

## Electronic Supplementary Information (ESI)

### Argyrodite sulfide coated NCM cathode for the improved interfacial contact in normal-pressure operational all-solid-state batteries

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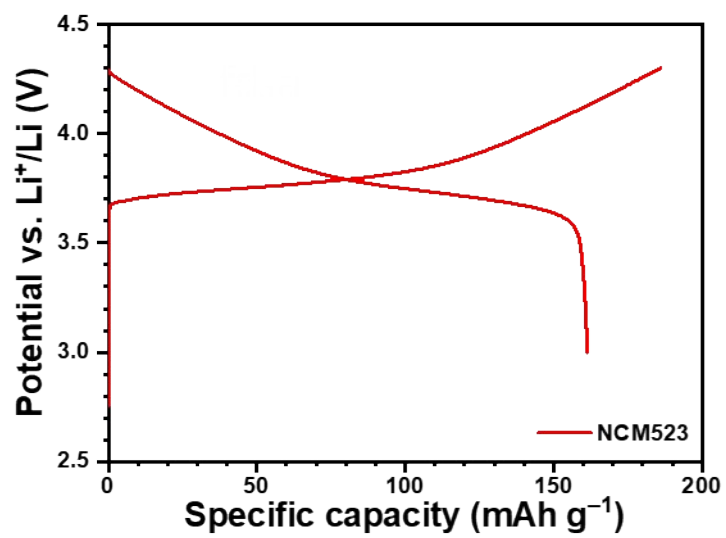
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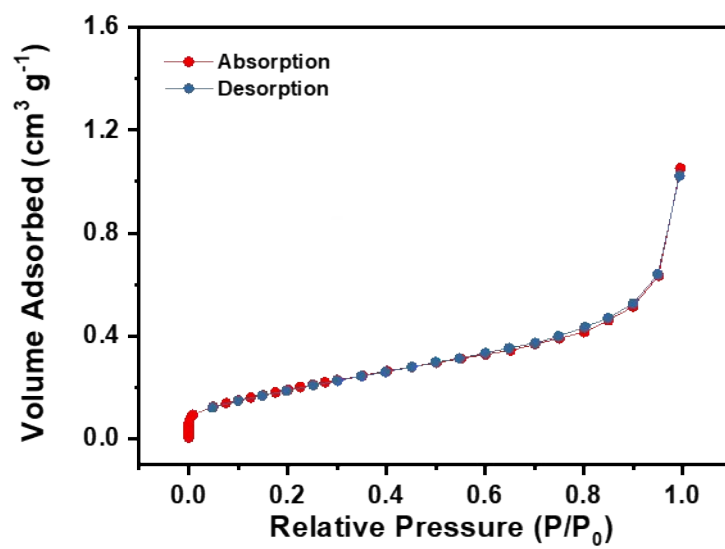
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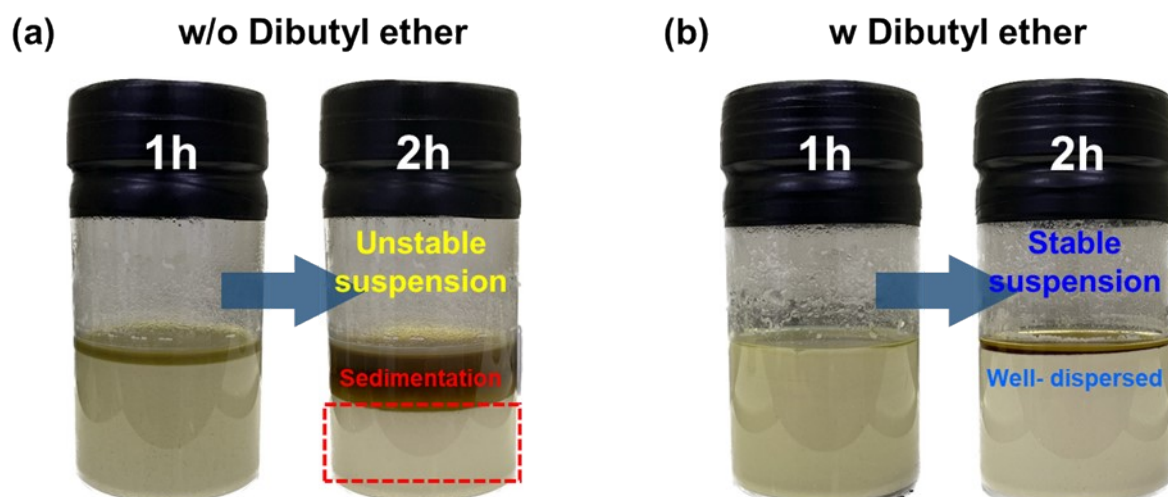
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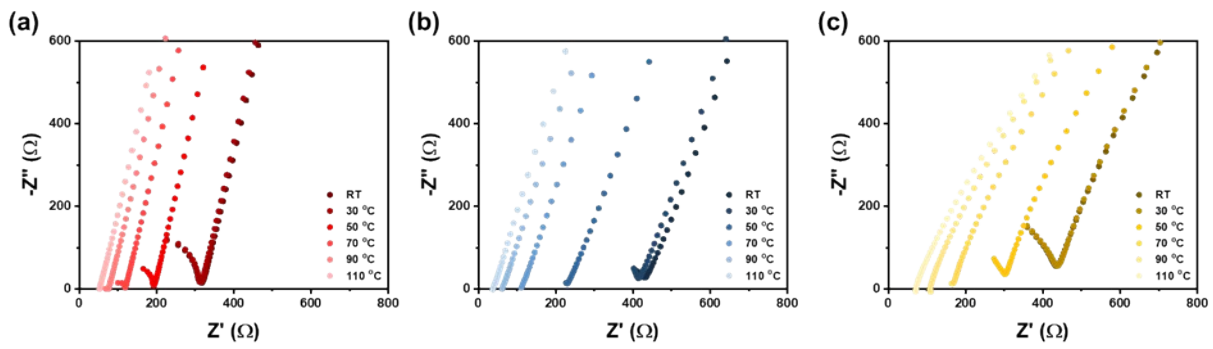
**Fig. S1** 1<sup>st</sup> charge–discharge voltage profile of NCM523 with liquid electrolyte.



