

Supporting Information for:

A new halospinel superionic conductor for high-voltage all solid state lithium batteries

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EXPERIMENTAL PROCEDURES

Materials synthesis

A simple approach based on mixing and heating of the precursors was used. Stoichiometric amounts of LiCl (Sigma-Aldrich, 99.9%) and ScCl₃ (Strem Chemical, 99.99%) were mixed together at the targeted ratio. The mixtures were pelletized and placed in a sealed quartz tube under vacuum. Li_{4-3x}Sc_xCl₄ ($0.64 \leq x \leq 0.8$) was heated to 650 °C for 48 hours with a ramp rate of 5 °C·min⁻¹.

X-ray and neutron powder diffraction and structure resolution

Powder X-ray diffraction (XRD) measurements on all materials were conducted at room temperature on a PANalytical Empyrean diffractometer with Cu-K α radiation that was equipped with a PIXcel bidimensional detector. XRD patterns were obtained in Debye-Scherrer geometry, with samples sealed in 0.5 mm (diameter) glass capillaries under argon. XRD patterns for phase identification (**Figure S1**) were obtained in Bragg-Brentano geometry, with the sample placed on a zero-background sample holder in an Ar-filled glovebox and protected by a Kapton film.

The time-of-flight (TOF) powder neutron diffraction pattern was collected on POWGEN at the Spallation Neutron Source (SNS) at the Oak Ridge National Laboratory. The sample (~1 g) was loaded into a vanadium can under an argon atmosphere and sealed with a copper gasket and aluminum lid. The samples were measured at 300 K, and a single bank wave with a center wavelength of 1.5 Å was used. Structure analysis was performed using the TOPAS V6 software package. The unit cell of Li₂Sc_{2/3}Cl₄ was identified through indexing the powder X-ray diffraction data, followed by locating the Cl and Sc positions. As Li possesses a negative neutron scattering length, the neutron pattern was refined using the Rietveld method¹ based on the structural model from powder X-ray data and difference Fourier mapping to initially locate the Li positions. All positions and atomic displacement parameters (ADP) were then fully refined in the absence of any constraints except for the ADP for the tetrahedral Li₃ site, which was fixed, due to its low occupancy and a stable refined ADP cannot be obtained.

Scanning electron microscopy

Material morphology and elemental analysis studies were performed using a Zeiss field emission scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy detector (EDX).

Ionic conductivity and activation energy measurements

Ionic conductivity was measured by electrochemical impedance spectroscopy (EIS). Typically, 150 mg of the $\text{Li}_2\text{Sc}_{2/3}\text{Cl}_4$ powder was placed between two stainless steel rods and pressed into a 10 mm diameter pellet by a hydraulic press at 3 tons for 1 min in an Ar-filled glovebox. EIS experiments were performed with 100 mV constant voltage within a frequency range of 1 MHz–100 mHz using a VMP3 potentiostat/galvanostat (Bio-Logic). For activation energy measurements, 160 mg of the $\text{Li}_2\text{Sc}_{2/3}\text{Cl}_4$ powder was placed between two stainless steel rods and pressed into a 10 mm diameter pellet by a hydraulic press at 3 tons for 3 min in a custom-made Swagelok cell, and the pellet was placed between two indium foils (10 mm diameter, Alfa Aesar, 99.99%, 0.125 mm thickness) in order to maintain a good interface as the temperature was varied. The impedance was measured from 35 MHz to 100 mHz at temperatures ranging from 30 to 60 °C using a MTZ-35 impedance analyzer (Bio-Logic).

Electrochemical measurements

For linear sweep voltammetry (LSV) measurements, 90 mg of $\text{Li}_2\text{Sc}_{2/3}\text{Cl}_4$ was filled into a polyether ether ketone (PEEK) cylinder and pressed at 2 tons for 1 min (10 mm diameter). To prepare the $\text{Li}_2\text{Sc}_{2/3}\text{Cl}_4$ -Super P carbon composite, $\text{Li}_2\text{Sc}_{2/3}\text{Cl}_4$ and carbon were mixed in a weight ratio of 7:3 and hand-ground in an agate mortar for 15 min. A mass of 5 mg of the composite was put into one side of the SE pellet to serve as a working electrode and pressed at 2 tons for another 1 min. On the other side of the pellet, a thin indium foil (10 mm diameter, Alfa Aesar, 99.99%, 0.125 mm thickness) was attached and ~0.3 mg Li powder (FMC Lithium) was spread over the indium foil. The cell was then placed into a stainless steel casing with a constant applied pressure of ~1.5 tons. The LSV measurement was performed with a scan rate of $0.01 \text{ mV} \cdot \text{s}^{-1}$.

