Electronic Supplementary Information

Design of densified nickel-rich layered composite cathode via the dry-film process for sulfide-based solid-state batteries

Dongjin Shin‡[a], Jae Seok Nam‡[a], Chi Thi Linh Nguyen [a], Younghoon Jo [a], Kyusik Lee [a], Soo Min Hwang [a], and Young-Jun Kim [a,b,*]

[a] *SKKU Advanced Institute of Nano Technology (SAINT), Sungkyunkwan University, Suwon 16419, Republic of Korea.*

[b] *Department of Nano Engineering, Sungkyunkwan University, Suwon 16419, Republic of Korea.*

‡These authors contributed equally to this work.

*Corresponding authors: yjkim68@skku.edu (Y.-J.K.)

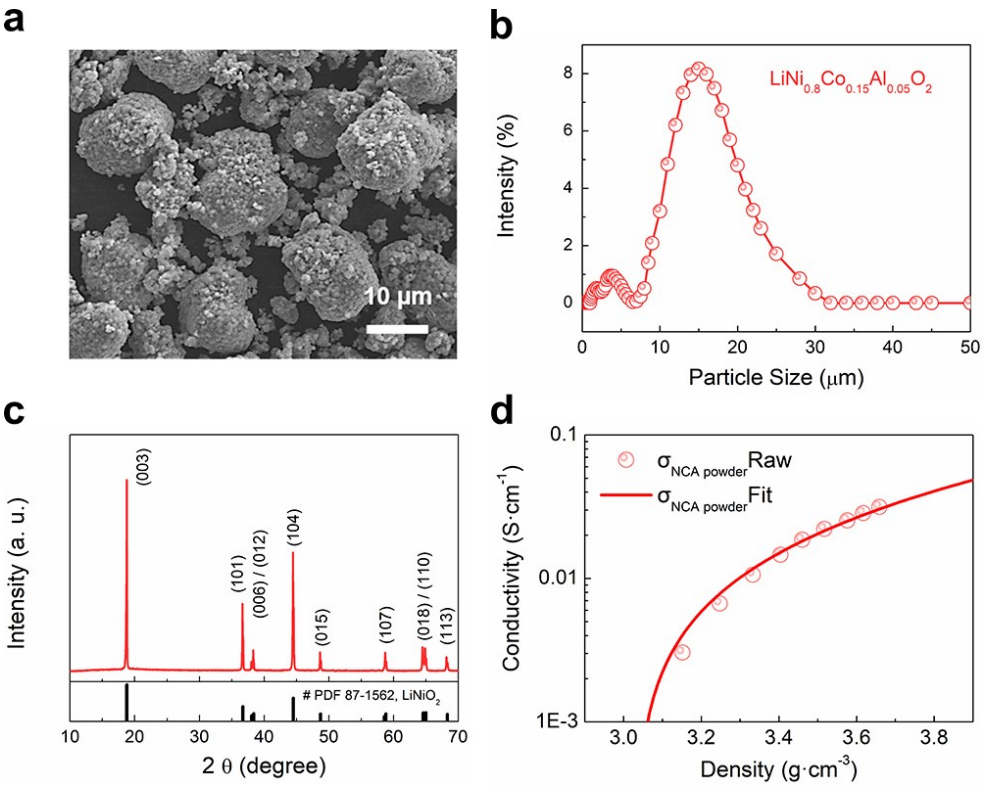

Fig. S1 (a) SEM Image, (b) Particle size distribution, (c) XRD patterns of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA); (d) Electronic conductivity of NCA powder as a function of density.