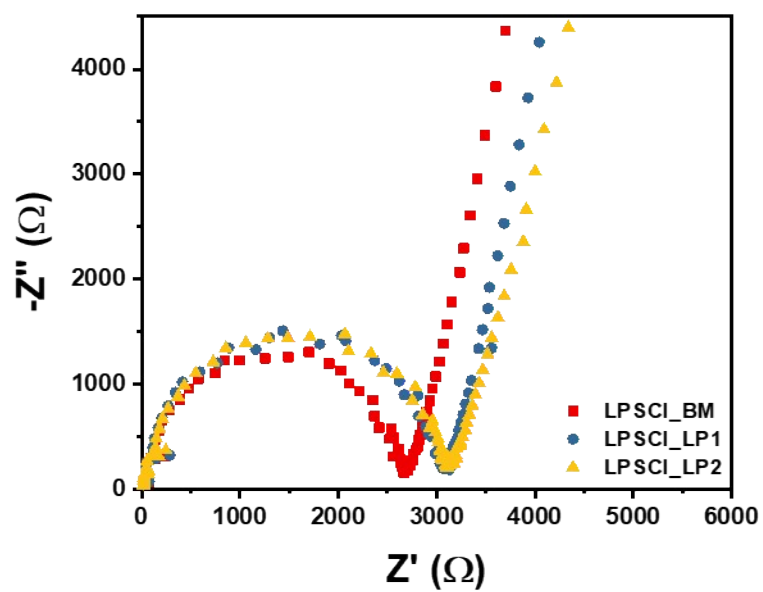
**Fig. S2** BET analysis of N<sub>2</sub> adsorption–desorption isotherm for NCM523.



