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Hierarchically Coated Halide Layers: Enhancing Performance at Composite Cathode Interfaces in Solid-State Li-Metal Batteries

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Experimental

Material preparation. The $Li_{5.4}PS_{4.4}Cl_{0.8}Br_{0.8}$ SEs were synthesized by mechanochemical milling in an inert Ar atmosphere using a high-energy planetary mill (Pulverisette 5 PL, Fritsch). The raw materials, LiCl (≥99%, Sigma Aldrich), LiBr (99.99%, Sigma Aldrich), P_2S_5 (99.99%, Sigma Aldrich), and Li_2S (99.9%, Sigma Aldrich), were mixed stoichiometrically. The mixture and ZrO_2 balls with diameters of 3 mm were loaded into a milling bowl. The ball-to-powder ratio was 20:1 (w/w). Milling was performed in two steps. The milling process, with 30 min of milling and 30 min of rest at 550 rpm, was repeated for 12 cycles. Next, milling was repeated for four cycles with a running time of 30 min and a rest rime of 15 min at 800 rpm. The synthesized $Li_{5.4}PS_{4.4}Cl_{0.8}Br_{0.8}$ was pulverized for use as the catholyte. The solvent was pre-mixed with heptane (99%, Sigma Aldrich) and dibutyl ether (99.3%, Sigma Aldrich) by stirring in a glove box. The synthesized $Li_{5.4}PS_{4.4}Cl_{0.8}Br_{0.8}$ and ZrO_2 balls were prepared in a bottle, and the mixed solvent was added. The ball mill bottle was sealed and milled at 300 rpm for 24 h using a ball mill machine. Subsequently, it was dried on a hot plate in a glove box at 100 °C for 1 h.

The synthesis procedure of halide ICEs is described below. LIC was synthesized via a well-known water-mediated route.[1] LiCl (≥99%, Sigma Aldrich) and $InCl_3$ (99.999%, Sigma Aldrich) precursors with a molar ratio of 3:1 were dissolved in deionized water (Sigma Aldrich) by stirring for 1 h. Additionally, the dehydration process was performed at 200 °C for 2 h under vacuum to evaporate water. For pulverization, the synthesized LIC powder, balls, and heptane (99%, Sigma Aldrich) as solvent, were placed in a bottle and sealed. The sealed container was then milled at 300 rpm for 24 h, and then dried on a hot plate in a glove box at 100 °C for 1 h. LYZC was synthesized via mechanochemical milling using a high-energy planetary mill (Pulverisette 7 PL, Fritsch) under an inert Ar atmosphere. LiCl (≥99%, Sigma Aldrich), YCl_3

(99.99%, Sigma Aldrich), and $ZrCl_4$ (99.9%, Sigma Aldrich) were mixed in stoichiometric ratios. The mixture and ZrO_2 balls with diameters of 7 mm were loaded in the milling bowl. The ball-to-powder was 35:1 (w/w). The sample were then milled for 18 cycles at 800 rpm. Each ball-milling run lasted 30 min and was paused every 10 min. LYZC was pulverized in the same process as that used for LIC, but at 200 rpm.

Material characterization. XRD (D8 Advance, Bruker) analysis with Cu Kα radiation (λ = 1.542 Å) were performed over the 2θ range of 10°–60° at a scan speed of 1.9° min^{-1} to analyze the crystal structures of d-couple cells. Because of air sensitivity, all samples were sealed in a glove box using a polyimide film. XPS (Nexsa, Thermo Fisher Scientific) was performed for S_{2p} and P_{2p} element analyses using an Al Kα source (1486.6 eV). The XPS samples were mounted on a sample holder, and sealed with a clamp in a glove box, and transferred to the XPS instrument without air exposure. The elemental composition and morphology of the halide-coated NCM particles were analyzed using SEM (Regulus 8230, Hitachi) combined with EDS (Ultim Max 170, Oxford). The samples were transferred from a glove box to the instrument via vacuum transfer (Hitachi). The halide SE-coated NCM coating layer was confirmed by TEM (Talos F200X, Thermo Fisher Scientific) and EDS (Super X-EDS system, Bruker). TEM images were obtained by scanning an electron beam at an acceleration bias of 200 keV. For the EIS measurements of SEs, the powder was placed in a mold with a 6 mm diameter and then pressed to 503 MPa to prepare the pellet. EIS was performed using an electrochemical testing system (EnergyLab XM, Solartron) in the frequency range of 1Hz to 1MHz with a current amplitude of 10 mV at room temperature.