For the fabrication of $\text{Li} | \text{Li}_2\text{Sc}_{2/3}\text{Cl}_4 | \text{Li}$ symmetric cells, ~100 mg of $\text{Li}_2\text{Sc}_{2/3}\text{Cl}_4$ powder was placed into a PEEK cylinder and cold-pressed at 3 tons for 1 min (10 mm diameter). On both sides of the SSE pellet, Li foil (99.9%, Sigma-Aldrich, 0.38 mm thickness) with a diameter of 10 mm was attached. The cell was subjected to constant uniaxial pressure using the screw of a stainless

steel framework with 4 Nm torque. Galvanostatic cycling of the symmetric cell was carried out at a current density and capacity of $0.1 \text{ mA}\cdot\text{cm}^{-2}$ and $0.1 \text{ mAh}\cdot\text{cm}^{-2}$ using a VMP3 potentiostat/galvanostat (Bio-Logic).

All-solid-state batteries employing the $\text{Li}_2\text{Sc}_{2/3}\text{Cl}_4$ SE in combination with a LiCoO_2 (LCO, Wellcos corporation) or $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NMC622, BASF) or $\text{LiNi}_{0.85}\text{Mn}_{0.1}\text{Co}_{0.05}\text{O}_2$ (NMC85, BASF) cathode and a Li-In alloy anode were assembled in an argon filled glovebox. LiCoO_2 , NMC622 and NMC85 powders were dried in a Buchi oven under vacuum at $200 \text{ }^\circ\text{C}$ for 20 h before use. $\text{Li}_{6.7}\text{Si}_{0.7}\text{Sb}_{0.3}\text{S}_5\text{I}$ was synthesized following our previously reported procedure.² First, $\sim 60 \text{ mg}$ of $\text{Li}_{6.7}\text{Si}_{0.7}\text{Sb}_{0.3}\text{S}_5\text{I}$ powder was placed into a PEEK cylinder and pressed at 2 tons for 1 min (10 mm diameter), and then $\sim 40 \text{ mg}$ of $\text{Li}_2\text{Sc}_{2/3}\text{Cl}_4$ was spread over one side of the SE pellet and pressed at 2 tons for another 1 min. The composite cathode mixtures were prepared by mixing LCO or NMC622 or NMC85 and $\text{Li}_2\text{Sc}_{2/3}\text{Cl}_4$ in an agate mortar in a weight ratio of 8:2. On the $\text{Li}_2\text{Sc}_{2/3}\text{Cl}_4$ side of the SE pellet, $\sim 6\text{-}9 \text{ mg}$ of the composite cathode mixture (corresponding to a capacity of $\sim 1\text{-}1.25 \text{ mAh}\cdot\text{cm}^{-2}$) was spread and pressed at 3 tons for 3 min. On the other side of the pellet, a thin indium foil (10 mm diameter, Alfa Aesar, 99.99%, 0.125 mm thickness) was attached and $\sim 1 \text{ mg}$ Li powder (FMC Lithium) was spread over the indium foil. The cell was placed into a stainless steel casing with a constant applied pressure of ~ 1.5 tons. Galvanostatic cycling of the cell was carried out in the voltage range of 3 - 4.3 V vs Li^+/Li for the LCO cell ($1\text{C} = 137 \text{ mAh}\cdot\text{g}^{-1}$) and 2.8 - 4.3 V or 2.8 - 4.6 V vs Li^+/Li for the NMC622 ($1\text{C} = 180 \text{ mAh}\cdot\text{g}^{-1}$) cell using a VMP3 (Bio-Logic) cyler.