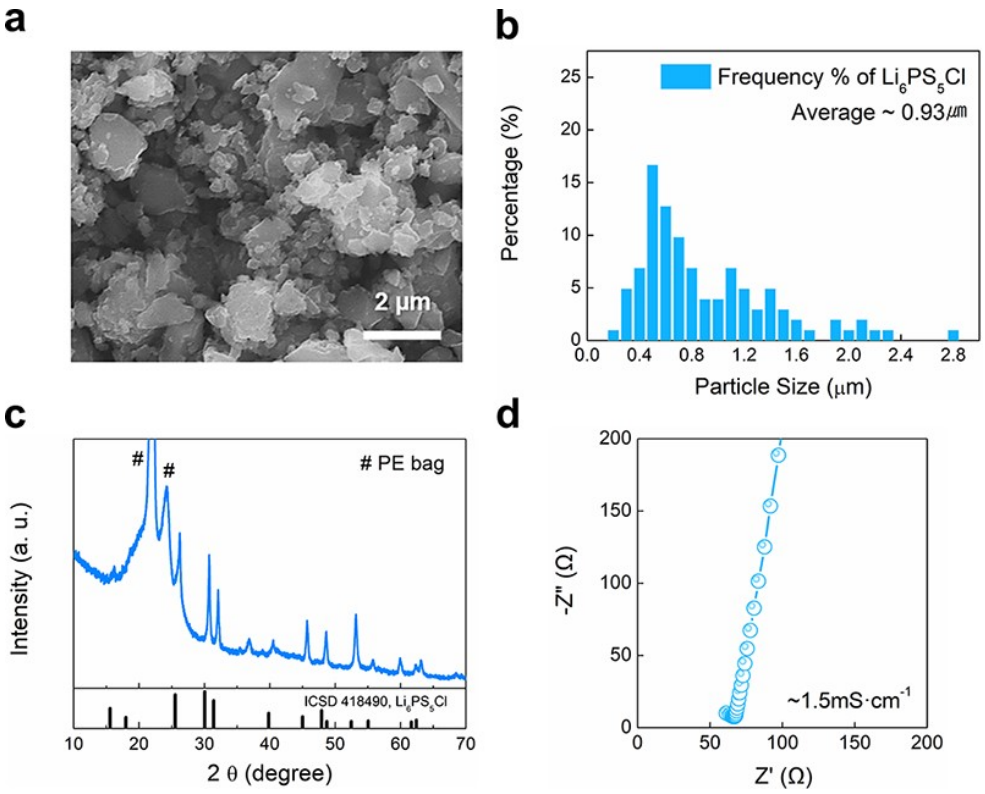

Fig. S2 (a) SEM Image, (b) Particle size distribution, (c) XRD patterns, (d) EIS measurement of Li_6PS_5Cl (LPSCl)

Table S1 Calculated porosity and volume ratio of NCA and Li_6PS_5Cl in composite cathode using theoretical density of NCA, Li_6PS_5Cl, SuperC65 and PTFE. The theoretical densities were assumed to be 4.45 g·cm^{-3}, 1.87 g·cm^{-3}, 1.6 g·cm^{-3} and 2.17g·cm^{-3}, respectively.[1, 2]

Modified contents	V_{theo} (cm^3) [a)]	V_{exp} (cm^3)	φ (%)	NCA (vol %)	Li_6PS_5Cl (vol %)
NCA 75wt%	0.302	0.357	15.95	46.85	34.19
NCA 77wt%	0.296	0.345	14.94	49.69	32.25
NCA 80wt%	0.287	0.333	14.43	53.62	28.71
NCA 83wt%	0.278	0.323	13.67	58.01	24.95
NCA 85wt%	0.271	0.313	13.44	60.92	22.17

a)

$$V_{theo} = \left[\frac{1g \times Cotent_{(NCA)}}{4.45\ [g/cm^3]} + \frac{1g \times Cotent_{(Li_6PS_5Cl)}}{1.87\ [g/cm^3]} + \frac{1g \times Cotent_{(SuperC65)}}{1.6\ [g/cm^3]} + \frac{1g \times C}{2.1}\right.$$

Table S2 Modified content of the NCA composite pellet (uniaxial pressing method) with experimental electrode density (D_{exp}) and loading level of NCA

Modified contents	NCA : Li_6PS_5Cl (wt%)	Super C65 : PTFE (wt%)	D_{exp} (g·cm^{-3})	Loading level of NCA (mg·cm^{-2})
NCA 75wt%	75 : 25	0 : 0	2.57 ± 0.08	~ 15
NCA 77wt%	77 : 23	0 : 0	2.64 ± 0.07	~ 15
NCA 80wt%	80 : 20	0 : 0	2.74 ± 0.04	~ 15
NCA 83wt%	83 : 17	0 : 0	2.86 ± 0.05	~ 15
NCA 85wt%	85 : 15	0 : 0	3.03 ± 0.03	~ 15

Table S3 Calculated porosity and volume ratio of NCA and Li_6PS_5Cl in composite pellet (uniaxial pressing method) using theoretical density of NCA, Li_6PS_5Cl. The theoretical densities were assumed to be 4.45 g·cm^{-3} and 1.87 g·cm^{-3}, respectively. [1, 2]

Modified contents	V_{theo} **(cm^3)** [b)]	V_{exp} **(cm^3)**	φ **(%)**	**NCA (vol %)**	**Li_6PS_5Cl (vol %)**
NCA 75wt%	0.389	0.302	22.33	43.31	34.36
NCA 77wt%	0.379	0.296	21.85	45.68	32.47
NCA 80wt%	0.364	0.287	21.43	49.26	29.30
NCA 83wt%	0.350	0.277	20.65	53.34	26.00
NCA 85wt%	0.330	0.271	17.82	57.88	24.30

b) $$V_{theo} = \left[\frac{1g \times Cotent_{(NCA)}}{4.45\ [g/cm^3]} + \frac{1g \times Cotent_{(Li_6PS_5Cl)}}{1.87\ [g/cm^3]}\right]$$

Reference

1. A. Zülke, I. Korotkin, J. M. Foster, M. Nagarathinam, H. Hoster, and G. Richardson, *J. Electrochem. Soc.*, 2021, **168**, 120522
2. P. Minnmann, L. Quillman, S. Burkhardt, F. H. Richter and J. Janek, *J. Electrochem. Soc.*, 2021, **168**, 040537

