

## **Infiltration-driven performance enhancement of poly-crystalline cathodes in all-solid-state batteries**

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Running title: Solid-electrolyte-infiltrated composite cathodes

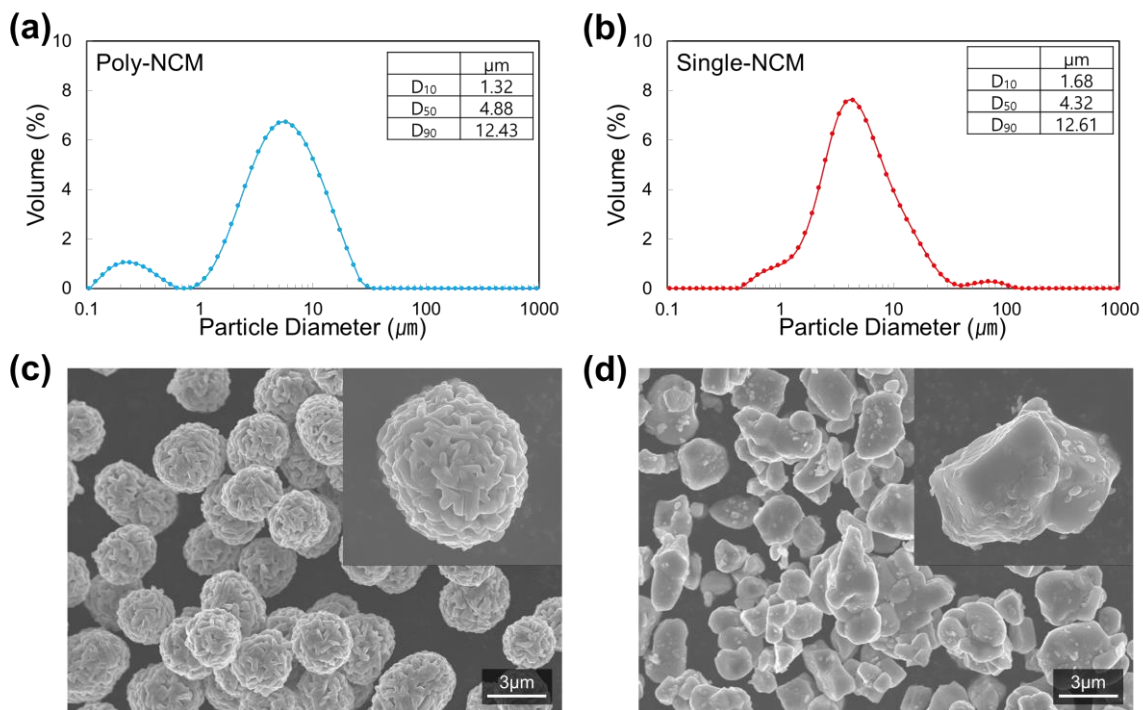


Figure S1 Characterization of poly- and single-crystalline NCM (poly-NCM and single-NCM, respectively) particles. Particle-size distributions of (a) poly- and (b) single-NCM. SEM images of (c) poly- and (d) single-NCM particles.

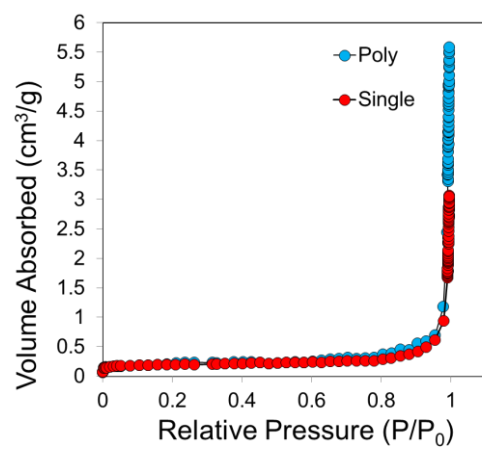


Figure S2 BET nitrogen adsorption-desorption isotherms of poly- and single-NCM electrodes.

