

[Supplementary Information]

# **Single-Step Wet-Chemical Fabrication of Sheet-Type Electrodes from Solid-Electrolyte Precursors for All-Solid-State Lithium-ion Batteries**

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## Supplementary Experimental

### Electrochemical characterization using liquid electrolyte cells

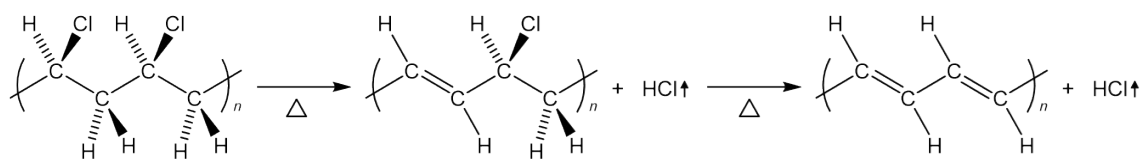
Cycling tests using liquid electrolytes were performed using 2032-type coin cells. NCM622 electrodes were prepared by spreading NCM622, Super C65, and poly(vinylidene fluoride) (PVDF) binder (KF1100, Kureha Inc.) on Al foil in a weight ratio of 90:5:5. Graphite electrodes were prepared by spreading graphite and PVDF binder on Cu foil in a weight ratio of 90:10. Li metal foil was used as both the counter and reference electrode. The loading amounts of NCM622 and graphite electrodes used in the liquid electrolyte cells were adjusted to be close to those used for the all-solid-state cells. Also, the porosities of NCM622 and graphite electrodes for liquid electrolyte cells were adjusted so that the volume fraction of the liquid electrolytes (49% and 42% for NCM622 and graphite electrodes, respectively) was close to that of SEs in the electrodes for all-solid-state cells (47% and 48% for NCM622 and graphite electrodes, respectively). A 1.15 M solution of  $\text{LiPF}_6$  dissolved in a mixture of ethylene carbonate (EC), ethylmethyl carbonate (EMC), and dimethyl carbonate (DMC) (2:5:3 v/v) with 5 wt.% fluorinated ethylene carbonate (FEC) and 0.5 wt.% vinyl carbonate (VC) as additives was used as the electrolyte. A porous polypropylene (PP)/polyethylene (PE)/PP tri-layer film (Celgard Inc.) was used as the separator.