LIST OF SUPPLEMENTAL FIGURES

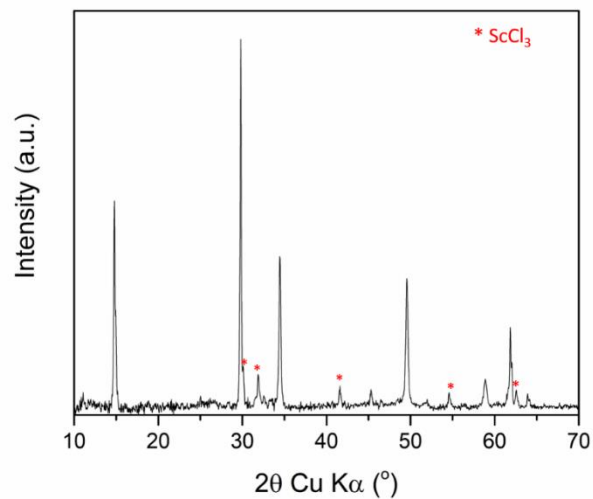


Figure S1. Powder X-ray diffraction of $\text{Li}_{1.6}\text{Sc}_{0.8}\text{Cl}_4$. All reflections correspond to the respective spinel phase except for the ScCl_3 impurity as marked.

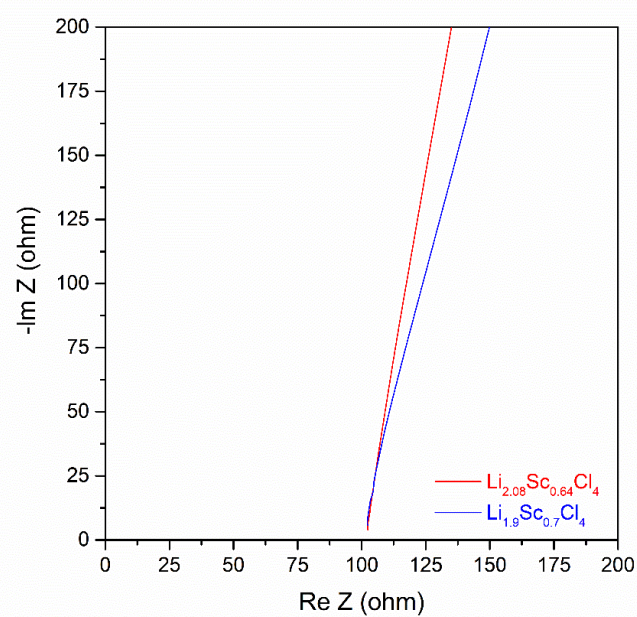


Figure S2. Nyquist plots of $\text{Li}_{2.08}\text{Sc}_{0.64}\text{Cl}_4$ (red) and $\text{Li}_{1.9}\text{Sc}_{0.7}\text{Cl}_4$ (blue) at room temperature.