Couple cell tests. A d-couple cell was manufactured to examine the reaction caused by diffusion between the electrolytes. The d-couple cells were produced as follows: $Li_{5.4}PS_{4.4}Cl_{0.8}Br_{0.8}$ and LIC (or LYZC) were mixed using a vortex mixer at a volume ratio of 50:50. The mixed SE powder were pelletized using a mold with a diameter of 10 mm at 452 MPa. A spacer with a thickness of 0.5 mm was attached to both sides of the pellet to form a CR2032 coin cell, which was vacuum-packed in an Al pouch. D-couple cells were stored and incubated at 70 °C for 300 h. CV was conducted to evaluate the electrochemical stability of the SE. Two types of CV measurement were used: either alone or in combination. An appropriate amount of argyrodite sulfide as an electrolyte layer was placed in a polyether-ether-ketone (PEEK) mold with a diameter of 10 mm and then pressed at 192 MPa. The working electrode was prepared by mixing SE ($Li_{5.4}PS_{4.4}Cl_{0.8}Br_{0.8}$, LIC, or LYZC) and VGCF in a weight ratio of 3:1 using a vortex mixer. The samples were pelletized at 305 MPa. The counter electrode was a Li-metal foil (200 μm thickness) with a diameter of 9 mm. The prepared cells were fastened to a custom-built mold assembly with a torque of 2 N-m. When using mixed two SEs, the working electrode was prepared by mixing two types of SE powders at volume ratios of 50:50 and 10 wt% of VGCF using a vortex mixer. CV curves were obtained using a potentiostat (SP-300, BioLogic) between 2.5 and 4.3 V at room temperature and a scan rate of 0.2 mV s^{-1}.

Dry coating process for CAMs. Non-coated NCM and 2 wt% of halide SE (LIC or LYZC) used as ICE were loaded into a container. It was coated using a planetary centrifugal mixer at 2,000 rpm in a dry room. After coating 2 wt% of halide SE, 3 wt% of halide SE (LIC or LYZC) was added to the container and the same process was performed. It was sieved at 53 μm in a glove box after 20 cycles of milling. The coated NCMs were vacuum dried overnight at 120 °C before use.

Fabrication and characterization of SSLMBs. Mixing was performed in three steps by using a laboratory mixer in a dry room. First, halide-coated NCM and $Li_{5.4}PS_{4.4}Cl_{0.8}Br_{0.8}$ in a volumetric ratio of 65:35 were mixed at 20,000 rpm for 3 min. VGCF (0.6 wt%) and PTFE (1 wt%) were then added respectively and mixed again with the same conditions. The mixed powder was ground in a glove box to form a sheet. A roll-calendering machine was used to thin the sheets. The folding and spreading processes were repeated when the thickness of the sheet reached 200 μm to make the sheet uniform. Finally, the thickness of the sheet was set at approximately 100 μm.

All the cells were assembled in a glove box. For cell assembly, a composite cathode sheet with a diameter of 12.95 mm was fabricated. The calculated mass loading of the composite cathode sheet was approximately 20 mg cm^{-2}. Additionally, $Li_6PS_5Cl_{0.5}Br_{0.5}$ SE powder (150 mg) and Li-metal foil (12.95 mm diameter, 200 μm thickness) were prepared. The $Li_6PS_5Cl_{0.5}Br_{0.5}$ SE powder was pressed at 134 MPa in a PEEK mold with a diameter of 13 mm. The as-prepared cathode sheet was added to one side of a $Li_6PS_5Cl_{0.5}Br_{0.5}$ pellet and pressed at 442 MPa. The Li-metal foil was placed in contact with a $Li_6PS_5Cl_{0.5}Br_{0.5}$ pellet. Finally, the cell was placed in a custom-built mold assembly and tightened with a torque of 4.9 N-m. The electrochemical performances of the cells were investigated using a cell test system (Model 4300K, Maccor) at 25 °C under normal atmospheric conditions in a sealed container. The initial charge–discharge voltage profiles were measured at 0.1C between 2.5 and 4.25 V (vs. Li^+/Li). The current density for 1 C-rate was established based on the theoretical capacity of 200 mAh g^{-1}, with the specific capacity calculated relative to the weight of the CAM in the composite cathode. The rate capability tests conducted on these cells at various C-rates (0.1, 0.33, 0.5, 1.0C). The long-term cycle tests of these three SSLMB cells were conducted at 0.5C for up to 100 cycles. During the long-term cycling, charged-state EIS spectra of the cells were obtained using an electrochemical testing system (EnergyLab XM, Solartron) in the frequency range of 0.1 Hz to 1 MHz with a current amplitude of 50 mV at room temperature.