### THF-solution-treated NCM622

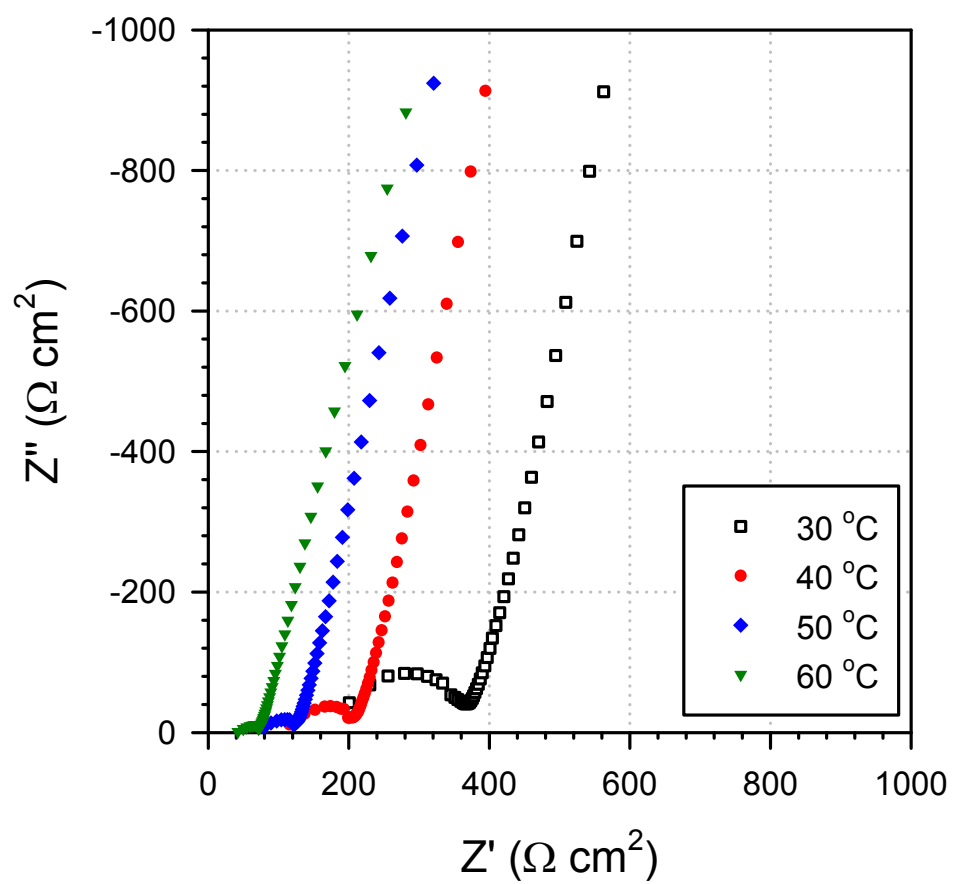
The THF-treated NCM622 powders were prepared by suspending pristine NCM622 powders in THF overnight and subsequently drying at 140 °C under vacuum. A stoichiometric mixture (0.5 g) of  $\text{Li}_2\text{S}$  and  $\text{P}_2\text{S}_5$  was reacted in 5 mL of THF overnight at room temperature to prepare the SE-precursor-THF-treated NCM622 powders. After 3 mL of supernatant was collected (Fig. S8a), 350 mg of pristine NCM622 powders were added and stored overnight at room temperature (Fig. S8b). After filtration and washing with THF, the resulting powders were obtained by heat treatment under vacuum at 140 °C. The electrochemical performances of the pristine, THF-treated, and SE-precursors-THF-treated NCM622 were compared by assembling NCM622/Li-In half-cells for each material. The NCM622 electrodes were fabricated by manually mixing the active powders, SE (LPSCI), and Super C65 in a weight ratio of 70:30:3. The cells were cycled at 0.1C (0.14 mA cm<sup>-2</sup>).

### ALD on NCM622 powders

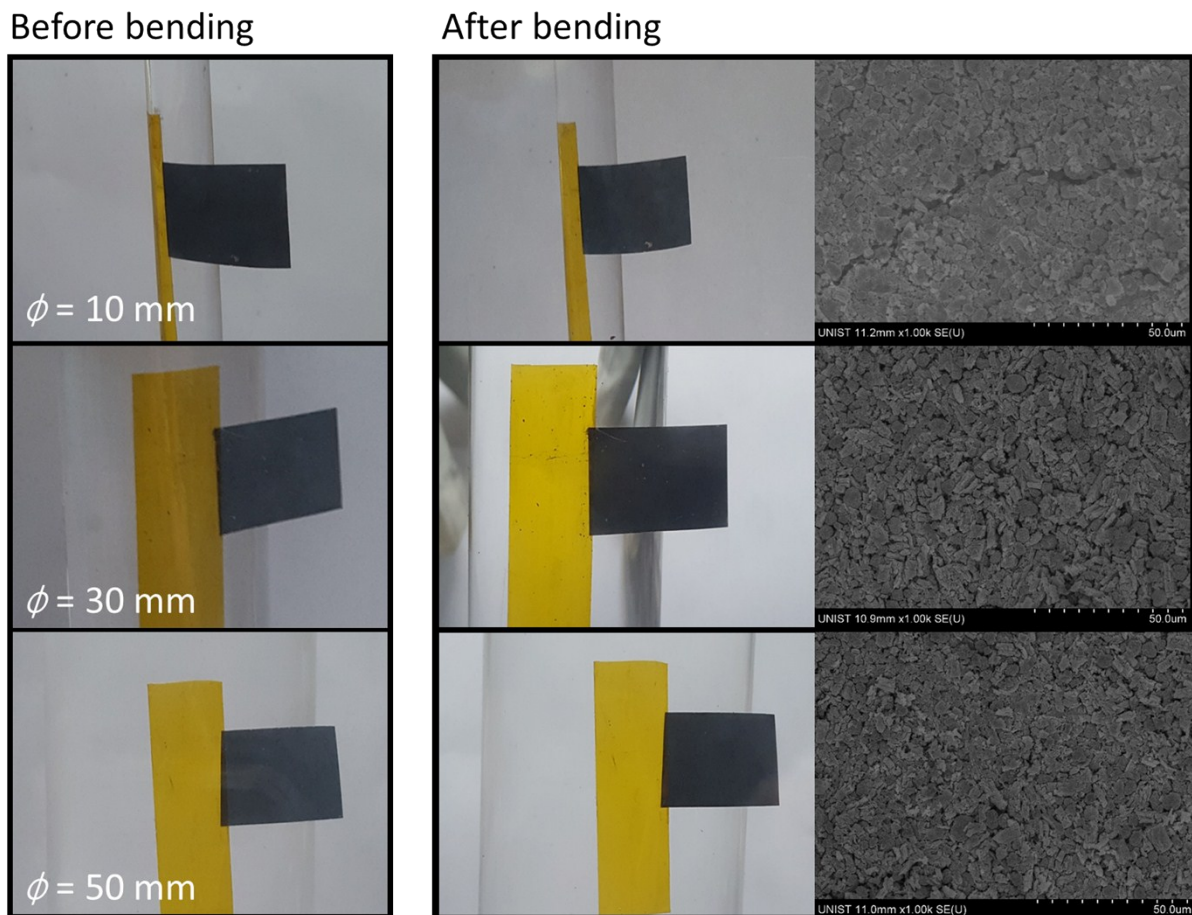
$\text{Al}_2\text{O}_3$  films were grown by ALD on NCM622 powders using a custom-made rotary ALD reactor, as described in our previous reports.<sup>44</sup> The ALD precursors were trimethylaluminum (TMA) and  $\text{H}_2\text{O}$ . During ALD, a porous stainless-steel cylinder containing the powders in the reaction chamber rotated at 140 rpm. ALD was conducted at 180 °C.