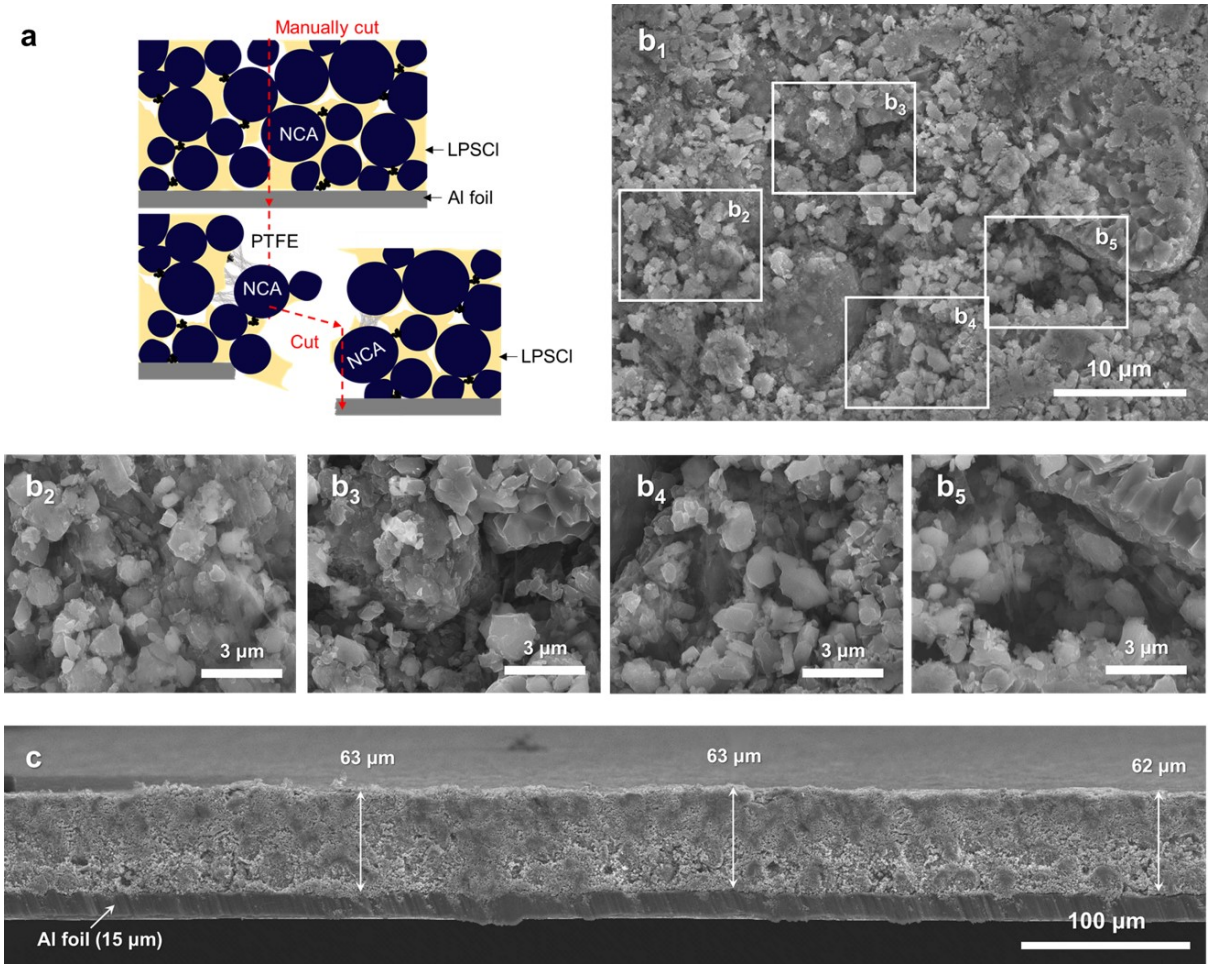

Fig. S3 (a) Schematics of the preparation of the cross-sectional surface of NCA 80wt% electrode with manual cut, and (b_1-b_5, c) cross-sectional SEM images of manually cut NCA 80wt% electrode.

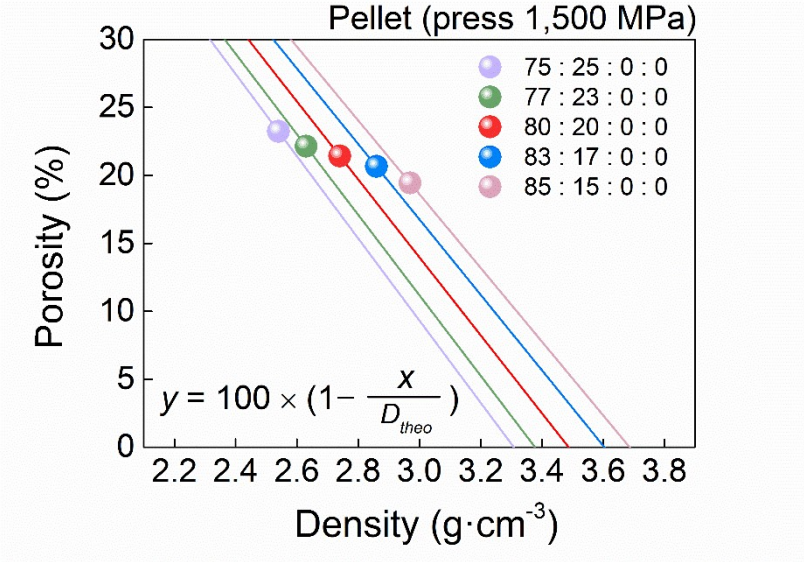

Fig. S4 Porosity plot of composite pellets with respect to the total summation of the standard density of NCA and LPSCl as a reference value of the theoretical density (see Table S1 and S2†).

