ABSTRACT: Solid-state batteries (SSBs) have received attention as a next-generation energy storage technology due to their potential to superior deliver energy density and safety compared to commercial Li-ion batteries. One of the main challenges limiting their practical implementation is the rapid capacity decay caused by the loss of contact between the cathode active material and the solid electrolyte upon cycling. Here, we use the promising high-voltage, low-cost LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (LNMO) as a model system to demonstrate the importance of the cathode microstructure in SSBs. We design Al$_2$O$_3$-coated LNMO particles with a hollow microstructure aimed at suppressing electrolyte decomposition, minimizing volume change during cycling, and shortening the Li diffusion pathway to achieve maximum cathode utilization. When cycled with a Li$_2$PS$_3$Cl solid electrolyte, we demonstrate a capacity retention above 70% after 100 cycles, with an active material loading of 27 mg cm$^{-2}$ (2.2 mAh cm$^{-2}$) at a current density of 0.8 mA cm$^{-2}$.

KEYWORDS: cathode microstructure, solid-state batteries, areal capacities, high-voltage cathodes, interfaces
inherent softness, and ability to form stable electrode−
electrolyte interphases.\textsuperscript{28−30} A Li_{0.25}In_{0.75} (Li−In) alloy anode was used to mitigate interfacial issues commonly reported for metallic lithium and isolate the degradation mechanisms occurring at the cathode.\textsuperscript{22,31} The shortened Li-ion diffusion length of the hollow structure facilitates uniform Li-ion extraction and prevents internal stress from accumulating in the particle.\textsuperscript{11,16,32} The Al_2O_3 layer deposited by atomic layer deposition (ALD) effectively attenuates the interfacial side reaction with the solid LPSCI electrolyte, thus enabling stable cycling even at high operating potentials. The combination of the Al_2O_3 capping layer and the hollow microstructure alleviates the volume change of the LNMO particles, thus improving the long-term cyclability of the SSB. Cathode composites prepared by a scalable dry-milling process demonstrate capacity retention above 70% after 100 cycles, with an active material loading of 27 mg cm\(^{-2}\) (2.2 mAh cm\(^{-2}\)) at a current density of 0.8 mA cm\(^{-2}\). To the best of our knowledge, this is the top-performing LNMO cathode in a SSB configuration.

Hollow LNMO (H-LNMO) particles were synthesized via a two-step method previously reported by our group and described in detail in the Methods section of the Supporting Information.\textsuperscript{18} X-ray powder diffraction (XRD) of the as-synthesized H-LNMO particles confirms the synthesis of phase-pure LNMO with its characteristic cubic crystal structure (Figure 1b).\textsuperscript{18,33,34} Scanning electron microscopy (SEM) images show spherical secondary particles of H-LNMO that are a few micrometers in diameter and composed of plate-shaped primary particles with a size of about 500 nm (Figure 1c). Dynamic light scattering (DLS) analysis of the as-synthesized powder (Figure S1) showed D50 and D90 values of 3.62 and 5.29 \(\mu m\), respectively, which are consistent with SEM observations.

Composite cathodes were prepared by mixing H-LNMO, LPSCI, and vapor-grown carbon fiber (VCF) in a weight ratio of 40:55:5, followed by a densification step at a uniaxial pressure of 500 MPa (see Methods section of the Supporting Information). Cross-section SEM images of the composite cathode show the intimate interfacial contact between H-LNMO and LPSCI and confirm that the hollow microstructure of LNMO was maintained after the densification step (Figure 1c).

Figure 1. (a) Schematic illustration of the Al_2O_3-coated H-LNMO in the composite cathode of SSBs. (b) XRD pattern of H-LNMO. (c) SEM image of the synthesized H-LNMO particles and cross-section SEM image of the H-LNMO particles after FIB sectioning.

