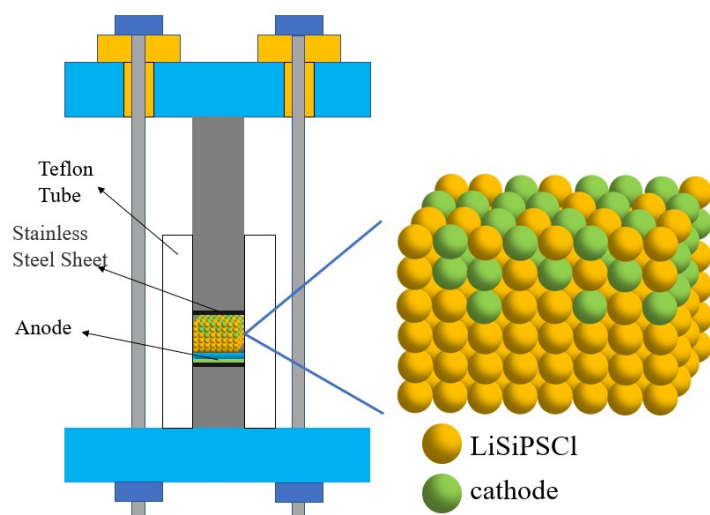


Fig. S2. Schematic diagram of assembled ASSLB.

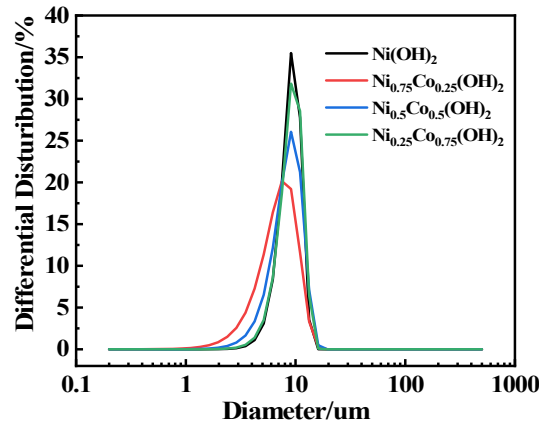


Fig. S3 Particle size distribution of the precursors.

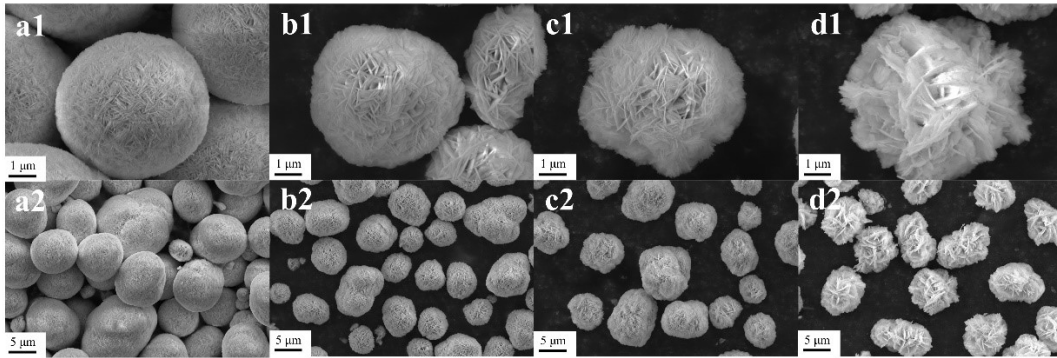


Fig. S4 SEM images of precursors of (a1-d2) LNO, N75, N50, and N25.