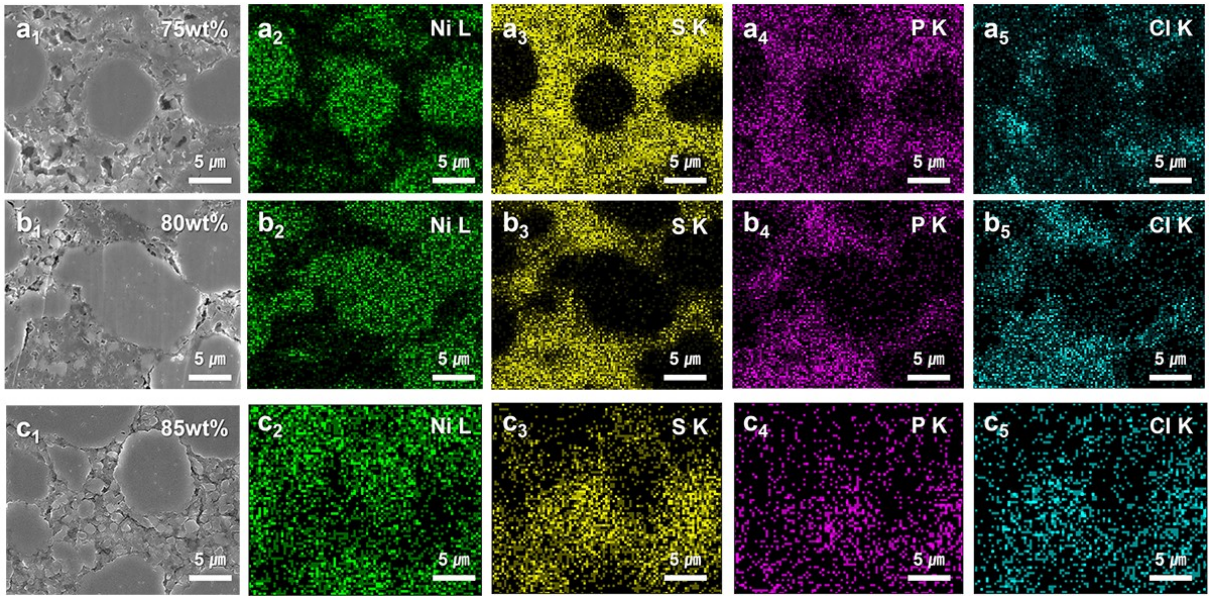

Fig. S5 Cross-sectional SEM image and corresponding EDS element mapping image of composite cathode with respect to content of NCA: (a_1) to (a_5) NCA 75wt%; (b_1) to (b_5) NCA 80wt%; (c_1) to (c_5) NCA 85wt%.

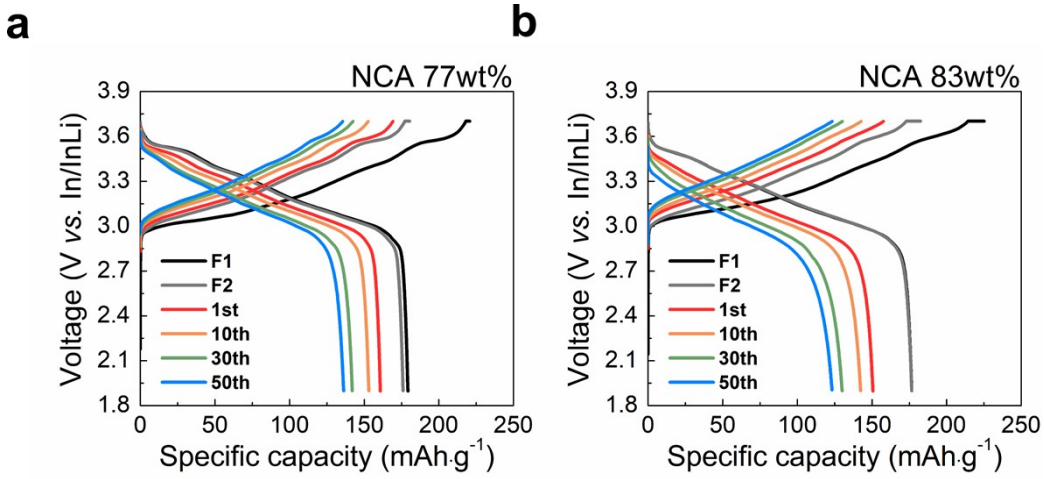

Fig. S6 Charge–discharge voltage profiles of SSBs composite cathodes with modified content of NCA (a) 77wt% and (b) 83wt%, measured in a voltage range of 1.9 V to 3.7 V *vs.* In/InLi at 0.1 C for 50 cycles after formation at 0.05 C for two cycles.