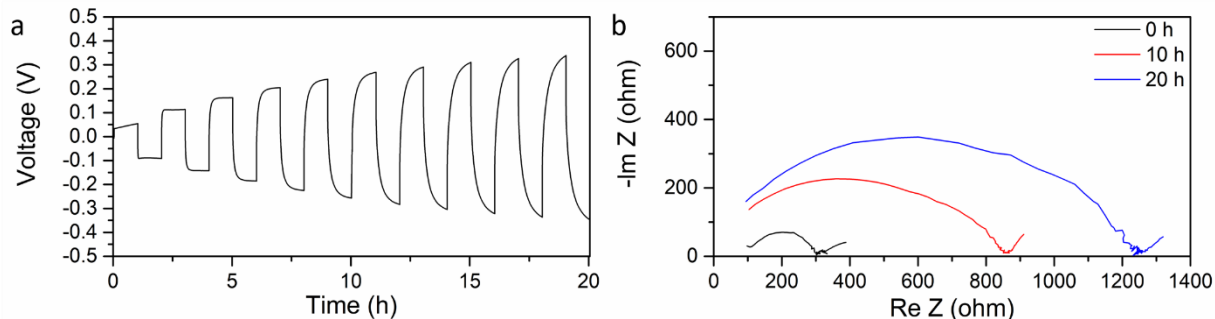


Figure S3. (a) Voltage profile of Li stripping/plating in a $\text{Li}/\text{Li}_2\text{Sc}_{2/3}\text{Cl}_4/\text{Li}$ symmetric cell, cycled at $0.1\text{mA}\cdot\text{cm}^{-2}$ and $0.1\text{mAh}\cdot\text{cm}^{-2}$ for 20 h; (b) corresponding Nyquist plots of the symmetric cell: before cycling (black), cycling for 10 h (red) and 20 h (blue). This figure shows the instability between $\text{Li}_2\text{Sc}_{2/3}\text{Cl}_4$ and Li metal, as Sc^{3+} can be reduced by Li to form an insulating interphase.

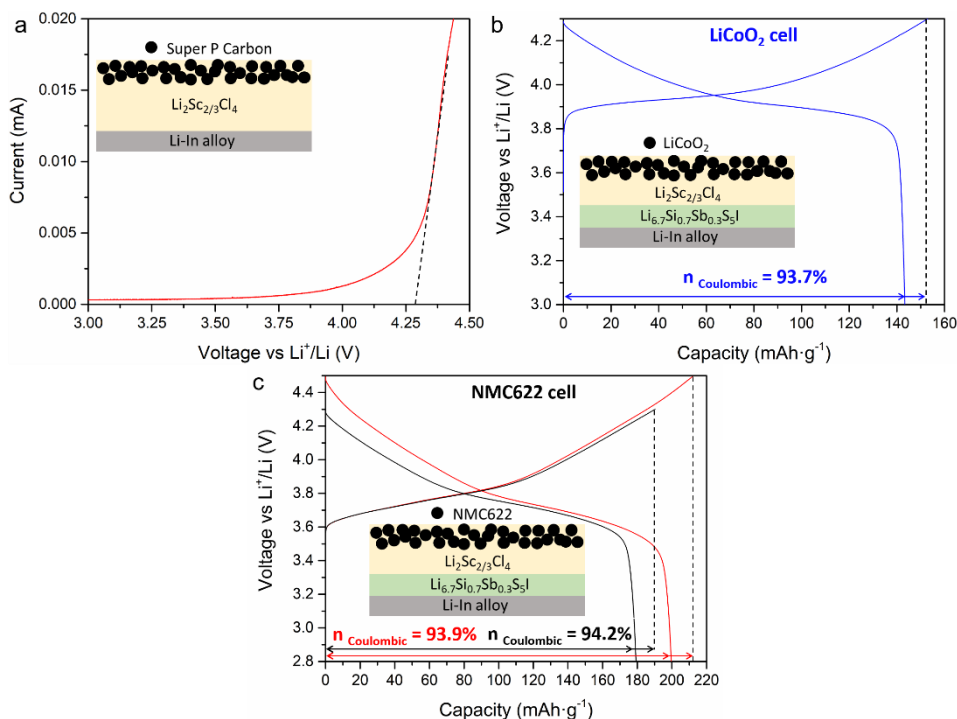


Figure S4. (a) Linear sweep voltammograms at a scan rate of $0.01\text{mV}\cdot\text{s}^{-1}$ with Li-In alloy as the reference; $\text{Li}_2\text{Sc}_{2/3}\text{Cl}_4/\text{Super P carbon}$ mixture (70:30wt%) as the counter electrode and $\text{Li}_2\text{Sc}_{2/3}\text{Cl}_4$ as the solid electrolyte layer. Initial charge/discharge curves of bulk-type ASSLBs of (b) LiCoO_2 cell cycled between 3V - 4.3V vs Li^+/Li and (c) NMC622 cell cycled between 2.8V- 4.3V and 2.8V- 4.5V vs Li^+/Li at room temperature at a rate of 0.1 C. Insets show cell configurations.

