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Densifying Solid Electrolytes through Surface Lubrication to Mitigate Shorting of Solid-State Batteries

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ABSTRACT: Lithium dendrite penetration has caused internal short-circuits that have limited the life of lithium metal allsolid-state batteries. Defects and pores in dry compacted solid electrolytes promote dendrite growth. This study introduces an organic molecular coating, 1-undecanethiol, that anchors strongly to the surface of $\text{Li}_6\text{PS}_5\text{Cl}$ and functions as an adsorbed lubrication layer, thus reducing interparticle friction, facilitating particle rearrangement and densification. Under a compacting pressure of 375 MPa, the 1-undecanethiol coated $\text{Li}_6\text{PS}_5\text{Cl}$ achieves a porosity of 1.7%, a substantial reduction from the porosity of 10.9% for $\text{Li}_6\text{PS}_5\text{Cl}$. As a result, Li symmetric cells incorporating the 1-undecanethiol densified $\text{Li}_6\text{PS}_5\text{Cl}$ pellet



exhibit up to a 4-fold increase in critical current density and demonstrate remarkable 4600 h cycling at a current density of 1 mA cm⁻². Likewise, the LillLiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ full cell shows a 4-fold increase in cycling current density. This work points to the potential of organic surface engineering to enable long-life solid-state batteries.

Il solid-state batteries (ASSBs) comprising a nonflammable solid electrolyte hold the promise of higher energy density and longer life by the use of lithium metal anodes.¹ Among solid-state electrolytes (SSEs) materials, sulfides such as $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSC), $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, and $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$ are particularly attractive due to their superionic conductivities (as high as ~10⁻² S cm⁻¹), low Young's modulus, and high deformability.² Among sulfide SSEs, Li-argyrodites family $\text{Li}_{6-y}\text{PS}_{5-y}\text{Cl}_{1+y}$, exhibit a much more stable interface with lithium than other sulfide SSEs.³

The occurrence of short-circuits due to the penetration of lithium dendrites, however, greatly limits the cycle life of lithium metal ASSBs.⁴ This issue is exacerbated by several factors, including low ionic conductivity at grain boundaries,⁵ electronic conductivity within the SSEs,⁶ low relative density of the SSEs,⁴ and pre-existing microstructural defects (such as cracks and pores) on the surface of and within the bulk of SSEs.⁷ It is thus crucial to obtain dense, dendrite-resistant SSEs layers.⁴

In academic settings, compacting pressures ranging from 370 to 530 MPa are typically required for the formation of LPSC pellets with porosities from 13.9 to 17.9% when the starting particles are ~5 μ m in size.⁸⁻¹⁰ Achieving fully dense (relative density >99%) sulfide SSEs necessitates even higher pressures,

e.g., above 600 MPa for Li₃PS₄.⁴ The need for these excessively high compaction pressures makes the process difficult and costly to implement and results in inhomogeneous residual stress.⁴ LPSC pellet density can also be improved by the utilization of smaller particles.¹⁰ Reducing particle size through ball milling, however, often lowers ionic conductivity due to the increased number of grain boundaries that resist lithiumion transport.⁹ On the other hand, increasing the compacting temperature above 250 °C can produce byproducts with low conductivity and reduce the critical current density (CCD).¹¹

To rationally design approaches to facilitate porosity reduction, the primary factors influencing the densification of sulfide SSEs must be considered. There are three essential processes during compaction: 1) grain boundary diffusion, 2) lattice diffusion, and 3) plastic deformation.¹² For instance, lithium (Li⁺) and thiophosphate (PS₄³⁻) ions in Li₂S-P₂S₅