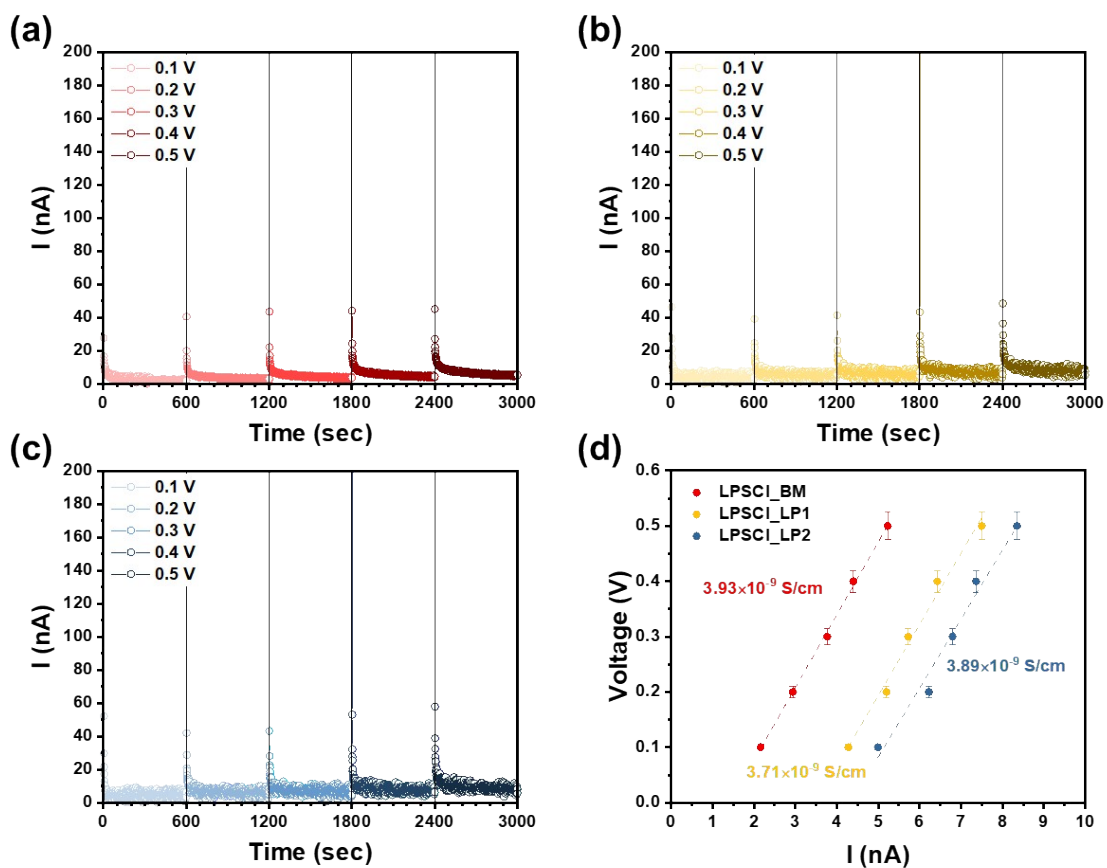
**Fig. S3** Results of liquid-phase synthesis of  $\text{Li}_6\text{PS}_5\text{Cl}$  precursors in solvent. Digital photographs of (a) without dibutyl ether and (b) with dibutyl ether (during synthesis without stirring).