Figure 2. (a) Cross-section SEM image and (b) EDS elemental mappings of the H-LNMO/LPSCI/VCF (40:55:5) cathode composite. (c) GCD curves of SSBs with a H-LNMO composite (40:55:5) cycled at a rate of 0.1 C. (d) Comparative GCD curves of SSBs with H-LNMO and PC-LNMO composites at a rate of 0.1 C. Ex-situ XANES spectra measured at the Ni K edge of (e) PC-LNMO and (f) H-LNMO in pristine, 3.4, 4.0, 4.4 (fully charged), and 2.75 V (fully discharged) states.

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2a). Energy dispersive X-ray spectroscopy (EDS) elemental mapping corroborates the homogeneous mixing of each component, which induces the formation of sufficient conduction pathways for both electrons and Li-ions (Figure 2b).

The electrochemical performance of the H-LNMO composite cathode was tested in a two-electrode setup, where a Li−In alloy acted as both the reference and counter electrodes and a LPSCl pellet acted as the solid electrolyte separator (see the Methods section of the Supporting Information). Galvanostatic charge−discharge (GCD) curves of the H-LNMO composite cathode exhibit a first discharge capacity of 83.4 mAh g−1 with an initial Coulombic efficiency of 60.3%, as shown in Figure 2c. The two plateaus at 4.0 and 3.4 V (vs Li+/Li−) correspond to the reduction of Ni4+ to Ni2+ and that of Mn4+ to Mn3+, respectively.35,36 The excess capacity on charge in the first cycle was attributed to LPSCl and VCF reacting at about 3.5 V to form a cathode−electrolyte interphase (CEI) composed of LiCl, S, and P2S5, which can act as a passivation layer in subsequent cycles.37,38 The GCD profile of the composite cathode without VCF confirms the absence of VCF-LPSCl side reactions (Figure S2).

In order to evaluate the effect of the hollow microstructure, the electrochemical properties of H-LNMO were compared to commercial polycrystalline LNMO (PC-LNMO). PC-LNMO secondary particles have a median particle size of 11 μm and are composed of primary particles with a size of 700 nm (Figure S3). They exhibited a discharge capacity of 10.1 mAh g−1 at a rate of 0.1 C and high voltage hysteresis (Figure 2d). We believe this behavior can be attributed to the longer diffusion length in PC-LNMO compared to that in the H-LNMO. This results in the faster formation of the Li-ion concentration gradient and consequently sets up an earlier trigger of the cutoff voltage. In addition, the larger particle size of PC-LNMO provides less contact area between the electrode particles and the solid electrolyte particles, which results in limited reaction kinetics and thus leads to a high overpotential and a reduced discharge capacity12,39 (Figure S4). Ex situ X-ray absorption near edge structure (XANES) analysis conducted on the pristine, charged, and discharged states of PC-LNMO and H-LNMO confirm the reversible redox activity of Ni (Figures 2e and f). However, the Ni redox swing in PC-LNMO is narrower than that in H-LNMO, thus confirming its partial (de)lithiation. To further clarify the effect of a shortened diffusion path in H-LNMO, single-crystalline LNMO (SC-LNMO, MTI) with a particle size of 3.8 μm was also electrochemically evaluated. SC-LNMO showed a discharge capacity of 21.1 mAh g−1 at a rate of 0.1 C, which was still far below the discharge capacity of H-LNMO, again highlighting the effect of the hollow microstructure of H-LNMO (Figure S5).

To mitigate the side reaction with LPSCl and increase the Coulombic efficiency, H-LNMO particles were coated with nanometer-thick layers of Al2O3 by atomic layer deposition (ALD) (see the Methods section of the Supporting Information).40−43 The XRD pattern of Al2O3-coated H-LNMO does not contain additional peaks ascribable to Al2O3, thus suggesting the deposition of a thin and amorphous layer (Figure S5). The presence of an Al2O3 layer was further confirmed by X-ray photoemission spectroscopy (XPS), where peaks characteristic of Al2O3 were observed in the Al 2p and 2s spectra at 75.9 and 120.8 eV, respectively (Figure S5).46 Scanning transmission electron microscopy (STEM) highlighted a discrete change in the atomic array between the
crystalline LNMO and an amorphous Al$_2$O$_3$ layer estimated to be about 1 nm thick after five cycles of ALD (Figure 3c). As the number of ALD cycles increased from two to eight, the thickness of Al$_2$O$_3$ also increased from 0.4 to 1.4 nm, as confirmed by both STEM and ellipsometry (Figures S6 and S7).