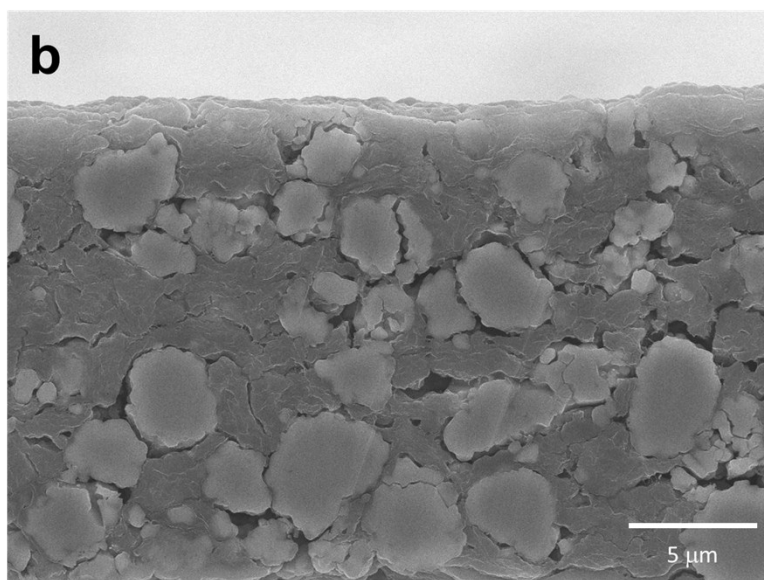
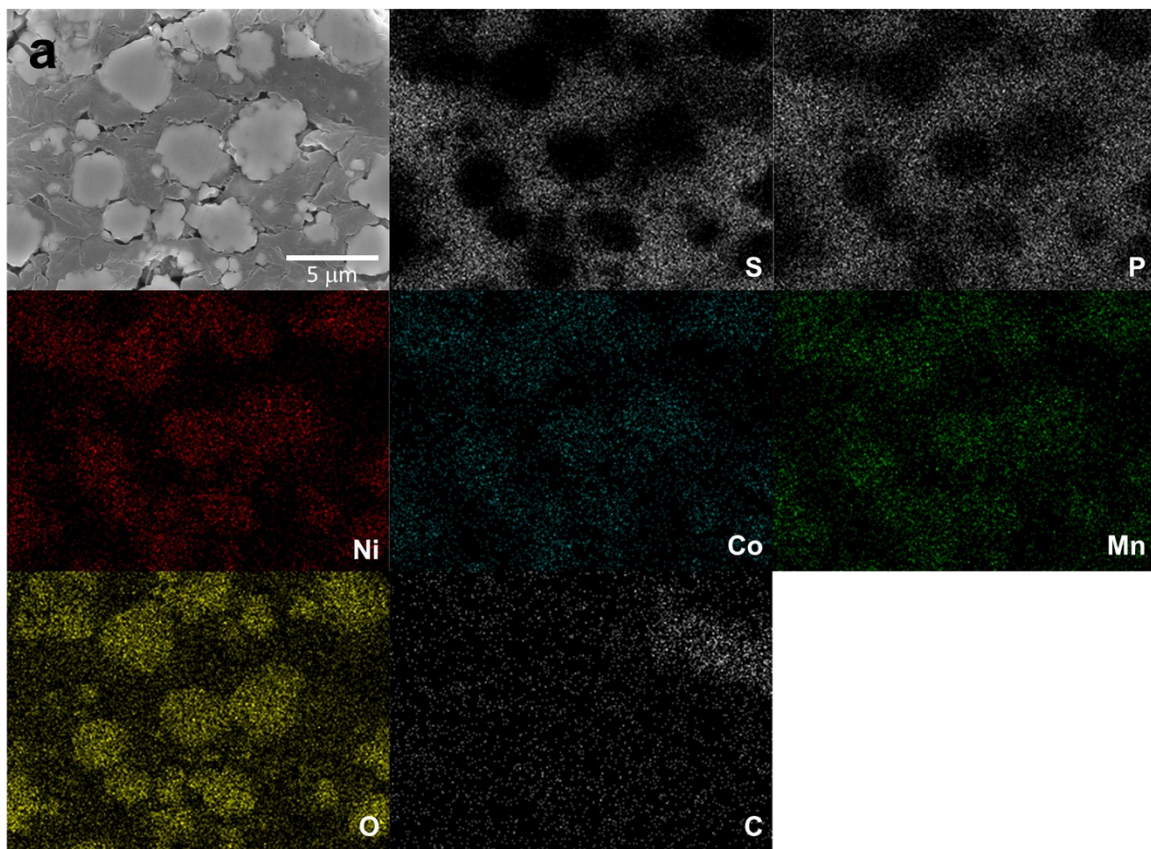
**Fig. S1.** Schematic diagram of dehydrochlorination of PVC.<sup>36</sup>