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(LPS) can diffuse at the grain boundaries. Plastic deformation primarily occurs due to the movement of dislocations under applied pressure.¹³ Consequently, the boundaries and voids between adjacent particles diminish with increasing pressure.¹ Nonetheless, the grain boundary diffusion is a slow process and the porosity of sulfide SSEs after plastic deformation remains greater than around 12% under a pressure of 370-530 MPa.^{14,15} Friction is a critical factor to consider as it can lead to inhomogeneous stress or deformation during dry compaction. Mechanistically, the friction can be attributed to 1) adhesion, the force required to rupture microscopic weldments formed between materials; and 2) abrasion, the force necessary to plow the peaks of a harder material through a softer one.¹⁶ Friction impedes particle rearrangement and halts further pore size reduction once the force around the pore reaches a steady state in the initial stage of densification.¹ To mitigate this friction and achieve higher pellet density, the field of powder compaction and metallurgy commonly employs lubricants as vital additives to enhance particle rearrange-ment.^{16,18} The reduction of interparticle friction promotes the particle arrangement, leading to microstructural changes during the initial stages of densification. This enhanced particle packing subsequently promotes a more uniform plastic flow in the later stages of densification, resulting in an increased pellet density. However, the use of a lubricant has yet to be considered for the densification of solid electrolytes.

■ THE CHOICE OF A LONG-CHAIN ALKYL THIOL TO LUBRICATE LI₆PS₅CL

A surface lubricant for SSEs particles should not significantly alter the critical properties of the material, in particular, ionic conductivity, while offering the possibility of reducing friction and facilitating compaction. In this study, we introduce an amphiphilic molecule, 1-undecanethiol (UDSH), that can chemically adsorb onto the LPSC SSEs surface, creating a strongly adsorbed lubrication layer (denoted as UDSH@ LPSC). UDSH is well-documented for forming self-assembled monolayers (SAM) on various substrates and is widely employed as a lubricant in industrial applications.¹⁹⁻²¹ The thiol headgroup is compatible with LPSC by forming S-S bonds with the surface of LPSC; no interaction with the Cl⁻ is observed. The crystal structure of LPSC, and its ion conduction properties are preserved (Figure S1).²² The S-S bonds are established between the S atoms in the thiol headgroup in UDSH and the S atoms on the surface of LPSC, leading to the formation of a multilayer coating of UDSH. A detailed study on the interaction between them has been published recently.²² The hydrocarbon tail of UDSH is expected to provide the necessary low adhesive force to reduce the interparticle friction. By chemically anchoring UDSH on the LPSC surface, the lubricant UDSH remains on LPSC surface during compaction which can effectively reduce friction between the powder particles, where significant frictional processes occur²³ (Figure 1). The introduction of UDSH effectively retains the ionic conductivity of the LPSC while effectively reducing pellet porosity, from 10.9% to 1.7% at 375 MPa at room temperature.

SURFACE LUBRICATION EFFECT OF UDSH ON LPSC

UDSH was mixed with LPSC using a planetary centrifugal mixer without milling balls. Consequently, the particle shape



Figure 1. Schematic illustration of the densification strategy for LPSC at room temperature. While LPSC typically retains voids and grain boundaries, exhibiting a porosity of 10.9%, the application of a UDSH adsorbed onto the LPSC surface reduces interparticle frictions, thereby reducing the pellet porosity to 1.7%. UDSH effectively forms a lubricating film around the LPSC particles.

and particle size distribution of UDSH@LPSC remained unchanged compared to those of the pristine LPSC, averaging approximately 5 μ m (Figure S2). The interaction between UDSH and LPSC is probed to be S-S bonding.²² The hydrocarbon tail aligns on the surface of LPSC. Following sample preparation, approximately 4-5 wt % of UDSH residue is present in the UDSH@LPSC.²² The UDSH residue remains chemically compatible with LPSC even after 1 week of aging in an Ar filled glovebox, as confirmed by X-ray photoelectron spectroscopy (XPS) analysis where no changes of the PS_4^{3-} units are observed (Figure S3). The 4-5 wt % concentration represents the optimal amount of UDSH required to achieve effective lubrication; higher concentrations appear to yield residual liquid during compaction (Figure S4). In the cryogenic transmission electron microscopy (cryo-TEM) images, an amorphous layer of ~ 3 nm in thickness is present at the LPSC particle surface in the UDSH@LPSC samples (labeled with dashed line), which we attribute to the UDSH adsorption (Figure S5a-b). The LPSC crystal structure remains intact after UDSH adsorption (Figure S5c).

