Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting Information

Mixed Ionic-electronic Conductivity of High-nickel, Single-crystal Cathodes Influencing the Cycling Stability of All-solid-state Lithium-ion Batteries

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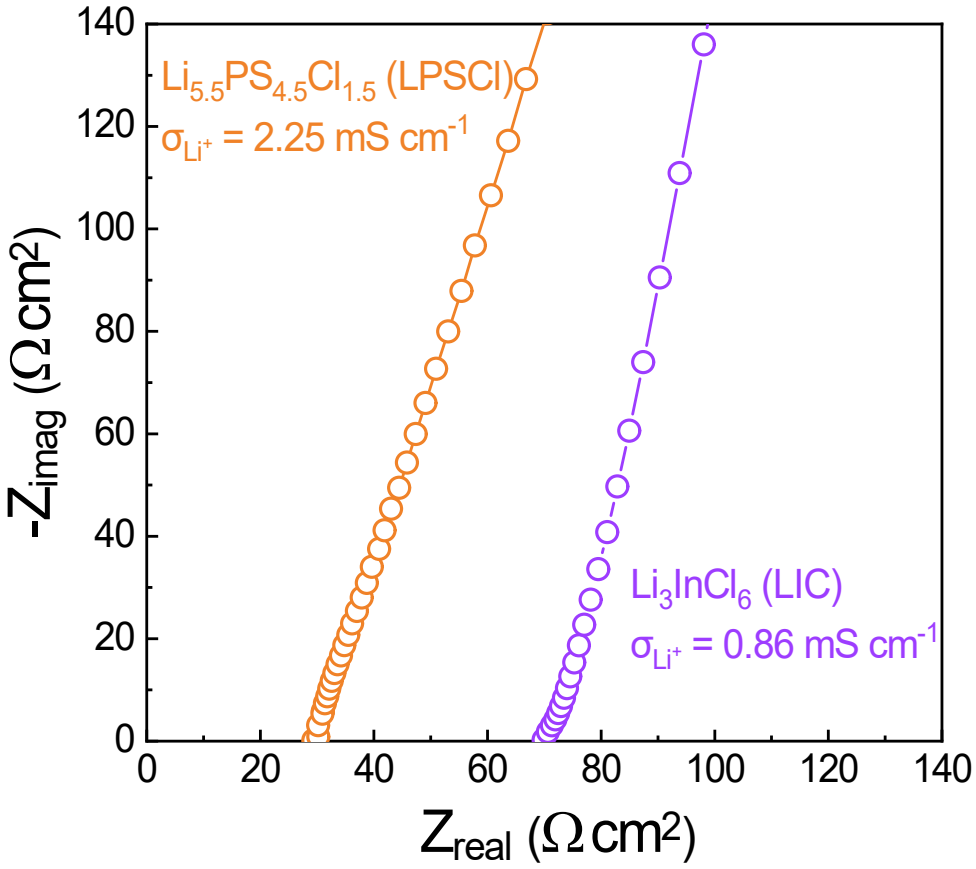

Fig. S1 Electrochemical impedance spectroscopy (EIS) curves of Li_3InCl_6 (LIC) and $Li_{5.5}PS_{4.5}Cl_{1.5}$ (LPSCl), illustrating their ionic conductivities (σ_{Li+}) after pressing under 370 MPa in a solid-state cell setup. The pellet thickness is around 0.6 – 0.7 mm.