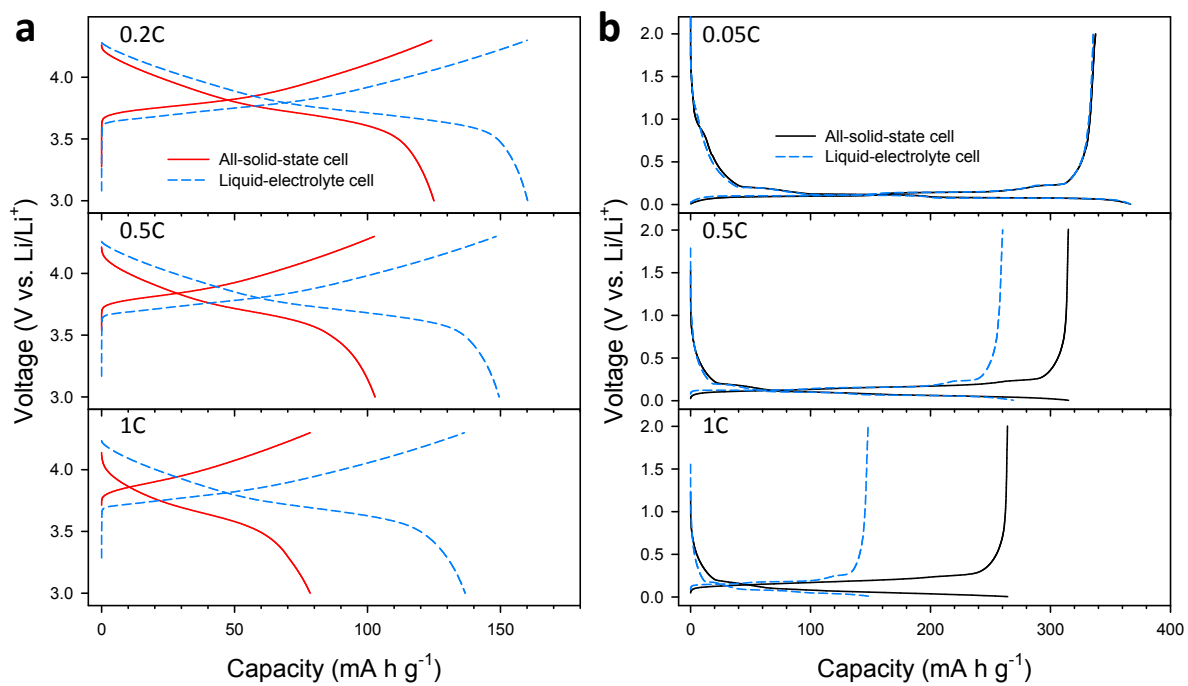
**Fig. S2.** Typical Nyquist plots of Li-ion-blocking Ti/SE/Ti symmetric cells.