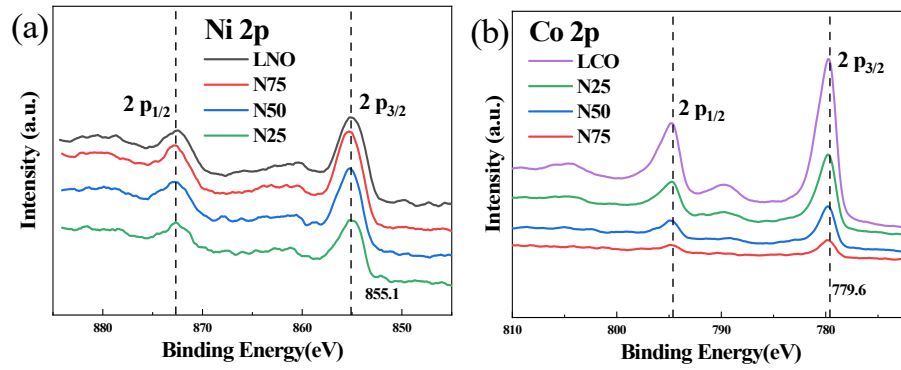


Fig. S5 X-ray photoelectron spectroscopy raw spectra of (a)Ni 2p and (b)Co 2p for cathode materials.

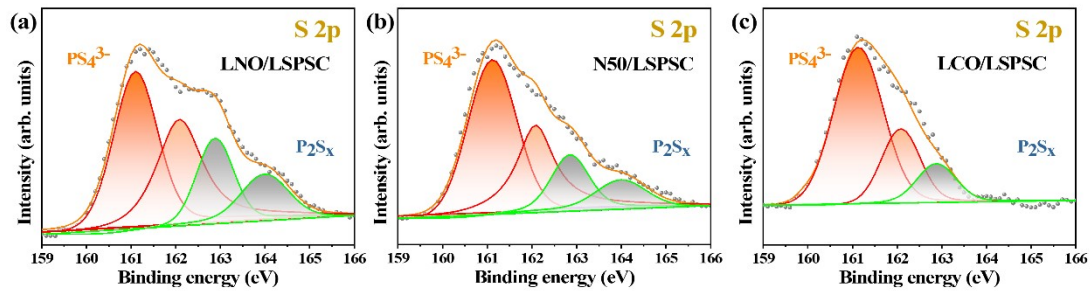
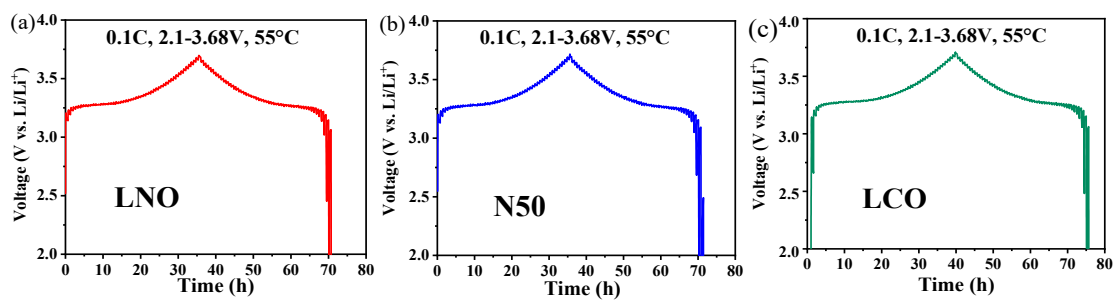
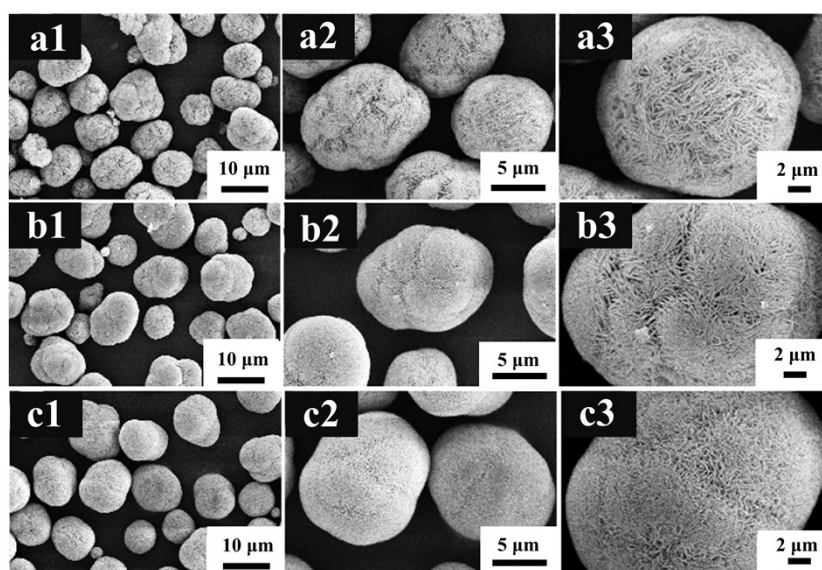