To identify the optimal thickness of the Al$_2$O$_3$ coating layer, H-LNMO samples with Al$_2$O$_3$ surface layers deposited by a different number of ALD cycles (two, five, and eight cycles) were evaluated electrochemically. As shown in Figure S8a, the discharge capacity of H-LNMO increased from 83.4 to 99.4 mAh g$^{-1}$ with two cycles of ALD. In addition, the initial Coulombic efficiency of H-LNMO with two ALD cycles improved to 81.4%, thus suggesting the mitigation of side reactions between LPSCl and coated LNMO at high operating potentials. Al$_2$O$_3$-coated H-LNMO with five ALD cycles improved to 81.4%, thus suggesting the mitigation of side reactions between LPSCl and coated LNMO at high operating potentials. Al$_2$O$_3$-coated H-LNMO with five ALD cycles exhibited an electrochemical performance similar to that of H-LNMO with two ALD cycles (Figure 3d). However, a comparison of the cycling performance between these two samples after 40 cycles revealed that the capacity retention of H-LNMO with five ALD cycles was 62.1%, significantly higher than that of H-LNMO with two ALD cycles (53.7%) (Figure S8b).

As previously reported in a separate study, a coating layer combined synergistically with a hollow structure can effectively mitigate the volume change of the cathode material, and the constraint becomes increasingly significant as the thickness of the surface layer increases.$^{18}$ Therefore, we speculate that the lower volume change of H-LNMO brought about by 1 nm of ALD-coated Al$_2$O$_3$ provides for improved capacity retention compared with thinner coating layers. Nonetheless, when the number of ALD cycles increased to eight, the capacity decreased to 91.1 mAh g$^{-1}$, as the insufficient Li-conductivity of the Al$_2$O$_3$ layer hinders Li-ion migration (Figure S8a). In summary, 1 nm of Al$_2$O$_3$ deposited using five cycles of ALD provided the best compromise between cycling stability and discharge capacity in this study, and we therefore focused the rest of the investigation on this system (denoted as Al$_2$O$_3$-H-LNMO). Plasma FIB cross-section SEM images of the PC-LNMO composite cathode exhibited contact loss between PC-LNMO and LPSCl after a few cycles, whereas the Al$_2$O$_3$-H-LNMO composite cathode maintained intimate interfacial
contact between $\text{Al}_2\text{O}_3$ and H-LNMO and LPSCl after 100 cycles, thus confirming that the hollow microstructure coupled with $\text{Al}_2\text{O}_3$ layer effectively mitigates the volume change of the LNMO cathode (Figures S9 and S10).

XPS measurements of H-LNMO and $\text{Al}_2\text{O}_3$-H-LNMO composite cathodes were performed to identify the influence of the $\text{Al}_2\text{O}_3$ coating layer on decomposition processes. The presence of oxidated sulfur and phosphorus compounds such as sulfites and phosphates, which result from the reaction between LNMO and LPSCl, was confirmed by the XPS analysis of the H-LNMO composite cathode after 50 cycles, whereas these compounds were barely detected in the $\text{Al}_2\text{O}_3$-H-LNMO composite cathode (Figure S11). This reveals that the $\text{Al}_2\text{O}_3$ surface layer effectively suppresses the interfacial reaction between LPSCl and H-LNMO, thus leading to the enhanced cycling performance of $\text{Al}_2\text{O}_3$-H-LNMO.