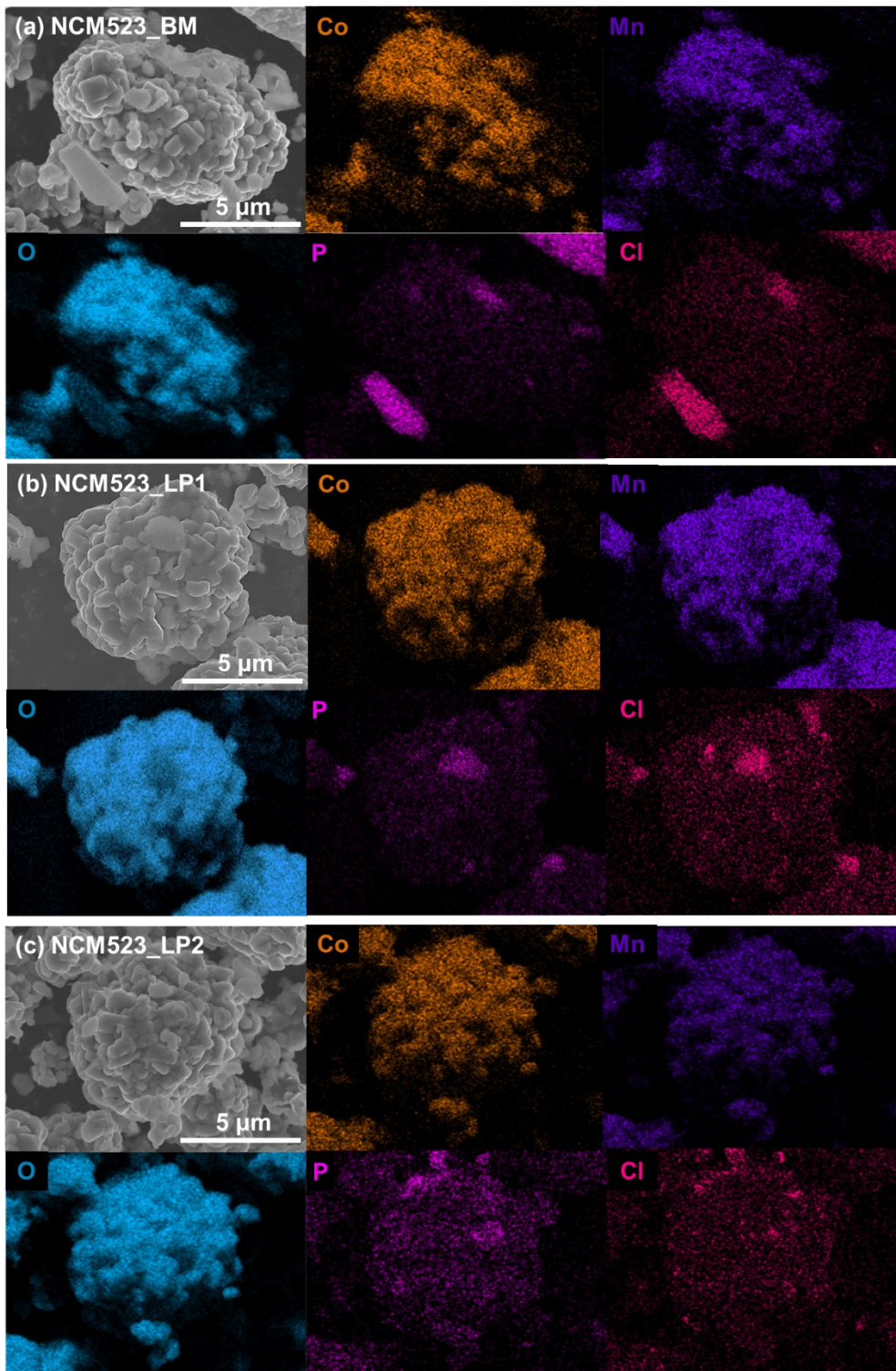
**Fig. S4** Nyquist plots of impedance spectra for (a) LPSCI\_BM, (b) LPSCI\_LP1, and (c) LPSCI\_LP2 with elevating temperature from RT to 110 °C at intervals of 20 °C.



**Fig. S5** Nyquist plots of impedance spectra for (a) LPSCI\_BM, (b) LPSCI\_LP1, and (c) LPSCI\_LP2 with heat-treatment at 180 °C.