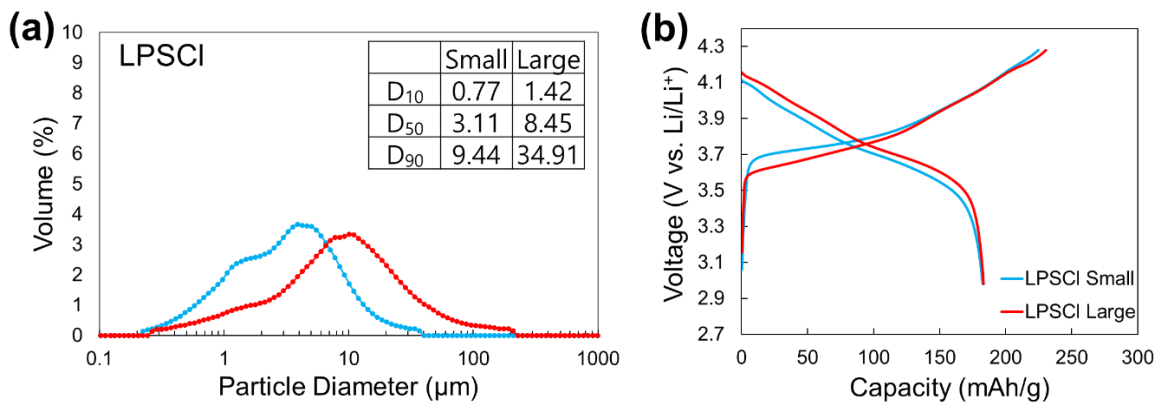


Figure S3 (a) Particle-size distribution analysis for LPSCI with small and large particles ( $D_{50}^{\text{Small}}$ : 3.11  $\mu\text{m}$ ,  $D_{50}^{\text{Large}}$ : 8.45  $\mu\text{m}$ ). (b) Electrochemical performances of electrodes infiltrated with SEs comprising small and large particles.

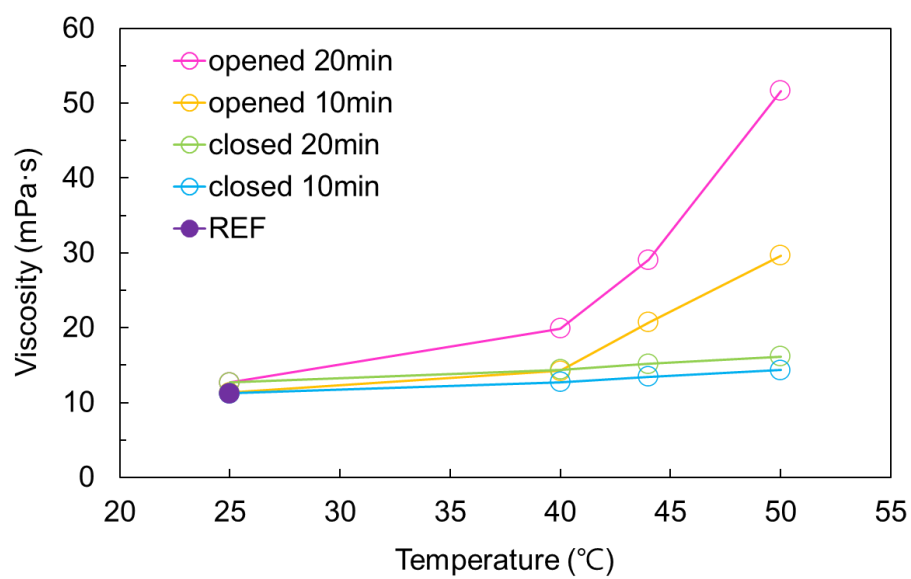


Figure S4 Variation of the SE-solution viscosity with the temperature, open/closed status, and time conditions, measured using a rheometer.