To quantitatively assess the lubrication capabilities of UDSH during LPSC compaction, we examined the powder rheology of the UDSH@LPSC and LPSC with the FT4 Powder Rheometer (Freeman Technology) in terms of compressibility, shear properties, and dynamic flowability in a dry room (dew point -45 °C). Compressibility measures changes in bulk density as a function of the applied normal stress. The shear test applies both vertical and rotational stress to determine the yield point-the force required for a consolidated powder at rest to begin flowing, which depend on interparticle friction.^{24–26} The vertical stress and shear stress (τ) required to initiate flow produced the yield locus (Figure S6). The angle of internal friction (φ) (AIF) is derived by the fitting line of yield locus in Figure S6 with the horizontal axis, with lower AIF values indicating reduced interparticle friction.²⁷ The dynamic flowability test, comprising stability and variable flow rate tests, quantifies the flowability and compressibility of UDSH@LPSC and LPSC by measuring the flow energy required to move the rotation blade through the powder (Figure S7). The key parameters derived from these measurements are summarized in Table 1.

Table 1. Powder Rheology Test Results of LPSC, UDSH@ LPSC, and UDCH@LPSC^a

Material	AIF, $^{\circ}$	NBFE, mJ/g	FRI
LPSC	35.72 ± 0.16	226.83 ± 1.31	2.51 ± 0.05
UDSH@LPSC	33.46 ± 0.09	278.28 ± 2.82	1.87 ± 0.04
UDCH@LPSC	34.11 ± 0.36	94.30 ± 6.14	4.32 ± 0.02

^{*a*}AIF - angle of internal friction; NBFE - normalized basic flowability energy; FRI - flow rate index; based on the average of 2 independent measurements. Data are presented as mean values \pm SD.

Normalized basic flow energy (NBFE) represents the energy per gram required to move the rotation blade downward from the top to the bottom of the powder column. Since NBFE is measured during the downward traverse in a confined environment, it largely reflects the powder's compressibility. More compact powders will require a higher NBFE for displacement.

normalized basic flow energy (NBFE)

$$= \frac{\text{downward flow energy}}{\text{sample mass}} (mJ/g)$$

The flow rate index (FRI) was calculated by taking the ratio of flow energy at a blade speed of 10 mm/s to that at 100 mm/ s. More adhesive powders typically exhibit greater sensitivity to changes in flow rate.²⁴

$$FRI = \left(\frac{\text{flow energy at 10mm/s}}{\text{flow energy at 100mm/s}}\right)$$

The compressibility test results show that the bulk density of both UDSH@LPSC and LPSC increases with applied normal stress, indicating improved particle packing (Figure 2a). UDSH@LPSC exhibits a consistently higher bulk density by 0.05-0.1 g mL⁻¹ across different levels of normal stress, suggesting the enhanced particle rearrangement and packing in UDSH@LPSC. AIF values of UDSH@LPSC $(33.46 \pm 0.09^{\circ})$ are lower than those of LPSC $(35.72 \pm 0.16^{\circ})$ from the shear test, demonstrating that the UDSH coating has reduced interparticle friction among LPSC particles (Figure 2b). Under confined conditions, the higher NBFE value for UDSH@LPSC $(278.28 \pm 2.82 \text{ mJ/g})$ compared to LPSC $(226.83 \pm 1.31 \text{ mJ/g})$ g) implies that the UDSH@LPSC powder exhibits superior packing under compression (Figure 2c). The lower FRI value for UDSH@LPSC (1.87 \pm 0.04) compared to LPSC (2.51 \pm 0.05) reveals that the UDSH coating reduces the cohesiveness of the powder, which is less sensitive to flow rate changes (Figure 2d).