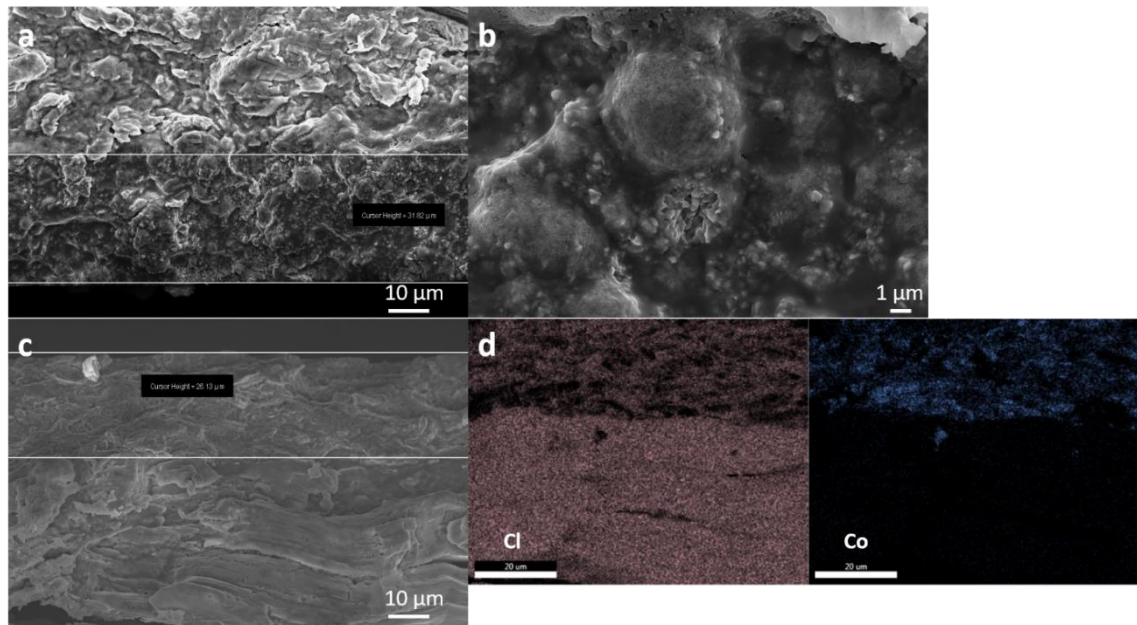


Figure S5. Cross-sectional SEM images of (a) the NMC622 cathode composite and Li₂Sc_{2/3}Cl₄ electrolyte section and (b) enlarged cathode composite section shows the NMC622 particles (spheres) are well embedded in the Li₂Sc_{2/3}Cl₄ matrix. (c) SEM cross-sectional images and (d) EDX mapping of the LiCoO₂ cathode composite and Li₂Sc_{2/3}Cl₄ electrolyte section, illustrating that the LiCoO₂ cannot be distinguished from the solid electrolyte; EDX mapping (Cl and Co) shows the LiCoO₂ particles and Li₂Sc_{2/3}Cl₄ are well mixed.