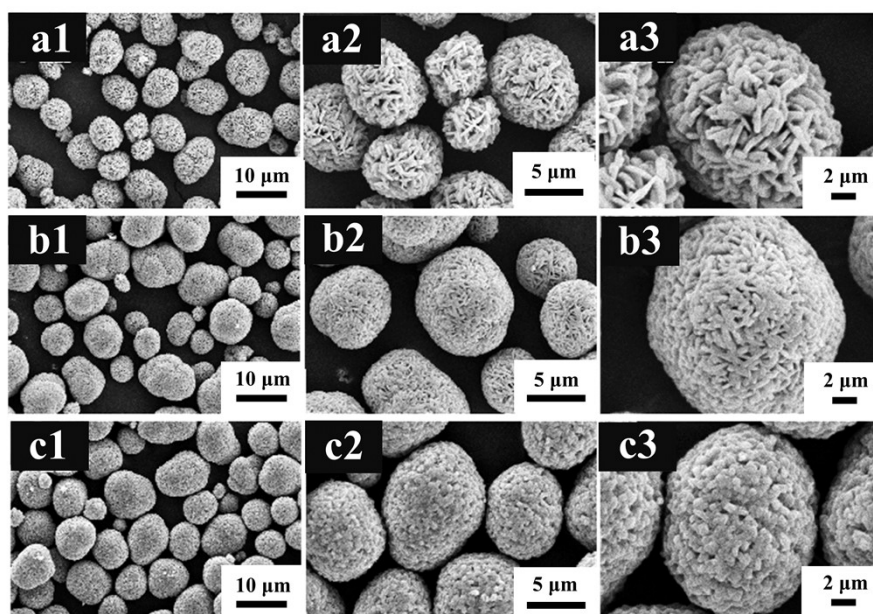
Fig. S6 XPS spectra of (a) LNO/LSPSC, (b) N50/LSPSC and (c) LCO/LSPSC mixture after 150h standing time.



**Fig. S7** Voltage-time patterns for the ASSLB assembled with (a) LNO, (b) N50 and (c) LCO cathode materials at a current density of 0.1C using the GITT test method.



**Fig. S8** SEM images of precursors of (a1-c3) NCM442, NCM622 and NCM811.



**Fig. S9** SEM images of (a1-c3) NCM442, NCM622 and NCM811.

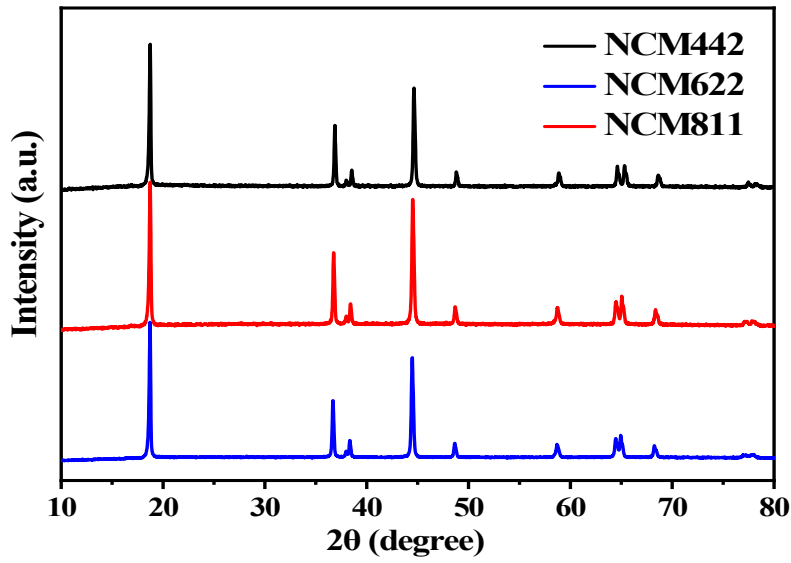


Fig. S10 XRD patterns of NCM442, NCM622 and NCM811.