To evaluate the role of the thiol headgroup in UDSH, we also conducted powder rheology measurements on undecanecoated LPSC (referred to as UDCH@LPSC) as a control, which lacks the thiol headgroup and therefore exhibits weaker adsorption to LPSC (Table 1). The AIF values of UDCH@ LPSC ($34.11 \pm 0.36^{\circ}$) are higher than UDSH@LPSC ($33.46 \pm 0.09^{\circ}$), indicating that the UDSH coating better reduces interparticle friction among LPSC particles. The approximately 3-fold lower NBFE of UDCH@LPSC ($94.30 \pm 6.14 \text{ mJ/g}$) compared to UDSH@LPSC ($278.28 \pm 2.82 \text{ mJ/g}$) and LPSC ($226.83 \pm 1.31 \text{ mJ/g}$) suggest that the UDCH coating does



Figure 2. Powder rheology and pellet compaction analysis of UDSH@LPSC and LPSC. (a) Bulk density as a function of the applied normal stress of the powder. Comparison of (b) angle of internal friction (AIF), (c) normalized basic flow energy (NBFE) and (d) flow rate index (FRI). Pellet porosity (e) and ionic conductivity (f) of UDSH@LPSC and LPSC prepared at various compacting pressures at room temperature. Data are presented as mean values \pm SD.

not enhance the compressibility of the powder. The greater increase in the FRI of UDCH@LPSC (4.32 ± 0.02) compared to UDSH@LPSC (1.87 ± 0.04) and LPSC (2.51 ± 0.05) reveals that the UDCH coating enhances the cohesiveness of the LPSC powder. The comprehensive characterization of powder rheology demonstrated the surface lubrication effect of UDSH which reduces mechanical interparticle friction and adhesion, resulting in improved flowability and compressibility of LPSC. And the presence of the thiol headgroup is critical.

We also investigated the influence of the hydrocarbon tail length in the thiols. Octanethiol (labeled as OCSH, which has $8 - CH_2-$), undecanethiol (labeled as UDSH, which has 11 $-CH_2-$), and hexadecanethiol (labeled as HESH, which has $16 - CH_2-$) are evaluated similarly by powder rheology (Table S1, Figure S8). While both UDSH and HESH modified LPSC samples show higher bulk densities and reduced AIF than pristine LPSC powder, UDSH offers the best compressibility in terms of highest bulk density, NBFE and smallest AIF and FRI. We suggest that the quality of the lubrication layer formed by UDSH is higher than thiols of other chain lengths, which was confirmed by atomic force microscopy (AFM) studies in our previous study.²² Overall, selecting the right chain length to yield a high-quality surface layer is crucial.

Thanks to the surface lubrication effect of UDSH, UDSH@ LPSC consistently exhibited 11% to 83% lower pellet porosity compared to LPSC across the entire compacting pressure range of 94 to 375 MPa at room temperature (Figure 2e). In Figure 2e, LPSC or UDSH@LPSC powders were pressed in a PEEK pressing die under varying pressures. At 375 MPa, UDSH@LPSC exhibits a pellet porosity as small as 1.7%, in contract to 10.9% porosity for LPSC. With UDSH, the compacting pressure can be reduced by 50%, to a range of 148-188 MPa, while achieving the same porosity as LPSC compressed at 375 MPa. In the microindentation test on UDSH@LPSC and LPSC pellets pressed at 375 MPa, the microhardness values of UDSH@LPSC and LPSC were 24.1 \pm 1.8 HV and 7.3 \pm 1.0 HV, respectively, based on the average of 4 independent measurements (errors correspond to one standard deviation) (Figure S9). This 4-fold increase in microhardness also indicates that the UDSH@LPSC has higher pellet density.²⁸ When the pellet is more densified, the lithium-ion pathway is expected to shorten. As a result, UDSH@LPSC exhibits higher ionic conductivity compared to LPSC, as shown in Figure 2f. At compacting pressures of 94, 188, 281, and 375 MPa, the average ionic conductivities of UDSH@LPSC are 2.37, 2.45, 2.60, and 2.93 mS cm⁻¹, respectively. In contrast, the average ionic conductivities of LPSC under the same pressures are 1.10, 1.43, 2.05, and 2.61 mS cm^{-1} , respectively. At the same time, the electronic conductivity of UDSH@LPSC is maintained within the same order of magnitude as LPSC, 6.9 vs 3.7×10^{-10} S cm⁻¹ (Figure S10).