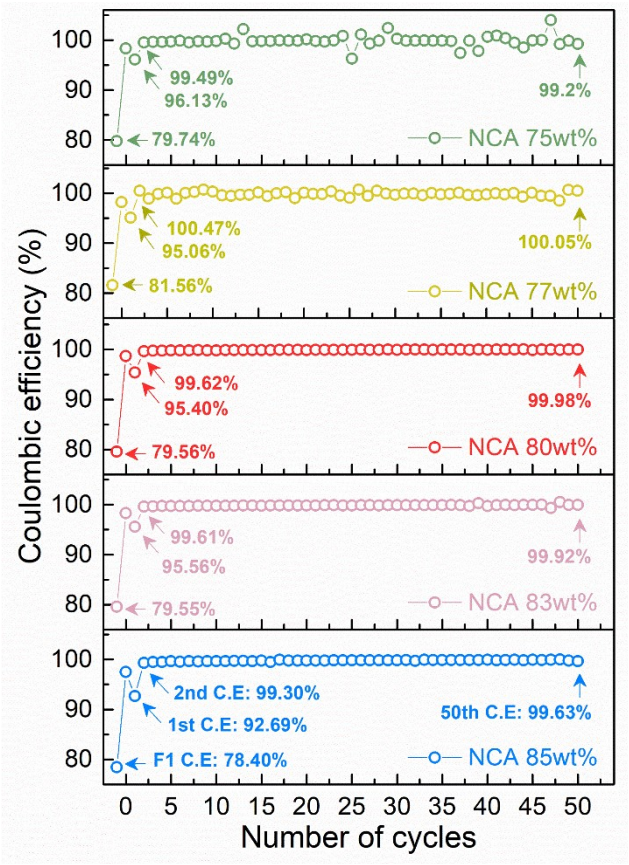

Fig. S7 Coulombic efficiencies during charge–discharge cycles of SSBs composite cathodes with modified content of NCA from 75wt% to 85wt% (top to bottom), measured in the voltage range of 1.9 V to 3.7 V vs. In/InLi at 0.1 C for 50 cycles after formation at 0.05 C for two cycles.

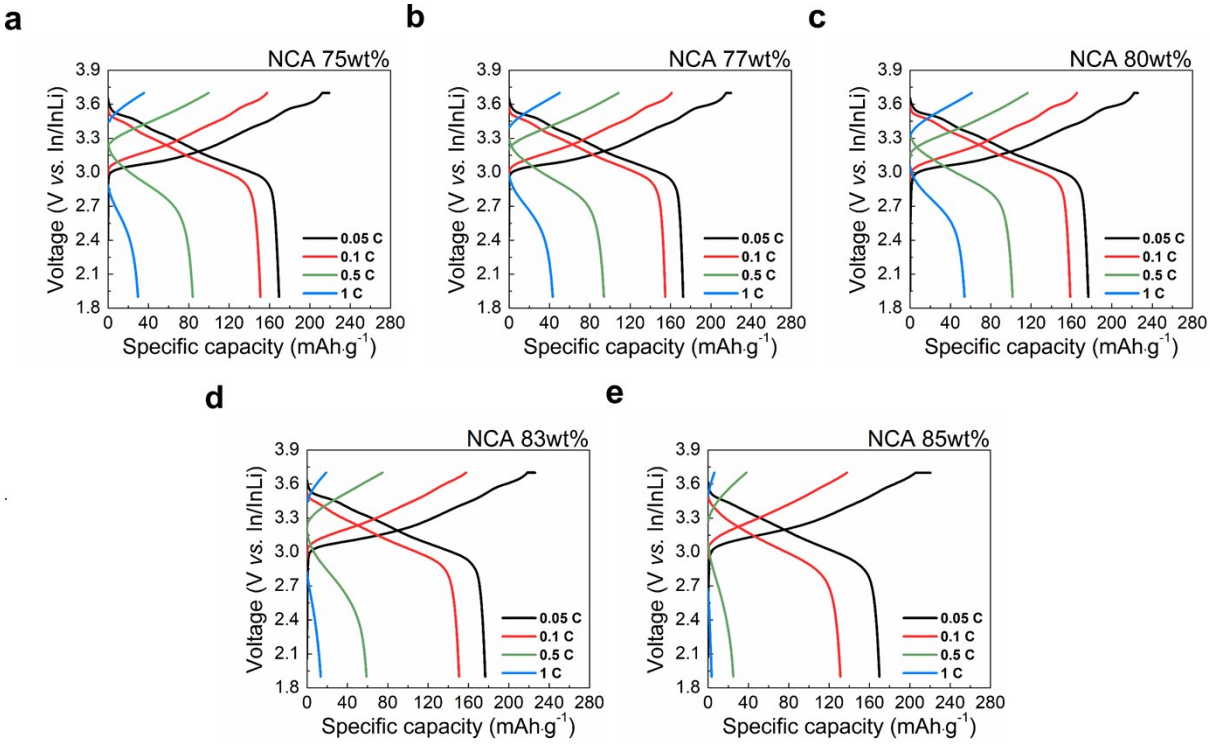

Fig. S8 Charge–discharge voltage profiles of composite cathode with modified content of NCA: (a) 75wt%, (b) 77wt%, (c) 80wt%, (d) 83wt% and (e) 85wt%, measured in voltage range of 1.9 V to 3.7 V vs. In/InLi at 0.05 C to 1C.