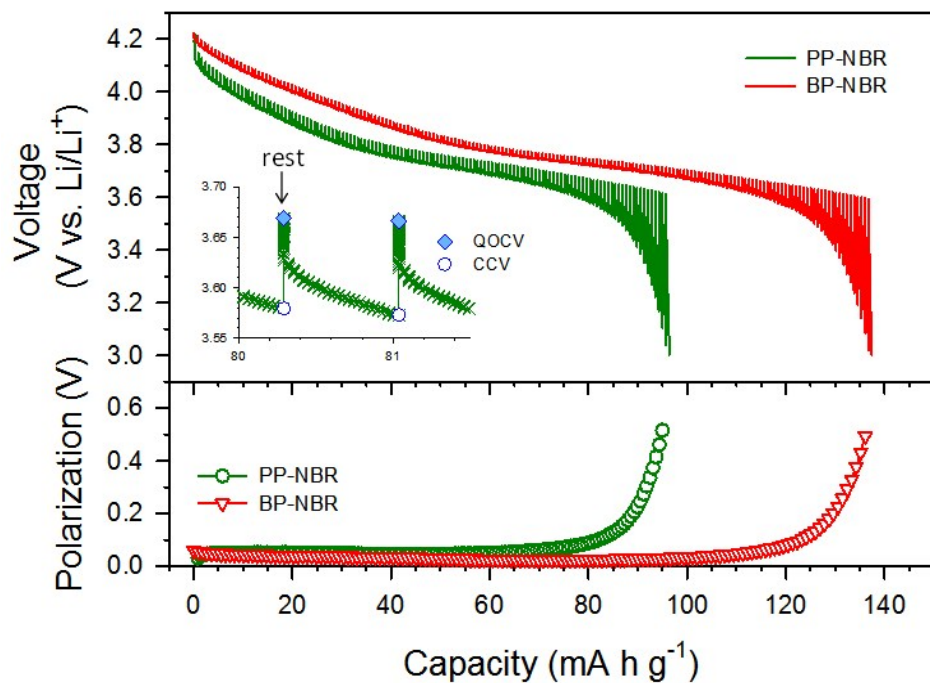
**Fig. S3.** Bending test results for the NCM622 electrode fabricated via the single-step wet-chemical route. Photographs of the electrodes before and after bending are shown. FESEM images of the electrodes after bending are also shown.



**Fig. S4.** Cross-sectional FESEM images of the NCM622 electrode fabricated via the single-step wet-chemical route and the corresponding EDXS elemental maps. a) is equivalent to Fig. 4a. The EDXS elemental maps are also shown. Another region is shown in b).

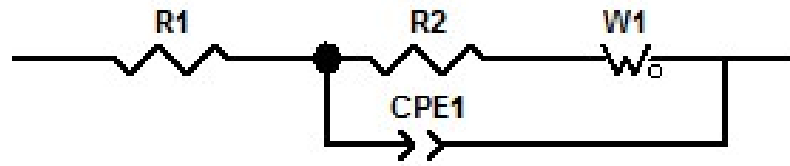


**Fig. S5.** Charge-discharge voltage profiles of a) NCM622/Li and b) graphite/Li cells using liquid electrolyte at different C-rates at 30 °C. The results are compared with those for all-solid-state cells in Fig. 6.