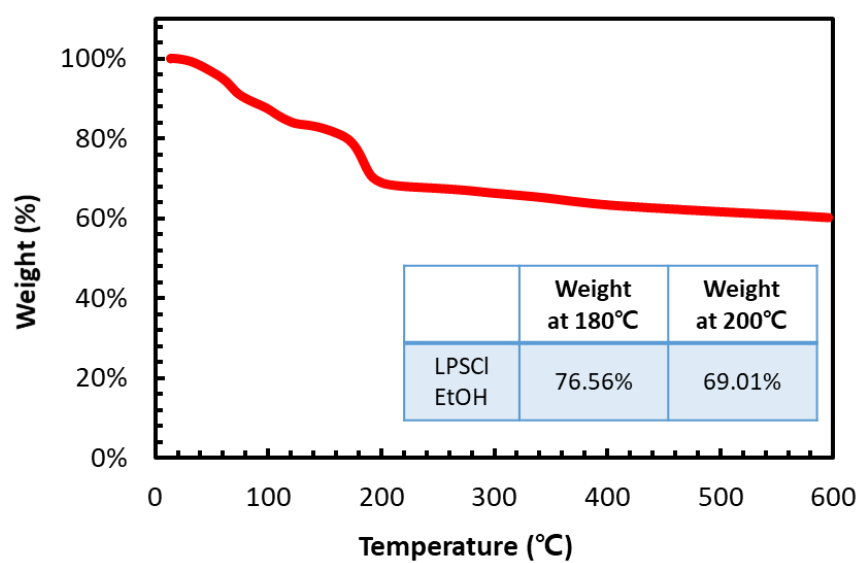


Figure S5 Thermogravimetric analysis of LPSCl dissolved in EtOH, which is used to optimize the recrystallization conditions of LPSCl.