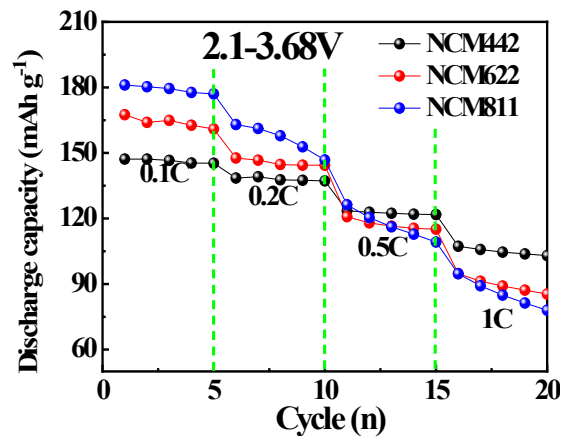
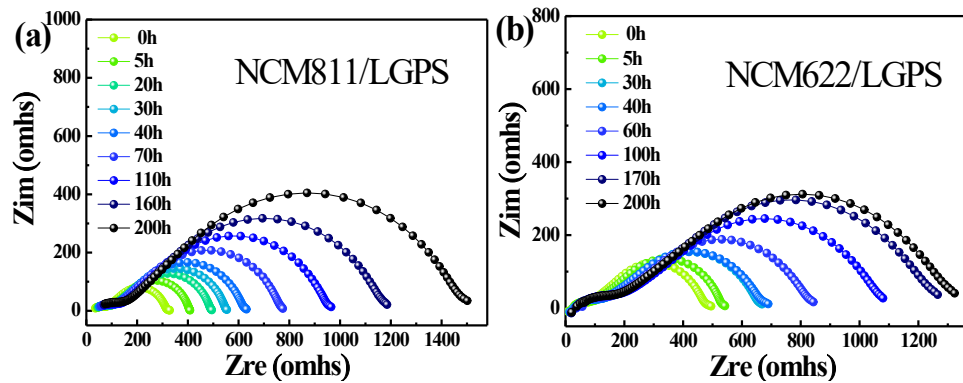
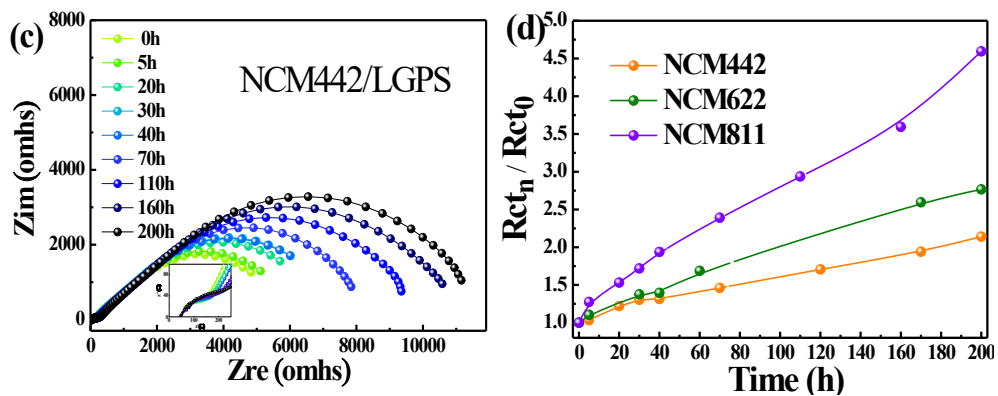


Fig. 11 Rate performance of  $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$  cathodes in ASSLB.





**Fig. S12** (a-c) Electrochemical impedance spectroscopy and (d) impedance increase comparison of  $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2/\text{LGPS}$  mixture with standing time.