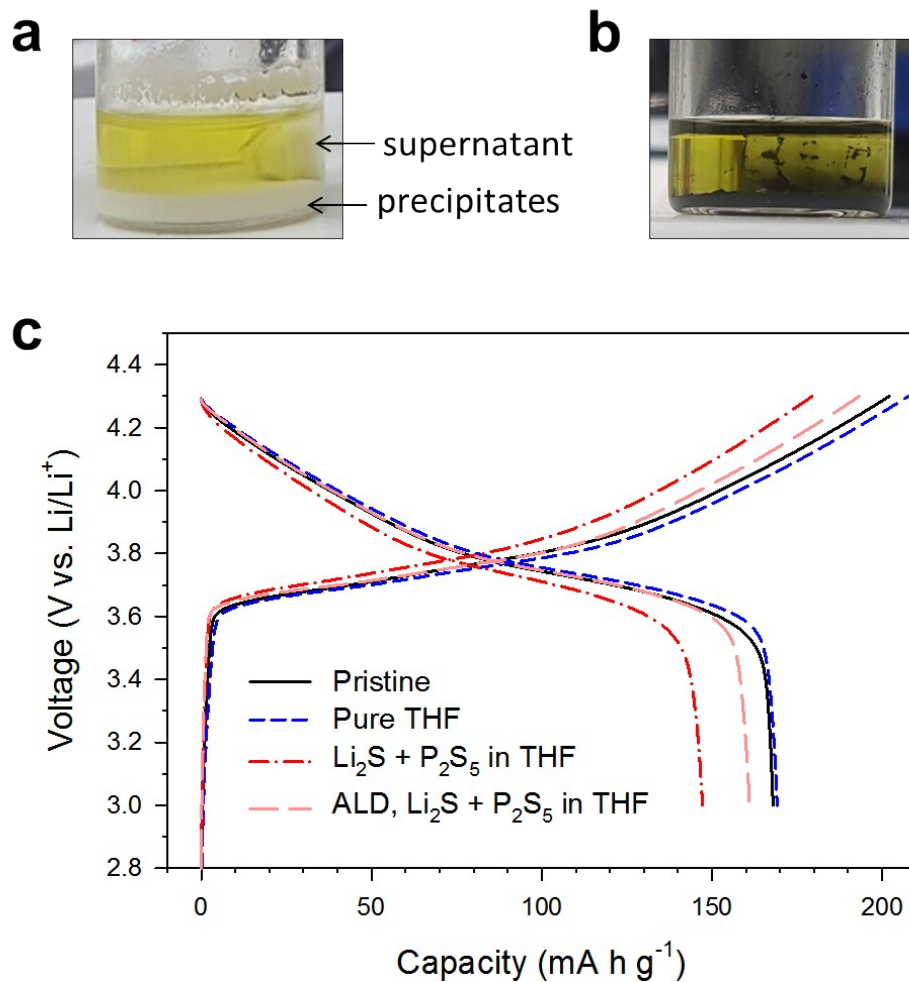


**Fig. S6.** Transient discharge voltage profiles and their corresponding polarization plots obtained by GITT for NCM622/Li-In cells, in which the NCM622 electrode was prepared from pristine and ball-milled LPS precursors (PP-NBR and BP-NBR, respectively). The closed-circuit voltage (CCV) and quasi-open-circuit voltage (QOCV) are shown in the enlarged view in the inset. The polarization curves were plotted by subtracting CCV from QOCV in the transient voltage profiles.