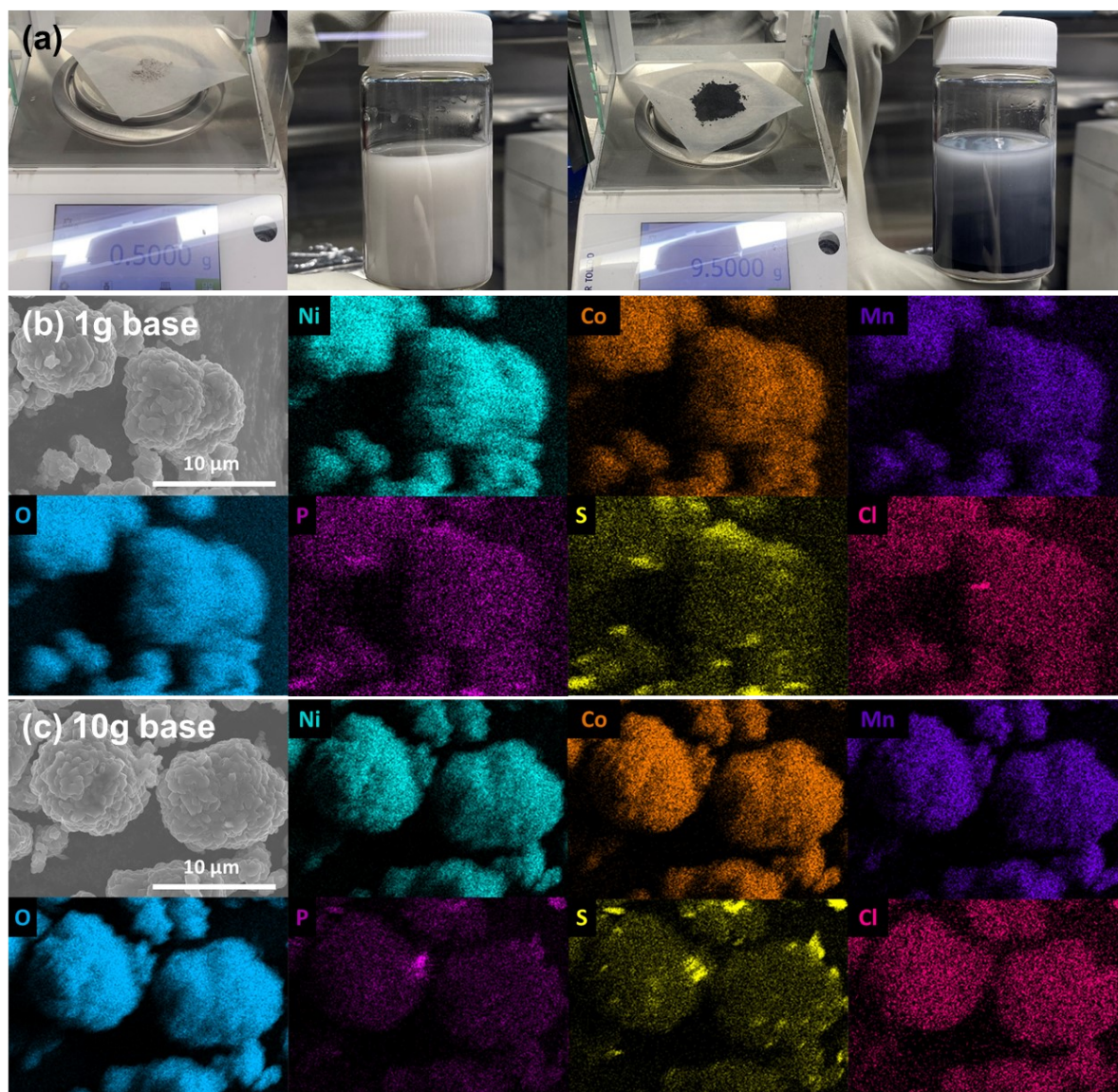


**Fig. S6** Chronoamperometry results of (a) LPSCI\_BM, (b) LPSCI\_LP1, and (c) LPSCI\_LP2 with an applied voltage of 0.1, 0.2, 0.3, 0.4, and 0.5 V. (d) Linear fits.