**Table S1** Particle size analysis of  $\text{Ni}_x\text{Co}_{1-x}(\text{OH})_2$  precursors.

Precursors	$D_{10}$ ( $\mu\text{m}$ )	$D_{50}$ ( $\mu\text{m}$ )	$D_{90}$ ( $\mu\text{m}$ )
$\text{Ni}(\text{OH})_2$	5.25	8.23	10.88
$\text{Ni}_{0.75}\text{Co}_{0.25}(\text{OH})_2$	3.45	6.5	9.73
$\text{Ni}_{0.5}\text{Co}_{0.5}(\text{OH})_2$	4.76	7.8	10.68
$\text{Ni}_{0.25}\text{Co}_{0.75}(\text{OH})_2$	5.75	8.37	10.64

**Table S2** Transition metal element content of  $\text{Ni}_x\text{Co}_{1-x}(\text{OH})_2$  precursors.

Precursors	Designed atomic ratio (%)		Measured atomic ratio (%)	
	Ni	Co	Ni	Co
$\text{Ni}_{0.75}\text{Co}_{0.25}(\text{OH})_2$	0.75	0.25	0.744	0.256
$\text{Ni}_{0.5}\text{Co}_{0.5}(\text{OH})_2$	0.5	0.5	0.503	0.497
$\text{Ni}_{0.25}\text{Co}_{0.75}(\text{OH})_2$	0.25	0.75	0.246	0.754

**Table S3** Lattice parameters of  $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ .

Samples	Lattice parameters		c/a	$I_{(003)/(104)}$
	a[ $\text{\AA}$ ]	c[ $\text{\AA}$ ]		
LNO	2.8847	14.2217	4.9301	1.001
N75	2.815	14.045	4.9893	1.20
N50	2.815	14.046	4.9896	1.23
N25	2.816	14.048	4.9886	1.42
LCO	2.8156	14.0564	4.9994	1.304

**Table S4** Initial charge/discharge capacities and coulombic efficiencies of  $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$  materials in liquid coin-cells.

Electrode materials	Initial capacity ( $\text{mAh g}^{-1}$ )		Coulomb efficiency (%)
	Charge	Discharge	
LNO	249.9	194.9	78.0
N75	216.4	175.9	81.3
N50	179.1	170.0	94.9
N25	168.6	153.4	91.0
LCO	159.3	145.6	91.4

**Table S5** Cycle performance of  $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$  materials in liquid coin-cells.

Electrode materials	6th Discharge capacity (mAh g <sup>-1</sup> )	100th Discharge capacity (mAh g <sup>-1</sup> )	Capacity retention (%)
LNO	164.2	124.3	78.0
N75	172.7	127.6	73.8
N50	160.3	129.8	80.9
N25	151.7	133.3	87.8
LCO	155.9	137.2	88.0

**Table S6** Initial charge/discharge capacities and coulombic efficiencies of LiNi<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub> materials in ASSLB

Electrode materials	Initial capacity (mAh g <sup>-1</sup> )		Coulomb efficiency (%)
	Charge	Discharge	
LNO	169.9	115.4	67.9
N75	216	181.5	84.0
N50	186.6	165.8	88.8
N25	169.4	150.3	88.7
LCO	160.8	147	91.4

**Table S7** Cycle performance and capacity retention of LiNi<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub> materials in ASSLB

Electrode materials	6th discharge capacity (mAh g <sup>-1</sup> )	100th discharge capacity (mAh g <sup>-1</sup> )	Capacity retention (%)
LNO	107.7	55	51.0
N75	181.6	95.1	52.3
N50	153	119.4	78.0
N25	144.1	122.4	84.9
LCO	144.8	122	84.2

**Table S8** The fitted EIS values of cycled ASSLB.

Electrode materials	Cycle numbers	Rs	Rf	Rct2
LNO	1	24.49	15.41	146.4
	100	25.91	11.51	648.5
N75	1	30.88	9.08	24.99
	100	27.86	12.94	104.3
N50	1	42.43	11.89	19.45
	100	40.87	10.42	54.87
N25	1	22.61	11.18	48.92
	100	25.52	11.51	78.36
LCO	1	27.01	14.89	10.58
	100	27.59	13.37	20.85