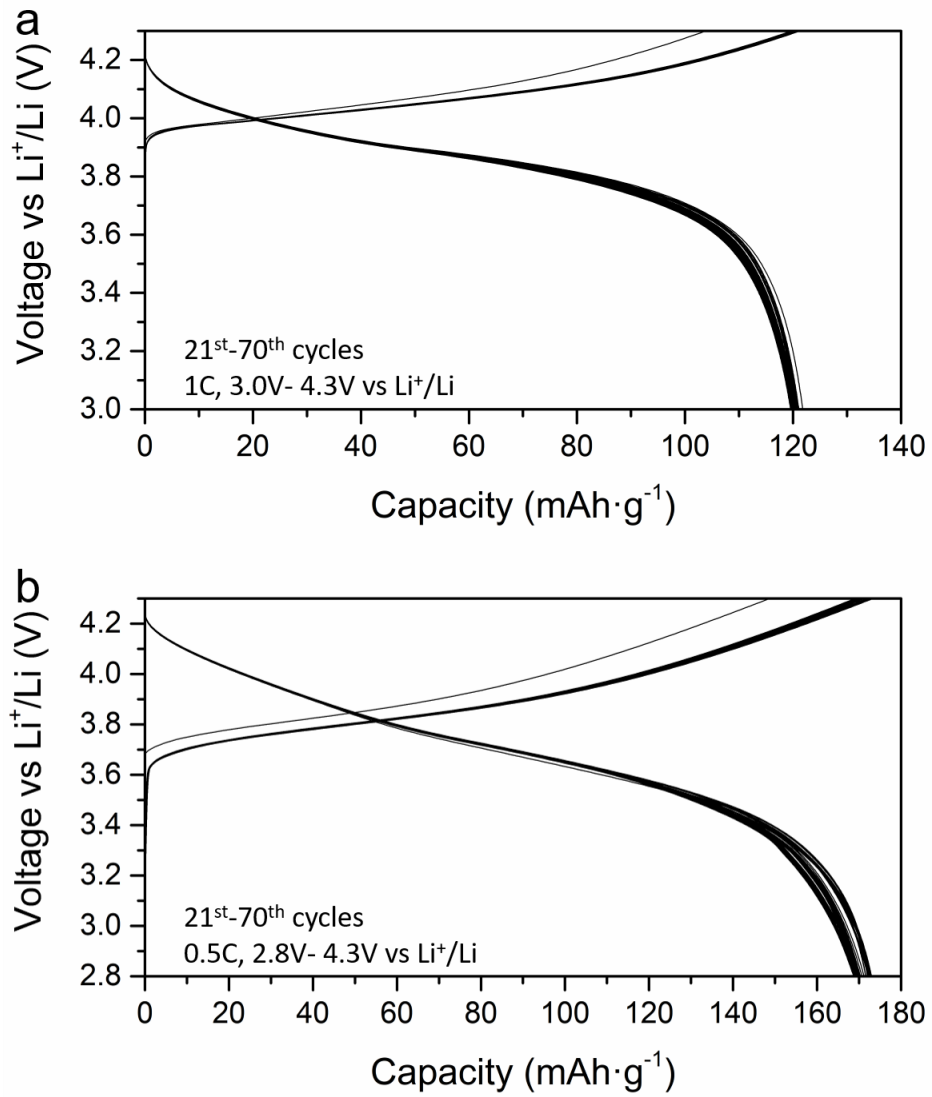


Figure S6. Charge-discharge curves corresponding to the 21st-70th cycles of ASSBs for a: (a) LiCoO₂ cell cycled at 1C and (b) NMC622 cell cycled at 0.5C.

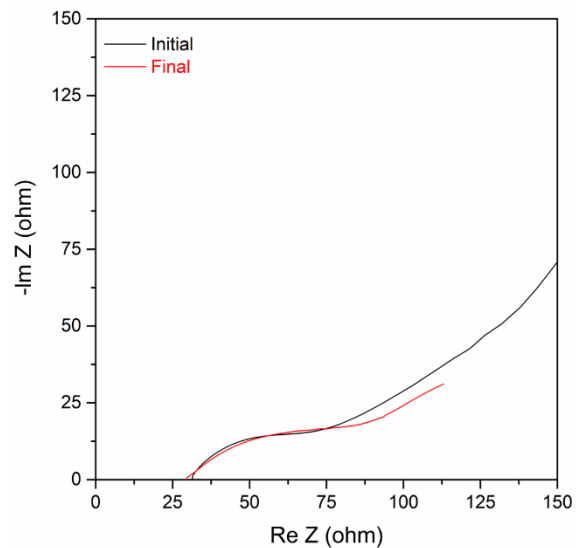


Figure S7. Nyquist plots of a LiCoO₂ ASSB at the initial state and after 70 cycles, showing no increase of internal resistance upon cycling.