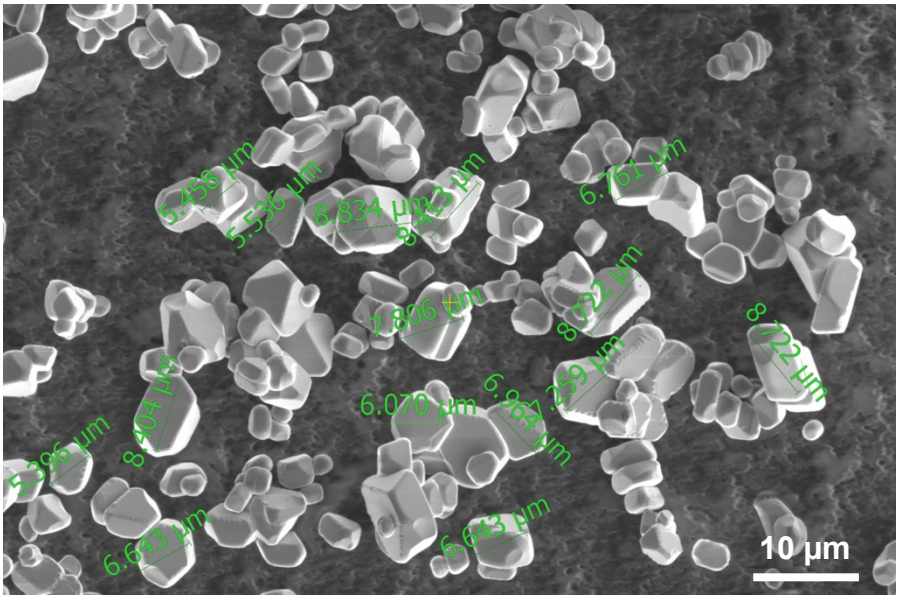

Fig. S2 Scanning electron microscope (SEM) images of SC-NC80 calcined with Na_2SO_4 at 840 °C. The particle size is 5 – 8 µm.

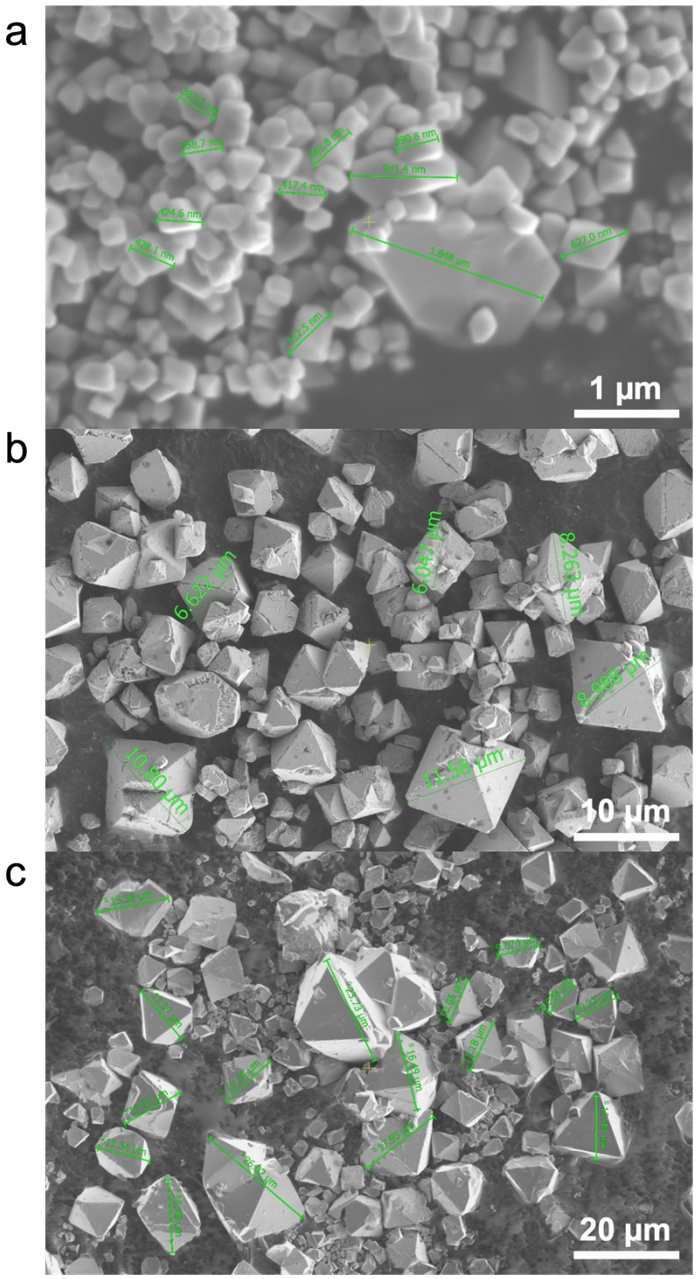

Fig. S3 SEM images of SC-NM80 calcined with Na_2SO_4 only at (a) 850 ^oC, (b) 870 ^oC, and (c) 900 ^oC. The particle sizes are 0.5 – 1 µm, 7 – 10 µm, and 10 – 25 µm, respectively.