DENSIFICATION VISUALIZATION OF UDSH ON LPSC

Focused ion beam (FIB) cross-section scanning electron microscopy (SEM) is used to visualize the pellet porosity and void distribution of LPSC and UDSH@LPSC pellets pressed at 375 MPa. We used the area as indicated with a white dashed box in Figure 3a-b for this comparison. Note that the top region of the images (right beneath the Pt capping layer) shows porosities likely due to hydrolysis of LPSC during sample transfer. The cross-sectional image of LPSC (Figure

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Figure 3. Evaluation of UDSH densification effect on LPSC. Scanning electron microscope (SEM) images of cryogenic temperatures focused ion beam (FIB) cross-section of (a) LPSC and (b) UDSH@LPSC pellets. The region marked by white dashed lines is used to illustrate the differences in porosities. The pores near the surface region are formed by hydrolysis during sample transfer. MicroCT 3D reconstructions of (c) LPSC and (d) UDSH@LPSC pellets with pores indicated by blue dots.

3a) distinctly reveals larger interconnected micrometer-sized cavities (marked in red circles), higher number of grain boundaries, and smaller grain size. In contrast, the UDSH@ LPSC pellet depicted in Figure 3b exhibits minimal voids, fewer grain boundaries, and larger grain size, approaching a nearly fully densified structure. The cross-sectional FIB-SEM of UDCH@LPSC in Figure S11 has a number of pores comparable to the pristine LPSC, which suggests UDCH does not have the densification effect. The powder rheology and cross-sectional FIB-SEM results indicate that the effectiveness of the UDSH is not just the result of having the liquid additives in LPSC. The presence of the thiol headgroup is essential. We attribute the S-S bonding between UDSH and LPSC to the formation of a stronger absorbed lubricant layer around the powder particles, which is crucial for densification.¹⁸ The UDSH lubricant layer adheres strongly to LPSC under a compacting pressure of 375 MPa. Energy dispersive spectroscopy (EDS) analysis reveals a higher carbon mass fraction and uniform carbon distribution in the UDSH@LPSC pellet crosssection, indicating that the lubricant layer remains after compaction without being concentrated near the pellet surface (Figure S12, Table S2).

We further conducted microcomputed tomography (micro-CT) to comprehensively assess the void distribution in LPSC and UDSH@LPSC pellets compacted at 375 MPa. The results of 3D reconstructed images are shown in Figure 3c-d, with blue dots indicating pores. The LPSC pellet shows a large number of voids distributed throughout the pellet (Figure 3c). In contrast, the densified UDSH@LPSC pellet displays significantly fewer voids (Figure 3d). The calculated porosities from the 3D reconstruction are 11.5% for LPSC and 2.2% for UDSH@LPSC, which aligns closely with the pellet porosity measurements. This observation confirms the effective densification of UDSH@LPSC at room temperature (20 ± 2 °C). While we use uniaxial compression in this study, the surface lubrication mechanism should still be operational if isostatic pressing, a more desirable approach, is used.

The confirmed surface lubrication effect of UDSH makes it a powerful densification agent at room temperature. This surface



Figure 4. Electrochemical performance of LPSC and densified UDSH@LPSC at room temperature. (a) LPSC and (b) UDSH@LPSC compacted at 375 MPa in a LillLi symmetric cell tested at step-increase current density. (c) CCD value of LPSC and UDSH@LPSC with

Figure 4. continued

electrolytes compacted at various pressures. (d) Voltage profile of LilUDSH@LPSClLi cell compacted at 375 MPa tested at a constant current density of 1 mA cm⁻². Voltage profiles of (e) LilLPSClNCM and (f) LilUDSH@LPSClLPSClNCM cells. The cells were cycled at C/ 20 for 2 formation cycles followed by cycling at C/5. C rate is defined as assuming a capacity of 200 mAh g⁻¹. (g) Capacity retention of Lil UDSH@LPSClLPSClNCM cell at 0.3 mA cm⁻² with loading of 1.5 mAh cm⁻², the sudden change in Coulombic efficiency is due to a software interruption.

lubrication layer helped LPSC from reducing interparticle friction, improving compressibility, particle rearrangement, and make a dense LPSC pellet.