Electrochemical impedance spectroscopy (EIS) spectra of H-LNMO/LPSCl/Li–In and $\text{Al}_2\text{O}_3$-H-LNMO/LPSCl/Li–In are shown in Figure 3e. It was not possible to deconvolute the contributions of the cathode and the anode to the reaction resistance, as previously reported. Therefore, an equivalent circuit model combining the contributions from both the anode and the cathode into one reaction resistance, $R_\text{q}$ (where $E$ stands for electrodes) was used to interpret the EIS spectra. The difference in resistance observed between the H-LNMO/LPSCl/Li–In and $\text{Al}_2\text{O}_3$-H-LNMO/LPSCl/Li–In systems can be directly attributed to the effect of the $\text{Al}_2\text{O}_3$ layer, as the anode is identical across both samples. The $R_\text{q}$ values of the coated and noncoated H-LNMO samples were 0.57 and 0.96 kΩ cm$^2$, respectively, after the first discharge (Figure S12 and Table S1). After 20 cycles, the increase in resistance was more significant for the H-LNMO system than for the $\text{Al}_2\text{O}_3$-H-LNMO system, highlighting the efficacy of the protective layer in terms of stabilizing the cathode–SE interface at high potentials. The effect of the active material fraction in the composite cathode was explored by comparing $\text{Al}_2\text{O}_3$-H-LNMO/LPSCl/VFC compositions with material ratios of 40:55:5 and 70:25:5. Although high cathode fractions naturally lower the fraction of solid electrolyte and increase the tortuosity of ionic paths, both composite cathodes delivered similar capacities of 94.9 (70 wt %) and 99.4 mAh g$^{-1}$ (40 wt %), which confirms the facile Li-ion diffusion in H-LNMO (Figure S13).

To demonstrate the benefits of H-LNMO in a realistic cathode configuration, a film-type composite cathode was fabricated using a polytetrafluoroethylene (PTFE)-based dry processing method (Figure S14). The fibrous network produced by PTFE under the shear stress of repeated grinding steps forms a cohesive composite cathode with good ionic and electronic transport. The GCD curves of $\text{Al}_2\text{O}_3$-H-LNMO/LPSCl/Li–In with pellet- and film-type composite cathodes are displayed in Figure 4a and b, respectively. The cells were cycled under constant current–constant voltage (CC–CV) charge and CC discharge to promote the full delithiation of the H-LNMO lattice. The first discharge capacities were 105.5 and 89.8 mAh g$^{-1}$ for the pellet- and film-type cathodes, respectively, at a C-rate of 0.1 C. After 100 cycles, the capacity retention of the cells cycled with the pellet- and film-type composite cathodes were 62.1% and 70.1%, respectively; thus, both cathodes displayed stable cycling performance even with a high active material loading (14 and 27 mg cm$^{-2}$ for pellet- and film-type composite cathodes, respectively) (Figure 4c). The enhanced capacity retention of the film-type composite cathode can be attributed to the ability of the PTFE fibrils to maintain the contact between LPSCl, $\text{Al}_2\text{O}_3$–H-LNMO, and VCF upon cycling. The areal capacities of pellet- and film-type composite cathodes were 1.51 and 2.46 mAh cm$^{-2}$, respectively, which were 7–10× higher than those of previously reported SSBs composed of LNMO and a sulfide electrolyte, thus confirming the importance of microstructure engineering cathode secondary particles to achieve high areal capacities and long-term cyclability in SSBs (Figure 4d and e and Table S2).

In conclusion, we have demonstrated that a hollow microstructure coupled with a stable surface layer significantly improves both the cycling performance and the rate capability of LNMO-based cathodes with a high active material loading. The hollow microstructure reduces the Li-ion diffusion path, leading to lower overpotentials and faster reaction kinetics at the electrode surface. The hollow secondary particle morphology coupled with the $\text{Al}_2\text{O}_3$ surface coating effectively mitigates both the volume change and the induced stress level in LNMO during lithium insertion and extraction, minimizing contact loss between the cathode and the solid electrolyte and resulting in improved cycling stability. This study highlights the importance of cathode microstructure engineering in SSBs and provides design strategies that can be extended to more traditional cathode chemistries.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.2c02426. Details on materials and methods, PSD curves of H-LNMO and PC-LNMO, EIS spectra and Arrhenius plot of LPSCl, SEM images of PC-LNMO, STEM images of $\text{Al}_2\text{O}_3$-coated H-LNMO after ALD cycles, and GCD curves of H-LNMO with an $\text{Al}_2\text{O}_3$ layer formed under a different number of ALD cycles (PDF)

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Notes
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