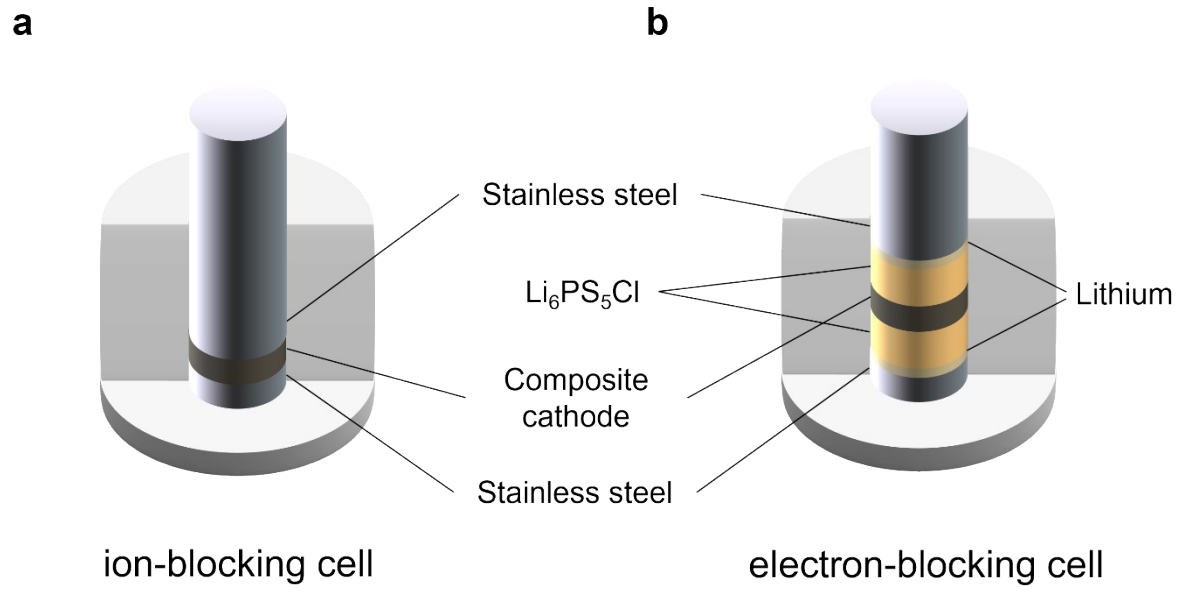

Fig. S9 Schematics configuration of (a) ion-blocking and (b) electron-blocking symmetric cell.

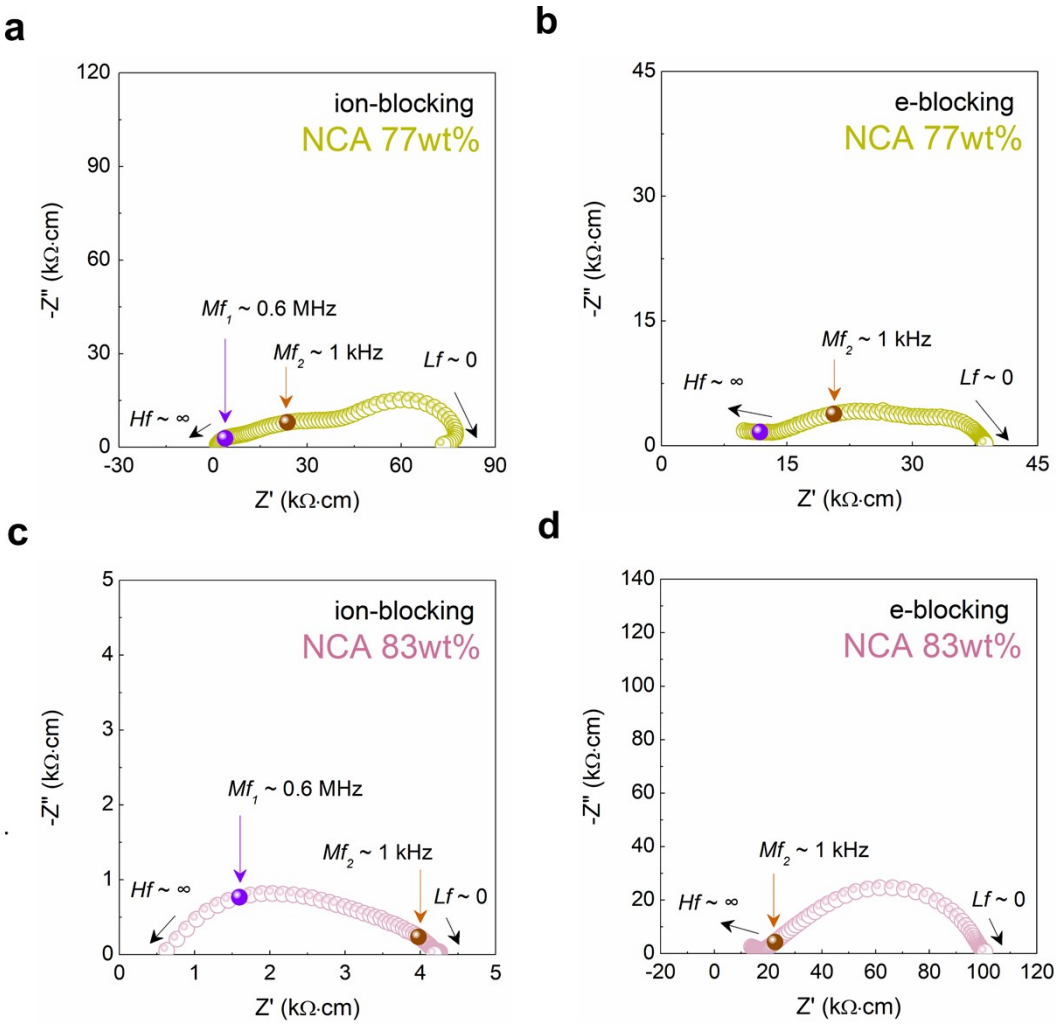

Fig. S10 Nyquist plots of ion-blocking [SS ‖ composite cathode ‖ SS] and electron-blocking [Li ‖ LPSCl ‖ composite cathode ‖ LPSCl ‖ Li] symmetric cells of composite cathode with modified content of (a) and (b) NCA 77wt%; (c) and (d) NCA 83 wt%.