**Fig. S7** SEM images of (a) NCM523\_BM, (b) NCM523\_LP1, and (c) NCM523\_LP2 with corresponding EDS mapping of Co, Mn, O, P, and Cl.





**Fig. S8** (a) Digital photograph of 10 g base coating process. SEM images of (b) 1 g base and (c) 10 g base of NCM523\_LP2 with corresponding EDS mapping of Ni, Co, Mn, O, P, S, and Cl.

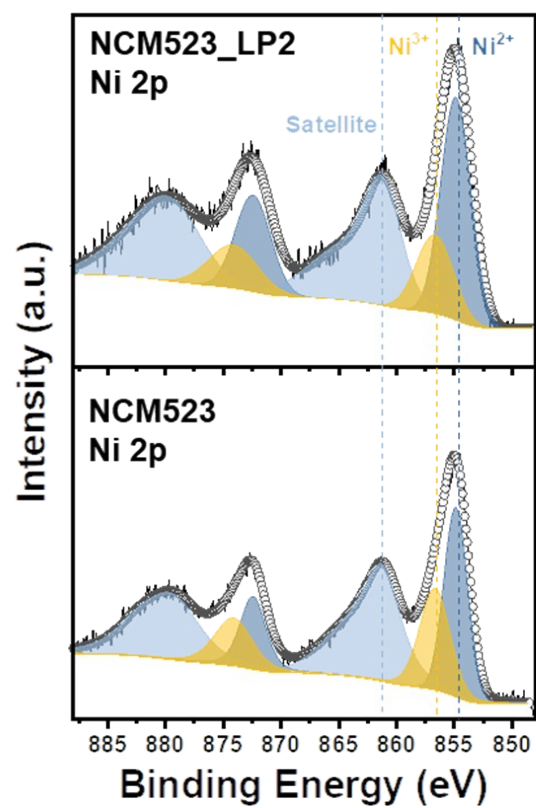


Fig. S9 Ni 2p XPS spectra of NCM523 and NCM523\_LP2.