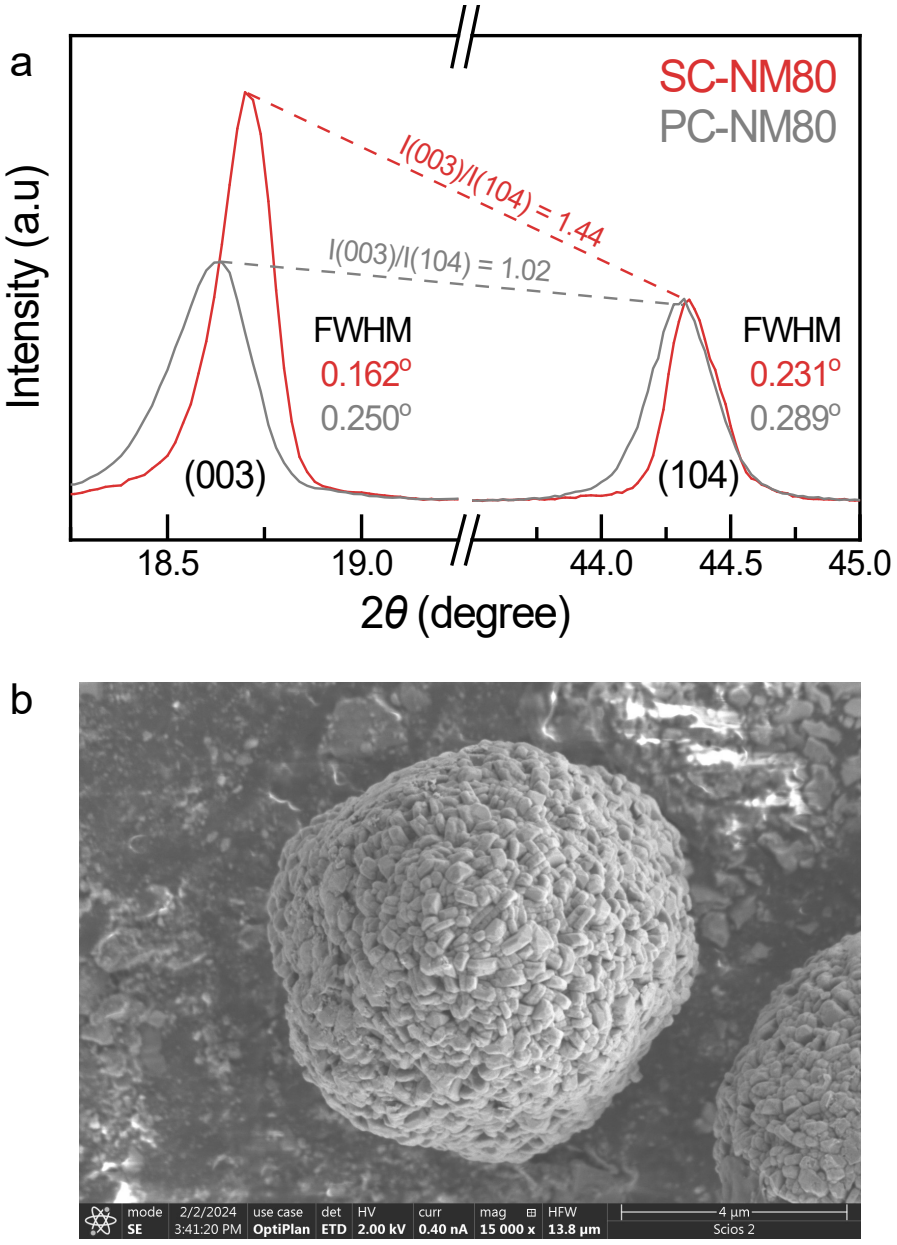

Fig. S4 (a) Comparison of the XRD patterns of single-crystalline NM80 (SC-NM80) and polycrystalline NM80 (PC-NM80). (b) SEM image of PC-NM80.