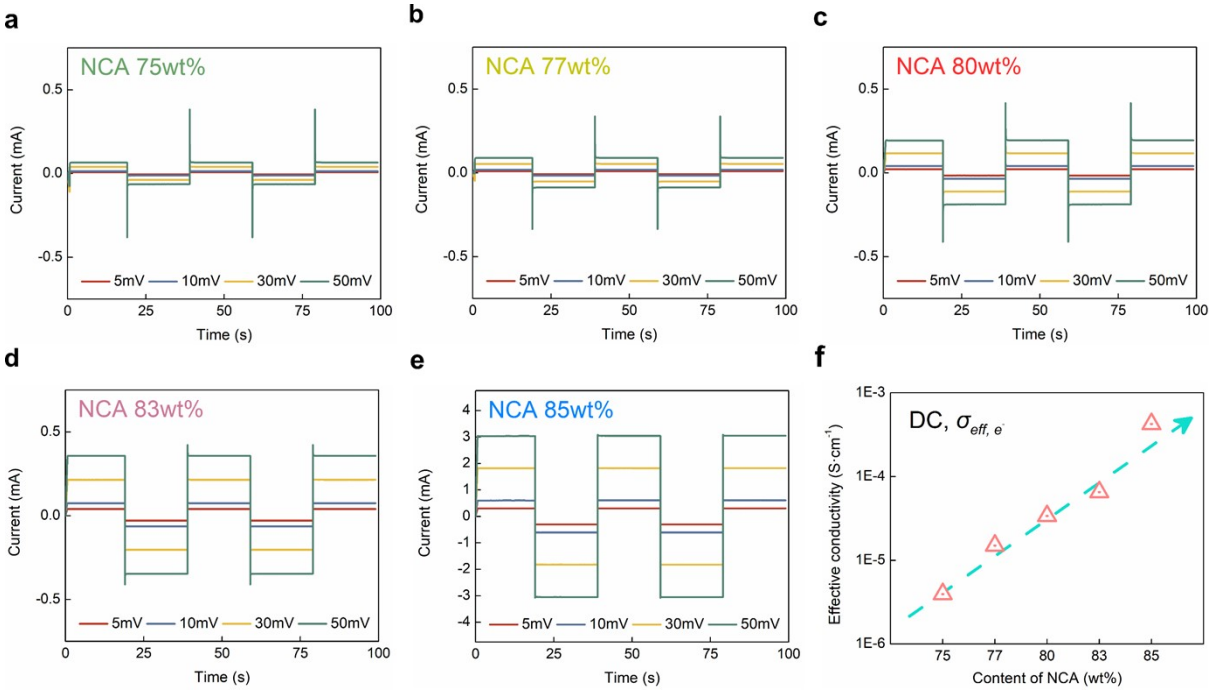

Fig. S11 DC polarization measurements at different voltage bias on ion-blocking symmetric cell containing composite cathode with modified content of NCA: (a) NCA 75wt%, (b) NCA 77wt%, (c) NCA 80wt%, (d) NCA 83wt%, and (e) NCA 85wt%; (f) measured electronic conductivity of each ion-blocking symmetric cell.