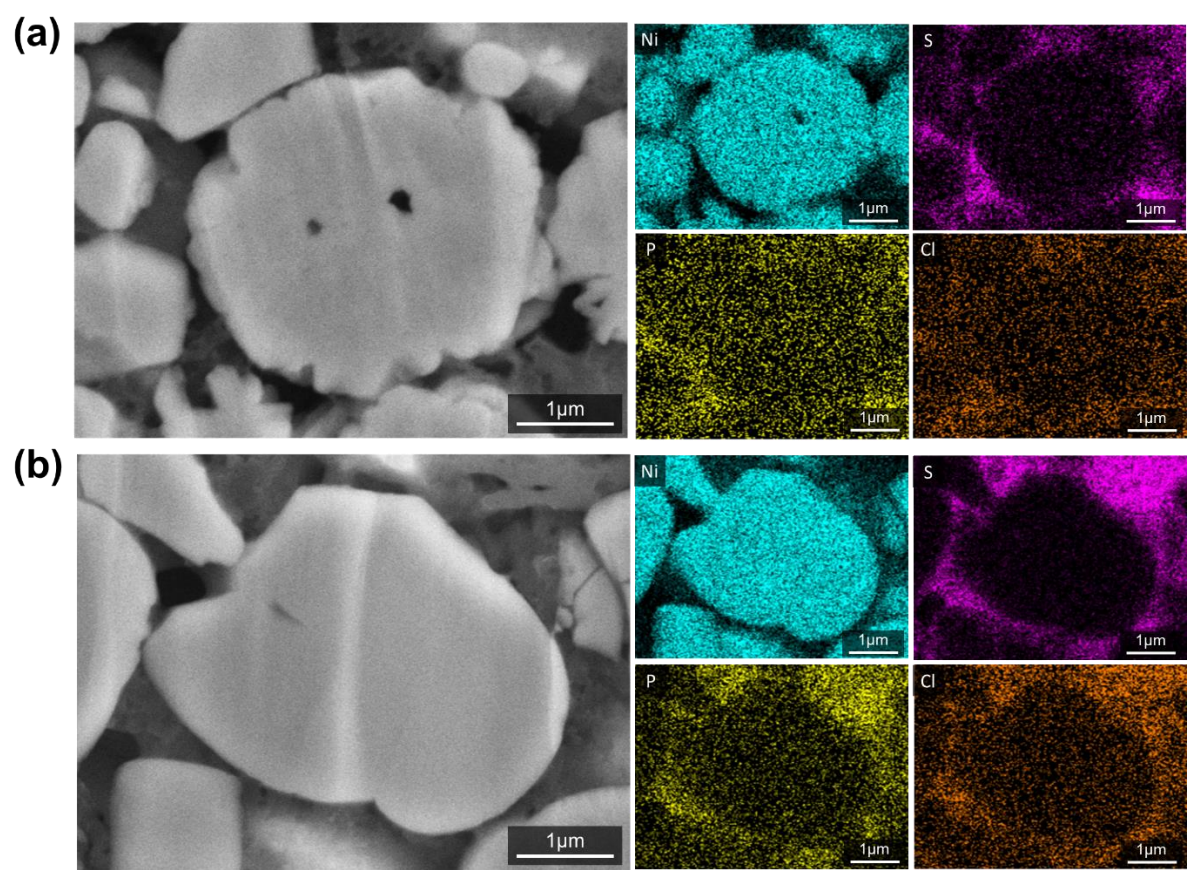


Figure S6 Magnified cross-sectional SEM and EDS images of SE-infiltrated NCM electrodes containing (a) poly- and (b) single-crystalline particles.

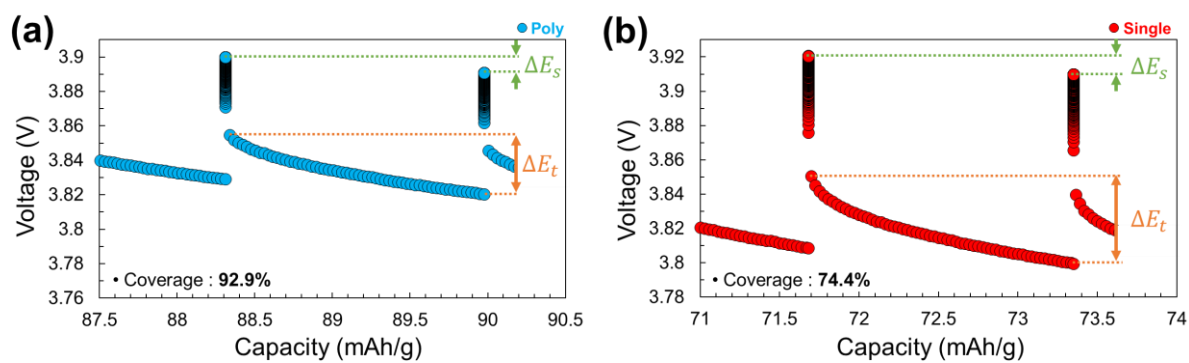


Figure S7 Enlarged section of the transient discharge voltage profile of obtained from GITT measurements for an LPSCl-infiltrated (a) poly and (b) single NCM electrode in an all-solid-state cell at 55 °C. The steady-state voltage change ( $\Delta E_s$ ) and the transient voltage change ( $\Delta E_t$ ) values used for obtaining the interfacial contact area are illustrated. A constant current of 0.5C was applied for 60 s, followed by resting for 1 h.