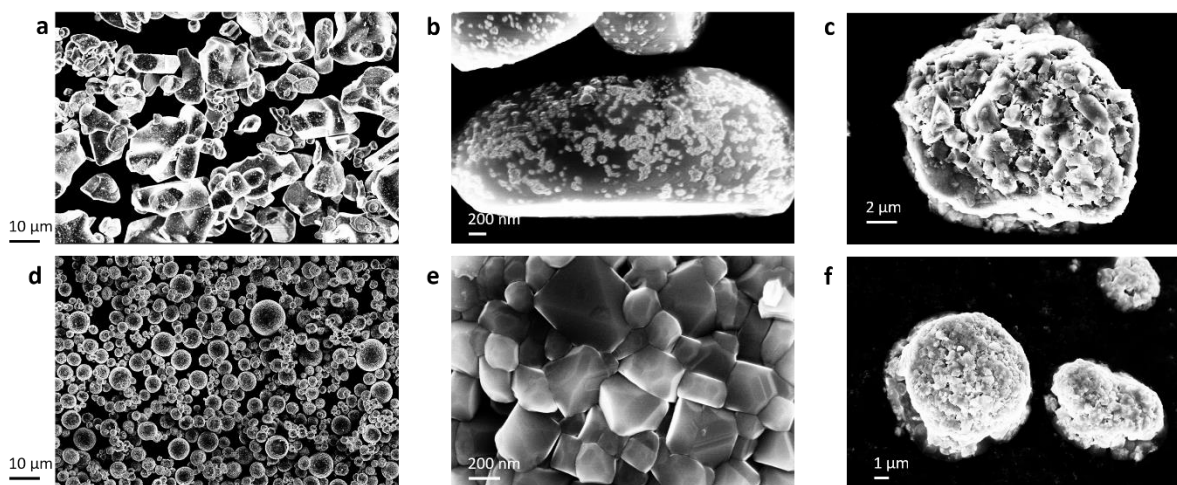


Figure S8. SEM images of pristine (a,b) LiCoO₂ particles and (d,e) NMC622 particles showing the particle size distribution and microstructure. SEM images of the particle morphology after hand-grinding with 20 wt% Li₂Sc_{2/3}Cl₄ shows (c) LiCoO₂ and (f) NMC622 particle surfaces are covered with the Li₂Sc_{2/3}Cl₄ solid electrolyte.

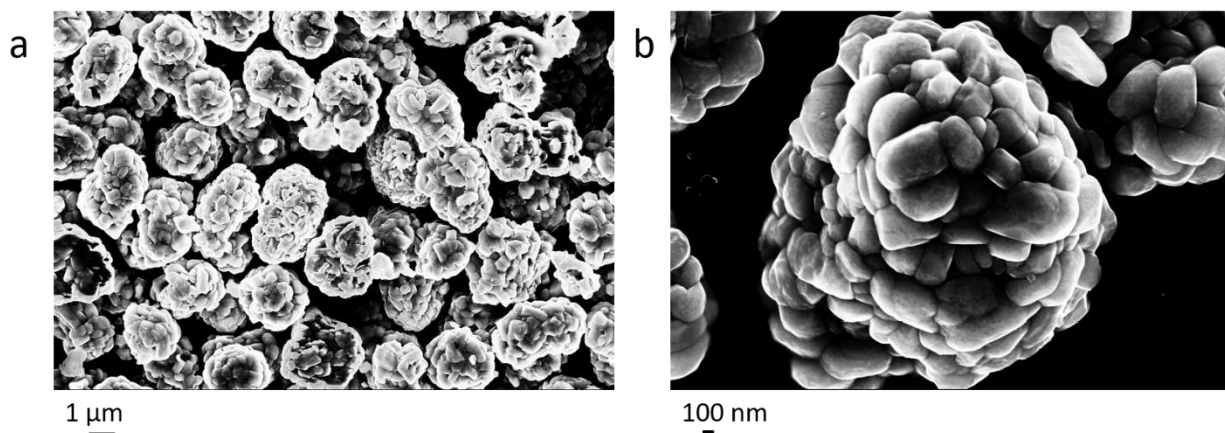


Figure S9. SEM images of NMC85 particles showing the (a) particle size distribution and (b) microstructure. NMC85 exhibits a small particle size compared to LCO and NMC622.

REFERENCES

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- 1 H. M. Rietveld, *J. Appl. Crystallogr.*, 1969, **2**, 65-71.
 - 2 L. Zhou, A. Assoud, Q. Zhang, X. Wu, L. F. Nazar, *J. Am. Chem. Soc.*, 2019, **141**, 19002-19013.