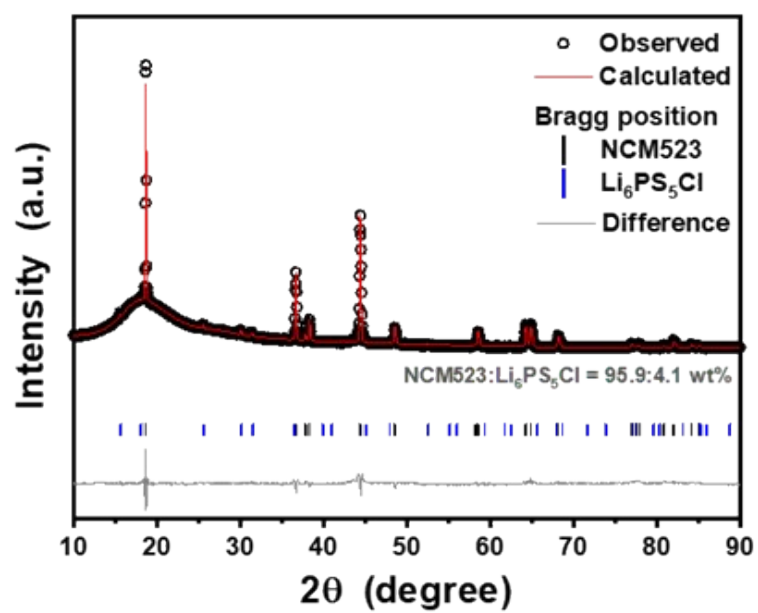
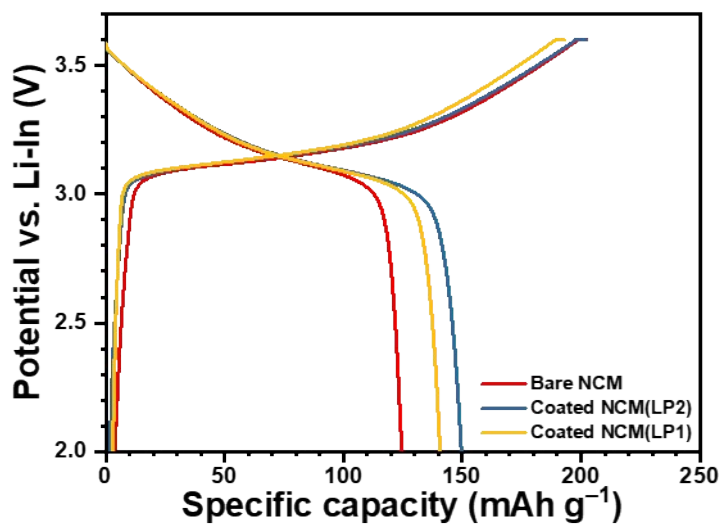
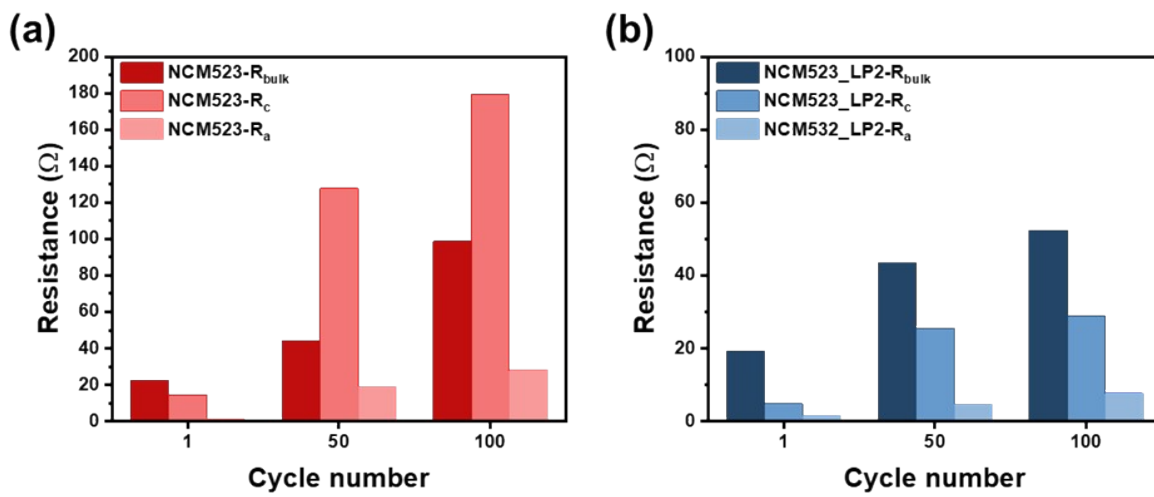