EFFECT OF DENSIFICATION ON LITHIUM PENETRATION RESISTANCE

The ultimate goal of this work is to mitigate lithium dendrite penetration by densifying the LPSC pellet. The evolution of the LilLPSC interface during compression and electrochemical cycling was evaluated using LillLi symmetric cells at room temperature (20 ± 2 °C). LPSC and UDSH@LPSC were compacted at a pressure of 375 MPa, and electrochemical impedance spectroscopy (EIS) was employed to monitor the symmetric cells maintained under open circuit conditions under a stack pressure of 30 MPa (Figure S13). The interfacial resistance and capacitance shown in Figure S14 were determined by fitting the data to the equivalent circuit. The evolution of the interfacial resistance value with time represents the stability of the interface. After 32 h, the interfacial resistance of LilLPSC abruptly dropped to zero, indicating Li metal penetration through the LPSC layer to short the cell²⁹ (Figure S14a). In contrast, the interfacial resistance as well as capacitance are relatively stable of Lil UDSH@LPSC after 40 h (Figure S14b). The steady-state increase in resistance may be attributed to interfacial reactions between the electrolyte and Li metal.³⁰

The effect of densification was further evaluated by measuring the critical current density (CCD) and cycling stability of the LillLi symmetric cells at a stack pressure of 30 MPa (Figure 4 and Figure S15-16). CCD is a commonly employed metric to measure the resistance of the SSEs to shorting due to lithium dendrite growth.³¹ When LPSC and UDSH@LPSC were pelletized at a pressure of 375 MPa, the LilLPSClLi cell experienced rapid shorting after 0.8 mA cm⁻² (Figure 4a). In contrast, the LilUDSH@LPSClLi cell exhibited a CCD of 3.2 mA cm⁻² (Figure 4b). CCD improvements of 0.9-2.4 mA cm⁻² (up to four times) were observed for electrolytes compacted at different pressures (Figure 4c). The relationship between cell shorting time and porosity is not monotonous.^{4,10} For high-porosity electrolytes where pores are connected, increased densification results in faster shorting due to reduced pore volume available for lithium infiltration.⁴ Below a porosity threshold, when pores become discrete, cell shorting is mitigated with further densification.⁴ For LPSC, the threshold is observed at 375 MPa, corresponding to a porosity of 10.9%, whereas UDSH@LPSC exhibits discrete porosity at a significantly lower pressure of 188 MPa, with a porosity of 10.5%. A control experiment was conducted to ascertain whether the higher pellet density of UDSH@LPSC or the presence of UDSH residue at the LilSSE interface contributes to the improvement in CCD. In this experiment, pristine LPSC was pelletized at 375 MPa, with 5 μ L of UDSH applied to each side, and a LillLi symmetric cell was assembled and tested under a pressure of 30 MPa (Figure S17). The resulting CCD of 0.7 mA $\rm cm^{-2}$ was nearly identical with that of pristine LPSC,

and the relationship between CCD and porosity suggests that the improvement in CCD is attributable to a denser electrolyte pellet rather than to the UDSH at the interface.