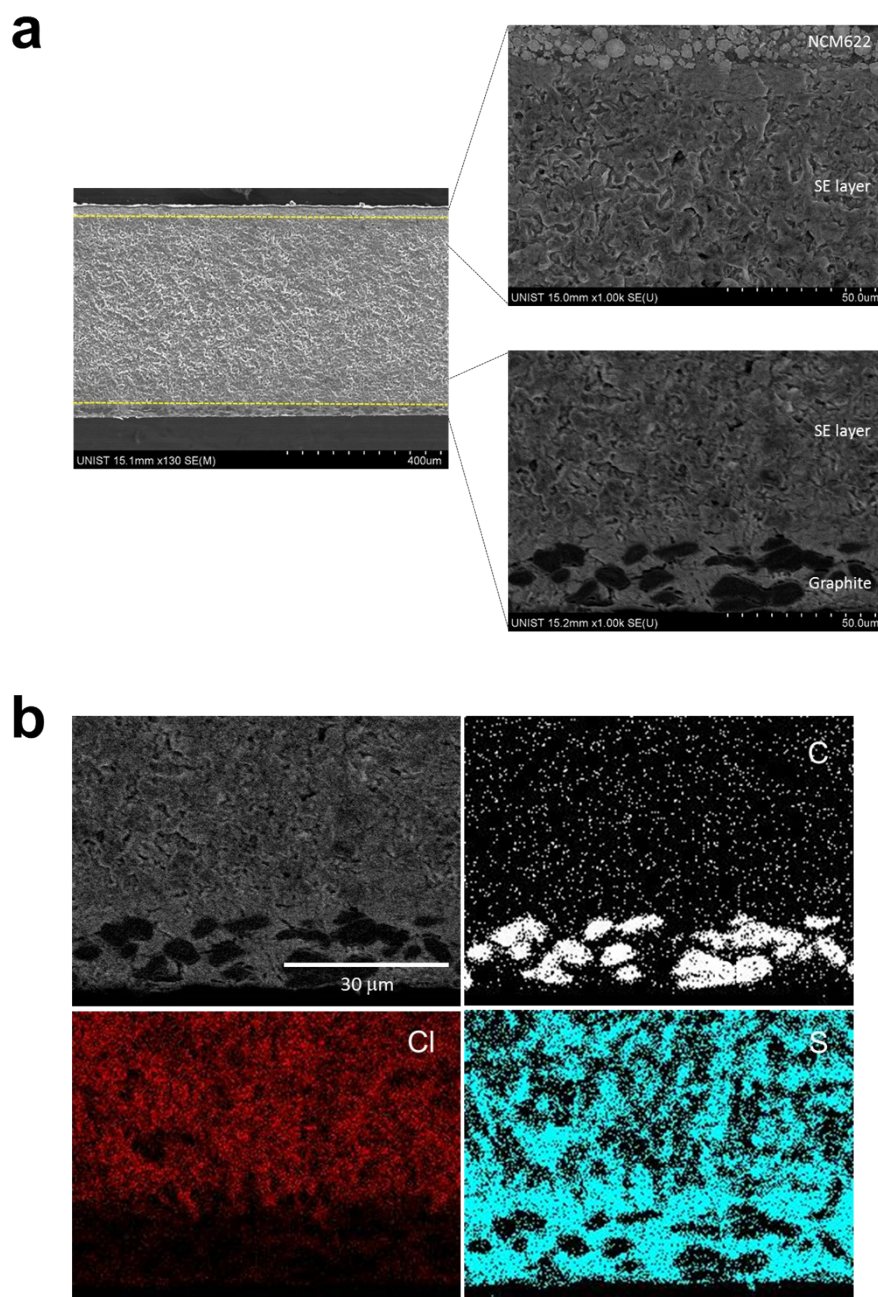




**Fig. S7.** Equivalent circuit model for fitting the EIS results in Fig. 6d. R1 and R2 are assigned as the resistances from SE layers and interfacial charge transfer, respectively.



**Fig. S8.** Photograph of a) the THF-solution containing the SE precursors of Li<sub>2</sub>S and P<sub>2</sub>S<sub>5</sub>, and b) NCM622 powders exposed to the SE-precursors-treated THF solution. The solution was prepared by adding NCM622 powders to the supernatant in a). c) First-cycle charge-discharge voltage profiles of NCM622/Li-In cells at 0.1C at 30 °C using pristine, pure-THF-treated, and SE-precursors-THF-treated bare and Al<sub>2</sub>O<sub>3</sub> ALD coated NCM622 (see the Supplementary Experimental Section for the preparation details).



**Fig. S9.** Cross-sectional FESEM images of the NCM622/graphite ASLB and their corresponding EDXS elemental maps. a) Low-magnification image and its enlarged views showing interfaces for NCM622 electrode/SE layer and graphite electrode/SE layer, indicating no noticeable mechanical failures at interfaces. b) FESEM image showing the interface for graphite electrode/SE layer and its corresponding EDXS elemental maps. The absence of chlorine signal in the graphite electrode in b) is because  $\text{Li}_3\text{PS}_4$  is used as SE for the graphite electrode while  $\text{Li}_6\text{PS}_5\text{Cl}$  for the SE layer.