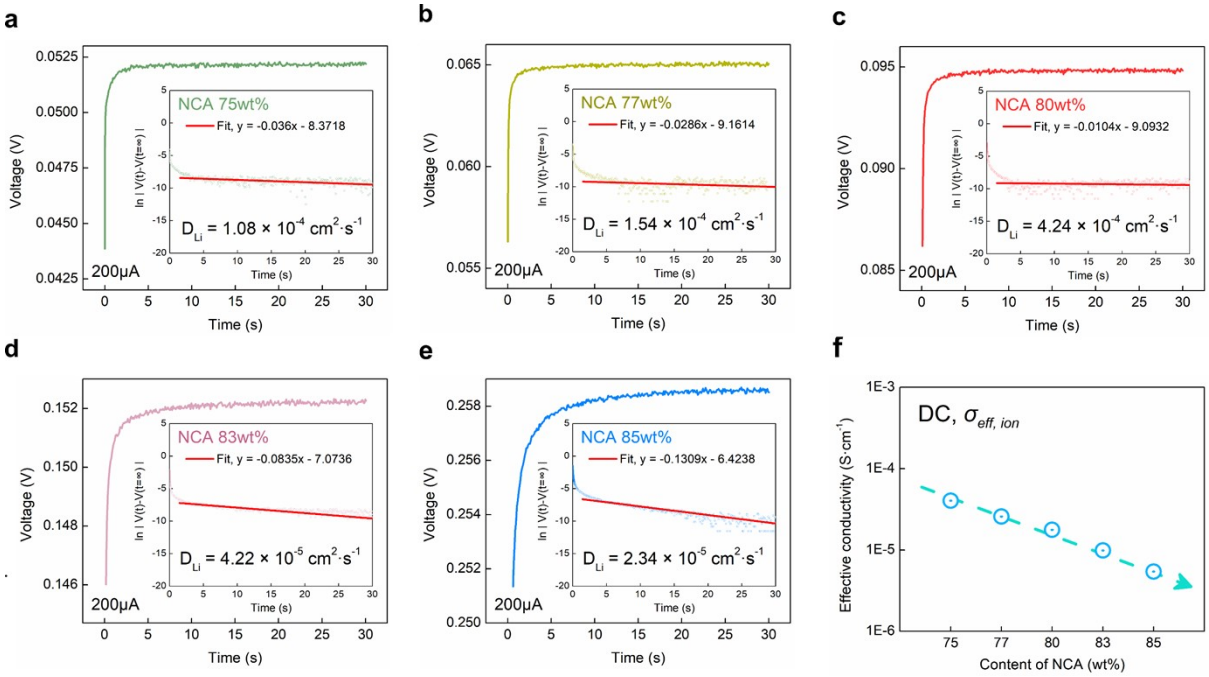

Fig. S12 DC polarization measurements at a current of 200 μA on electron-blocking symmetric cell containing composite cathode with modified content of NCA. The slope of the ln| U(t)-U (t = ∞) | *vs.* t plots indicate the diffusion coefficient of composite cathodes (inset): (a) NCA 75wt%, (b) NCA 77wt%, (c) NCA 80wt%, (d) NCA 83wt%, and (e) NCA 85wt%.; (f) measured ionic conductivity of each electron-blocking symmetric cell.

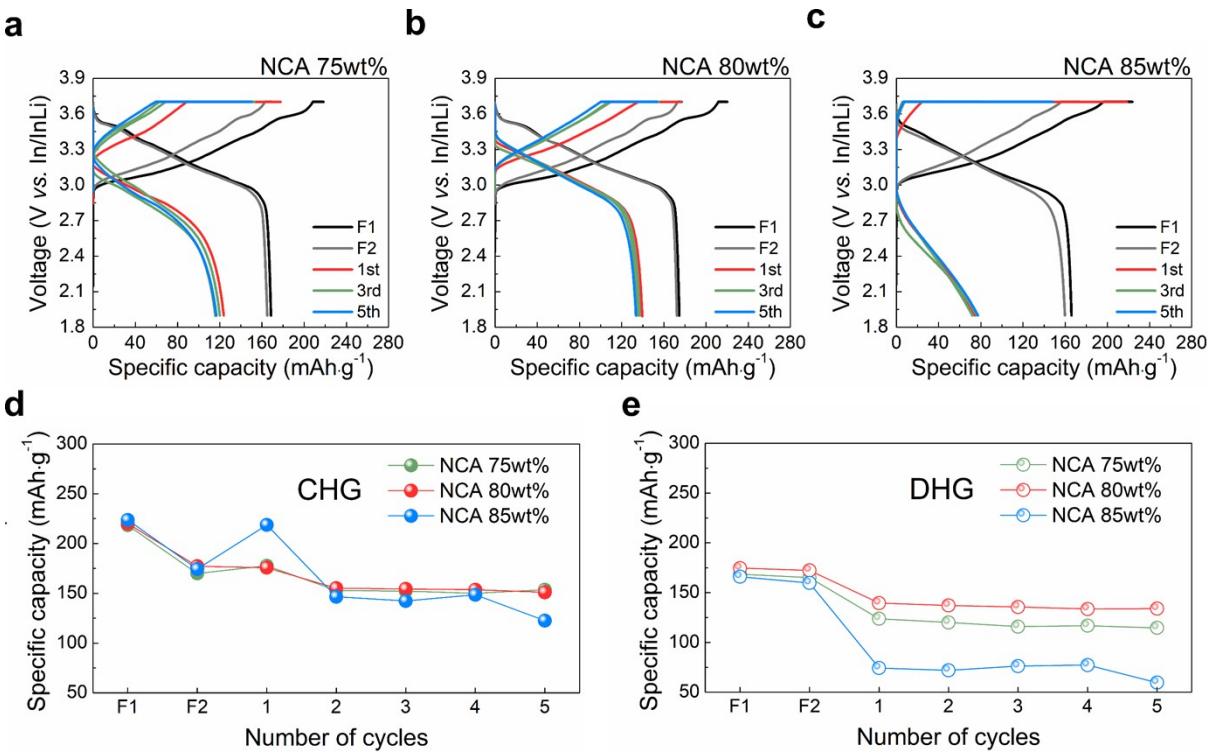

Fig. S13 Voltage profiles of composite cathode with modified content of (a) NCA 75wt%, (b) 80wt% and (c) 85wt%, measured in the voltage range of 1.9 V to 3.7 V *vs.* In/InLi at 0.5 C followed by CV charging with a cut-off condition of 0.05 C for 5 cycles after formation at 0.05 C for two cycles; (d) charge and (e) discharge capacity retention with composite cathode.