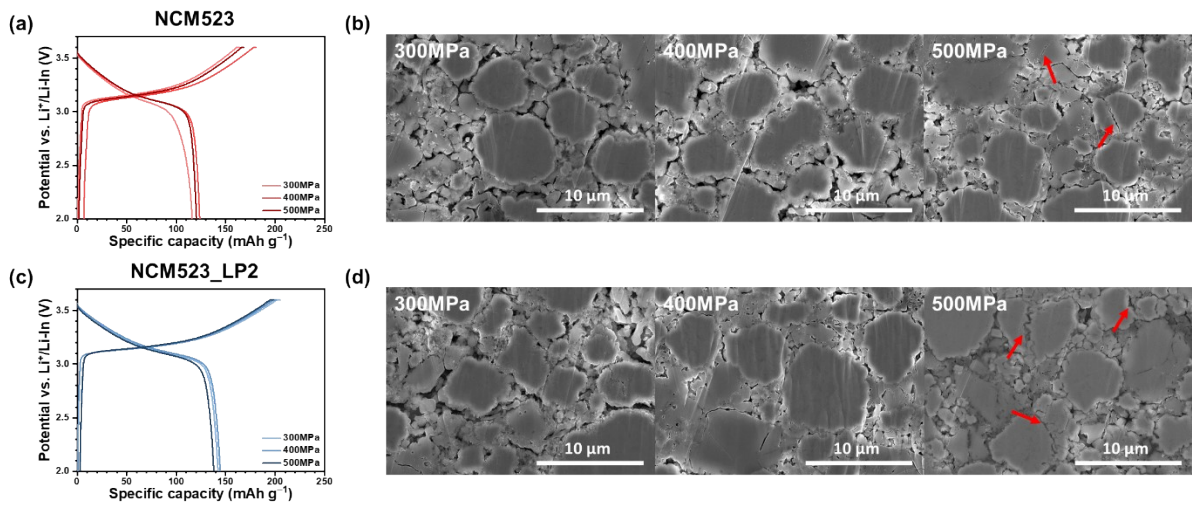
Fig. S10 Rietveld refinement results of the XRD patterns of NCM523\_LP2.



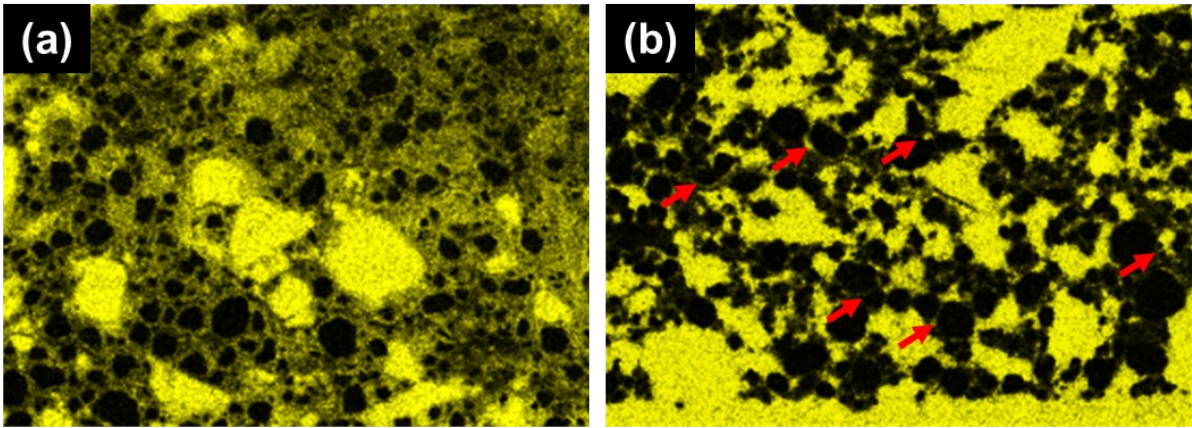
**Fig. S11** 1<sup>st</sup> charge–discharge voltage profiles of all-solid-state cells with composite cathode featuring NCM523, NCM523\_LP1, and NCM523\_LP2.



**Fig. S12** Fitted values for impedance spectra of all-solid-state cells with (a) NCM523, and (b) NCM523\_LP2 in Fig. 4e.



**Fig. S13** Electrochemical characterization of all-solid-state cells employing bare NCM523 and NCM523\_LP2 with variable fabrication pressure. (a, c) 1<sup>st</sup> charge–discharge voltage profiles. Cross-sectional SEM images of composite cathode with (b) NCM523, and (d) NCM523\_LP2 applying variable fabrication pressure. Red arrows indicate micro cracks in cathode active material.



**Fig. S14** Corresponding EDS mapping of S in Fig. 5a and b. Pristine state of composite cathode with (a) NCM523, and (b) NCM523\_LP2. Red arrows indicate intimate contacts.