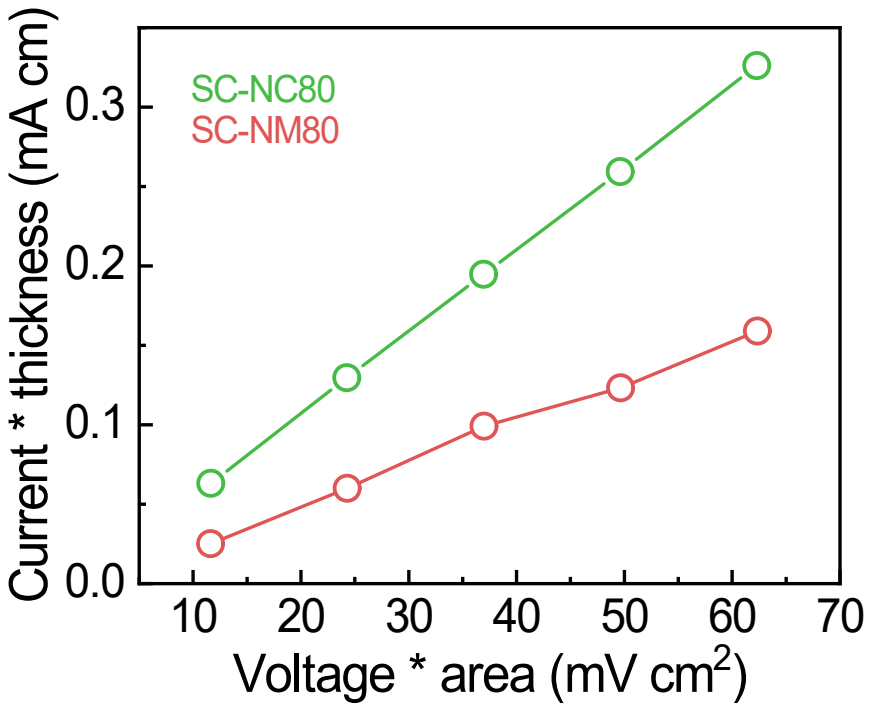

Fig. S5 Current vs. voltage curves of ion-blocking cells containing electrodes with purely SC-NC80 or SC-NM80 from DC polarization testing. The current axis and voltage axis are scaled by the electrode thickness and area, respectively, to reveal the slope that corresponds to the electronic conductivity of the cathode sample.