The microstructures of cells after cycling were obtained by SEM (Regulus 8230, Hitachi) using a vacuum transfer holder (Hitachi) after ion milling. Ion milling was performed using a FIB (Quanta 3D FEG, Thermo Fisher Scientific) equipped with a vacuum transfer holder (ALTO 2500, Gatan) to prevent exposure of the samples to air. XPS (Nexsa, Thermo Fisher Scientific) of the cells after cycling was performed for S_{2p} and Y_{3d} element analysis using Al Kα source (1486.6 eV). The samples for XPS measurements were mounted on a sample holder, sealed with a clamp in a glove box, and transferred to the XPS instrument without air exposure. To analyze the cell surface after cycling, TOF-SIMS (TOF-SIMS 5, IONTOF) was performed in the positive ion mode using Bi_3^+ species. To minimize the effect of mass interference, the spectroscopy mode was used for surface analysis to enable a high signal intensity and mass resolution [FWHM = 4317 at mass-to-charge ratio = 57.94 (Ni^+)]. The analysis area was set to 100 × 100 μm^2, rasterized to 128 × 128 pixels, and scanned 100 times. All TOF-SIMS data were evaluated using SurfaceLab 6 (IONTOF GmbH) software, and the spectra were normalized to the total ion signal. To observe the microstructures of the cells, cross sections of the cells were machined using an ion milling system (Ar blade 5000, Hitachi) and characterized using SEM (Regulus 8230, Hitachi) combined with EDS (Ultim Max 170, Oxford). The samples were transferred from the glove box to the instrument using a vacuum transfer holder (Hitachi).

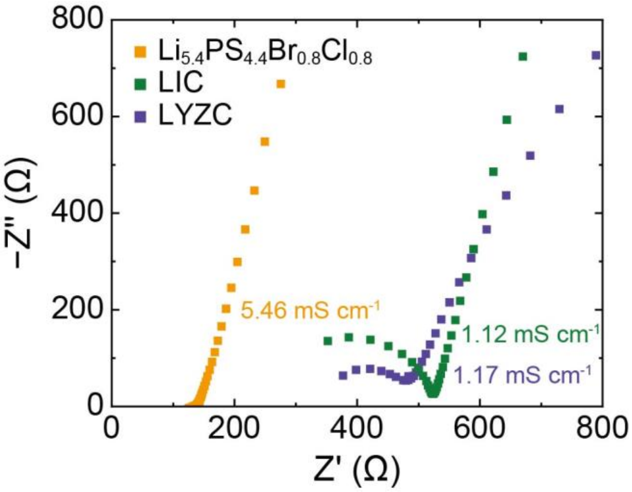

Fig. S1 Electrochemical impedance spectroscopy (EIS) spectra of as-synthesized solid electrolytes at room temperature. LIC and LYZC indicate Li_3InCl_6 and $Li_{2.5}Y_{0.5}Zr_{0.5}Cl_6$, respectively.

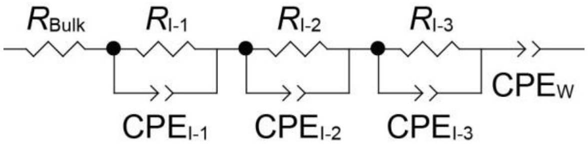

Fig. S2 An equivalent circuit model for fitting EIS spectra of three solid-state Li-metal battery (SSLMB) cells.