The effectiveness of densification in mitigating dendrite penetration is further examined by imaging the interface between Li and the electrolyte layer. As an example, SEM images of LilLPSClLi cross-section reveal evidence of Li dendrite penetration into the LPSC pellet after cycling at 0.1 mA cm⁻² for 5 cycles (Figure S18a). In contrast, the SEM cross-section of LilUDSH@LPSC|Li cycled under the same conditions displays a clean interface with no observable lithium penetration (Figure S18b). Next, we conducted a comparison of extended cycling. A LilLPSClLi cell shorted after 12 h at 0.1 mA cm⁻² (0.1 mAh cm⁻²) and shorted immediately at 1 mA cm⁻² (1 mAh cm⁻²) (Figure S19). Conversely, a LilUDSH@ LPSCILi cell demonstrated superior performance, cycling for 4600 h at 1.0 mA cm⁻², 1.0 mAh cm⁻² (Figure 4d). This represents over 3 orders of magnitude improvement in cycling duration compared to LPSC. The increased stability under open circuit, 4-fold higher CCD and over 3 orders of magnitude longer cycling demonstrated the significant benefit of densification enabled by the use of UDSH.

To understand the effect of UDSH on the redox stability of LPSC, we measured cyclic voltammetry (CV) by using LPSC or UDSH@LPSC mixed with vapor grown carbon fiber (VGCF) as a composite electrode. The CV profiles of both LPSC (Figure S20a) and UDSH@LPSC (Figure S20b) exhibited peaks at 2.65 V due to the oxidation of the bridging sulfur in PS_4^{3-} in LPSC.³² Notably, with UDSH adsorption, the current intensity remained comparable. In fact, the reduction peak for the UDSH@LPSC sample was weaker, indicative of the potential of UDSH in mitigating parasitic reactions, which is a topic of future study. These findings indicate that the thiol functional group does not introduce additional decomposition reaction versus Li/Li⁺.

Finally, Figure 4e-g illustrates the galvanostatic cycling performance of LillLiNi_{0.80}Co_{0.1}Mn_{0.1}O₂ with a capacity loading of 1.5 mAh cm⁻² at room temperature (20 ± 2 °C). In Figure 4e, the cell fabricated utilizing pristine LPSC experiences an initial shorting at the onset of charging at 0.3 mA cm⁻² after formation cycles. In contrast, the cell incorporating UDSH@LPSC (Figure 4f-g) demonstrates a higher discharge capacity of 160 mAh g^{-1} and retains 80% of its capacity after 50 cycles at 0.3 mA cm⁻². This finding provides compelling evidence of the remarkable densification effect of UDSH on LPSC, particularly in mitigating lithium dendrite penetration in lithium metal all solid-state batteries. We note that postcycling analysis of both LPSC and UDSH@ LPSC by XPS shows a comparable increase in the intensity of Li-S signals, which is associated with the reaction between argyrodites and lithium metal³ (Figure S21). The observed enhancement in stability is thus due to the densification effect.

We have shown that a long chain thiol, 1-undecanethiol, can be used to effectively densify the Li_6PS_5Cl solid electrolyte. The -SH end group anchors to the surface of the solid electrolyte, which is essential for a strongly bonded lubrication layer surrounding the LPSC particles. The hydrocarbon tail of the thiol forms the lubrication layer that effectively facilitates the particle rearrangement and reduces friction during compaction to promote densification and reduce porosity. The UDSH-modified solid state electrolyte reduced the LPSC pellet porosity by 11% to 83% compared to pristine LPSC at various compacting pressures. In the LillLi symmetric cells, the densified LPSC enables up to 4-fold higher critical current density and over 3 order of magnitude longer cycle life at 1 mA cm⁻². Our results demonstrate the potential of surface engineering to facilitate the processing of solid-state batteries.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.4c03387.

Experimental methods, SEM, FIB-SEM, TEM results, powder rheology, microindentation, electronic conductivity and battery performance (PDF)

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Author Contributions

MC.L. and P.L. conceived the idea and designed the experiments. MC.L., E.L, S.F. W.Y. carried out the experiments and measurements. S.W. carried out the FIB-SEM. J.G. carried

out the 3D reconstruction. J.O., M.S. and J.L. helped with discussion. MC.L., J.L. and P.L. prepared the manuscript with contributions from all authors. P.L. supervised the research.

Notes

The authors declare the following competing financial interest(s): P.L., MC.L., J.O. and M.S. have filed a U.S. patent application based on this work. The remaining authors declare no competing interests.

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