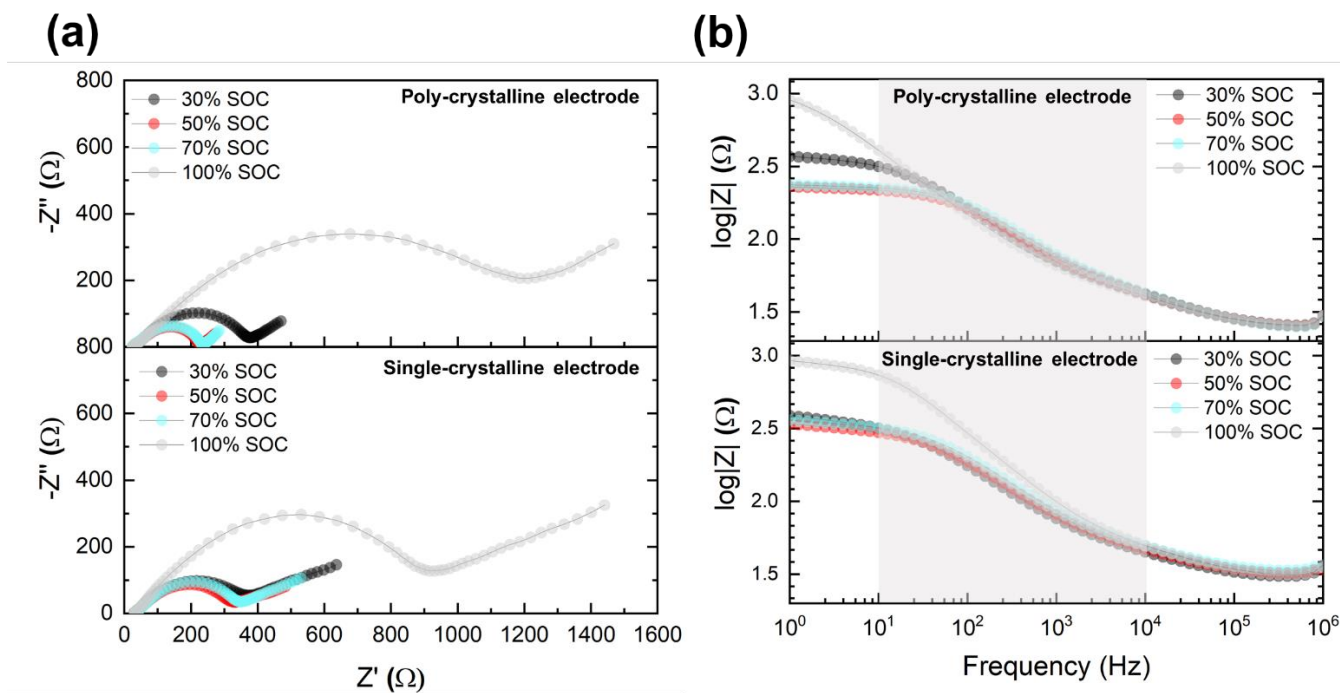


Figure S8 (a) Nyquist plots and (b) bode plots of LPSCl-infiltrated Poly- or Single- NCM/Li all-solid-state cell at different state of charge(30% SOC, 50% SOC, 70% SOC, 100% SOC).

**Table S1.** Comparison of Cell Performance of Previously Reported ASSBs<sup>a</sup>

| ref                     | Cathode               |                   |                                                                                  | Anode                   | SE                                                                        | Capacity<br>(mAh g <sup>-1</sup> ) | C-Rate      | Cyc<br>(th) | T<br>(°C) |
|-------------------------|-----------------------|-------------------|----------------------------------------------------------------------------------|-------------------------|---------------------------------------------------------------------------|------------------------------------|-------------|-------------|-----------|
|                         | CAM(wt%)              | Carbon(wt%)       | Other(wt%)                                                                       |                         |                                                                           |                                    |             |             |           |
| Song <i>et al.</i> (31) | LCO <sup>b</sup> (97) | Super C65(2)      | Li <sub>6.5</sub> P <sub>0.5</sub> Ge <sub>0.5</sub> S <sub>5</sub> l<br>PVDF(1) | Li-In                   | Li <sub>6</sub> PS <sub>5</sub> Cl <sub>0.5</sub> Br <sub>0.5</sub> (600) | 135                                | 0.2C        | 100         | 30        |
| Kim <i>et al.</i> (33)  | LCO(97)               | Super P(2)        | Li <sub>6</sub> PS <sub>5</sub> Cl<br>PVDF(1)                                    | graphite<br>PVDF<br>SSE | Li <sub>6</sub> PS <sub>5</sub> Cl-nonwoven(70)                           | 100                                | 6C          | 100         | 100       |
| Kim <i>et al.</i> (38)  | NCM622(96)            | Super P(2)        | Li <sub>6</sub> PS <sub>5</sub> Cl<br>PVDF(2)                                    | Li-In                   | Li <sub>6</sub> PS <sub>5</sub> Cl(800)                                   | 140                                | 0.1C        | 30          | 55        |
| <b>This Study</b>       | <b>NCM811(96)</b>     | <b>Super P(2)</b> | <b>Li<sub>6</sub>PS<sub>5</sub>Cl<br/>PVDF(2)</b>                                | <b>Li</b>               | <b>Li<sub>6</sub>PS<sub>5</sub>Cl(700)</b>                                | <b>196</b>                         | <b>0.1C</b> | <b>30</b>   | <b>55</b> |

<sup>a</sup>We selected the data with cycling performance (>10 cycles) as comparison and excluded the data with only rate performance and without cycling performance.

<sup>b</sup>LCO(LiCoO<sub>2</sub>)