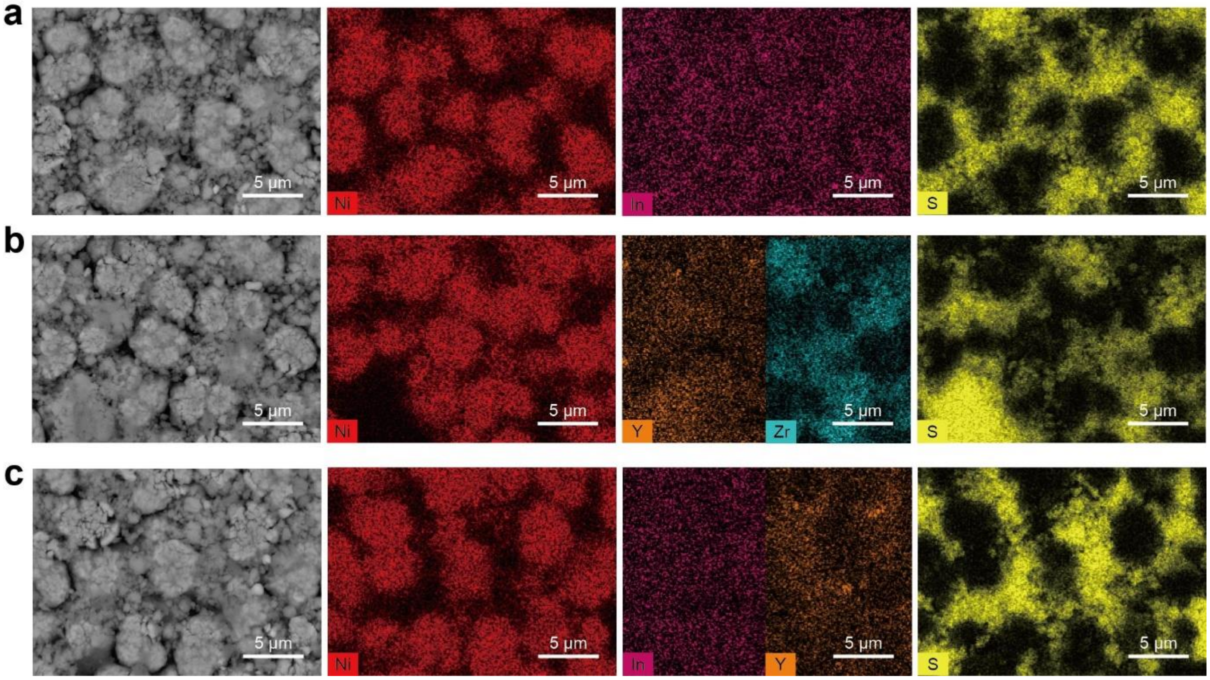

Fig. S3 Scanning electron microscopy (SEM) images and corresponding energy-dispersive X-ray spectroscopy (EDS) mappings of as-fabricated SSLMB cells, (a) In5-, (b) YZr5-, and (c) YZr3In2-cell.

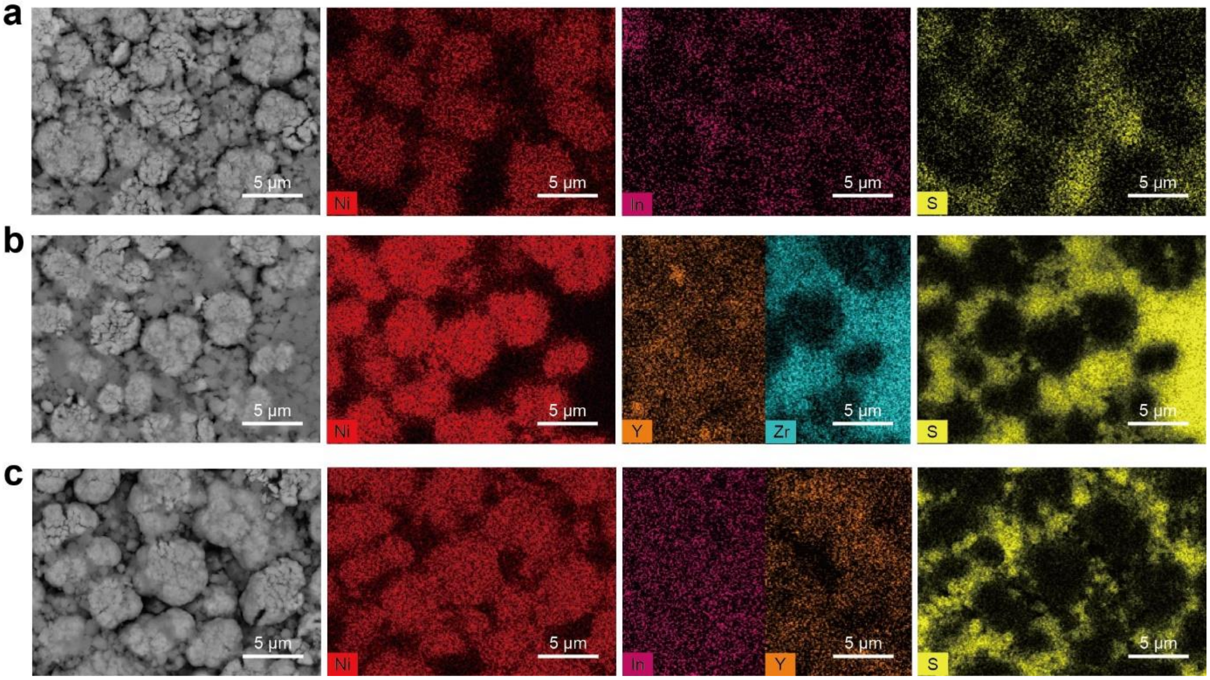

Fig. S4 SEM images and corresponding EDS mapping of SSLMB cells, (a) In5-, (b) YZr5-, and (c) YZr3In2-cell, after 100 cycles.

References

1. X. Li, J. Liang, N. Chen, J. Luo, K. R. Adair, C. Wang, M. N. Banis, T.-K. Sham, L. Zhang, S. Zhao, S. Lu, H. Huang, R. Li and X. Sun, *Angew. Chem. Int. Ed.*, 2019, **58**, 16427–16432.