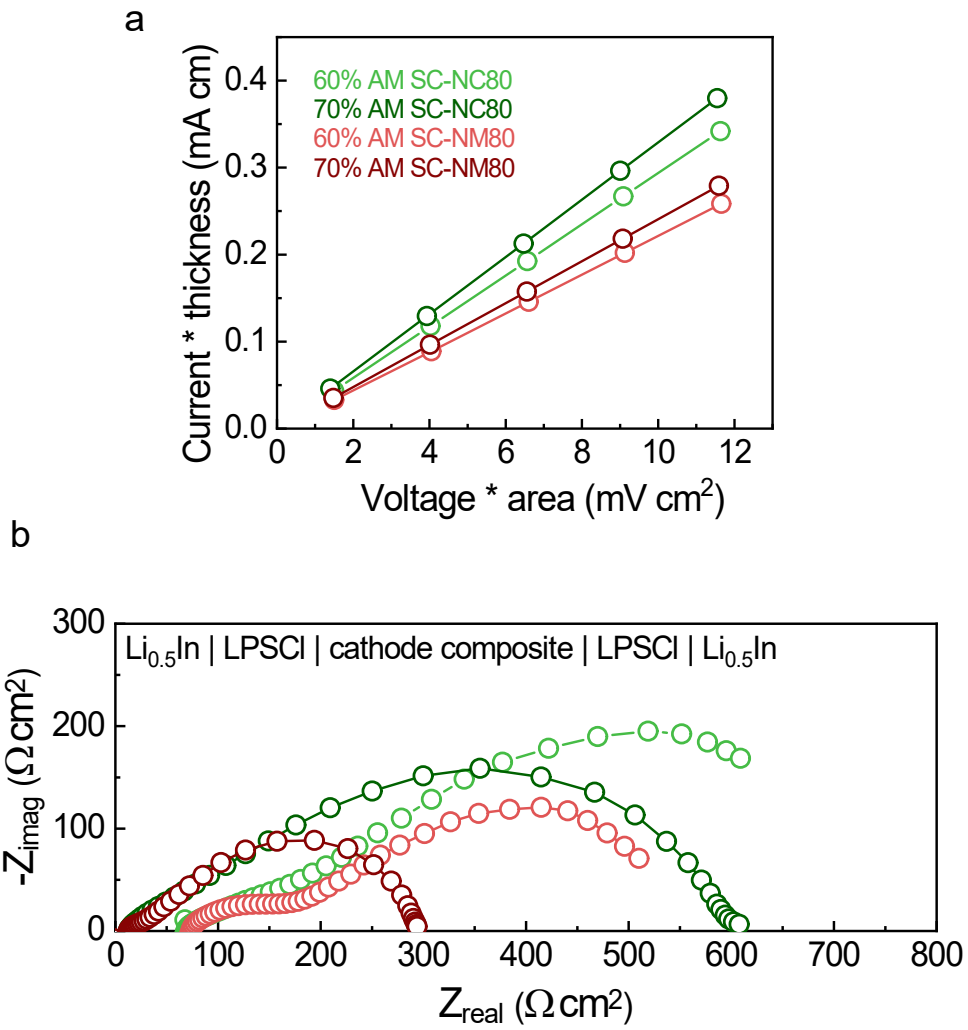

Fig. S6 Conductivity measurements of SC-NC80 and SC-NM80 with 60% or 70% AM in the cathode composites. (a) Current vs. voltage curves of ion-blocking cells containing various cathode composites from DC polarization testing. The current axis and voltage axis are scaled by the electrode thickness and area, respectively, to reveal the slope that corresponds to the electronic conductivity of the cathode composite. (b) EIS curves of the cathode composites in an electron-blocking symmetric ASSB. In this test, the loading of 60% and 70% of SC-NC80 is around 1.5 times higher than that of 60% and 70% of SC-NM80, giving a false indication that the impedance of SC-NC80 cathode composites is higher.

Table S1 XRD Rietveld refinement parameters of SC-NC80.

$LiNi_{0.8}Co_{0.2}O_2$ (SC-NC80)						
Space group: R-3m		I(003)/I(104) = 2.74			$FWHM_{(003)}$ = 0.151	
a = 2.8672(1) Å		*c* = 14.1695(9) Å			*V* = 100.879(8) Å^3	
R_p = 19.5		R_{wp} = 22.8		R_{exp} = 9.84	χ^2 = 5.38	
Atom	Wyckoff position	x	y	z	β_{iso}[1]	Occupancy
Li1	3a	0	0	0	0.943	1
Ni1	3b	0	0	0.5	0.295	0.8
Ni2	3a	0	0	0	0.295	0
Co	3b	0	0	0.5	0.295	0.2
O	6c	0	0	0.2318(4)	u_{11} = 0.0103 u_{33} = 0.0077	2

Table S2 XRD Rietveld refinement parameters of SC-NM80.

$LiNi_{0.8}Mn_{0.2}O_2$ (SC-NM80)						
Space group: R-3m		I(003)/I(104) = 1.44			$FWHM_{(003)}$ = 0.162	
a = 2.8796(3) Å		*c* = 14.2372(14) Å			*V* = 102.238(17) $Å^3$	
R_p = 17.9		R_{wp} = 19.5		R_{exp} = 10.3	χ^2 = 3.61	
Atom	Wyckoff position	x	y	z	β_{iso}[1]	Occupancy
Li1	3a	0	0	0	0.943	0.9653(3)
Li2	3b	0	0	0.5	0.943	0.0347(3)
Ni1	3b	0	0	0.5	0.295	0.7653(3)
Ni2	3a	0	0	0	0.295	0.0347(3)
Mn	3b	0	0	0.5	0.295	0.2
O	6c	0	0	0.2366(4)	u_{11} = 0.0103 u_{33} = 0.0077	2