Spraying Li₆PS₅Cl and silver-carbon multilayers to facilitate large-scale fabrication of all-solid-state batteries

Doerrer, Christopher; Metzler, Michael; Matthews, Guillaume; Bu, Junfu; Spencer-Jolly, Dominic; Bruce, Peter G.; Pasta, Mauro; Grant, Patrick S.

DOI: 10.1016/j.device.2024.100468

License: Creative Commons: Attribution (CC BY)

Citation for published version (Harvard):
Doerrer, C, Metzler, M, Matthews, G, Bu, J, Spencer-Jolly, D, Bruce, PG, Pasta, M & Grant, PS 2024, 'Spraying Li₆PS₅Cl and silver-carbon multilayers to facilitate large-scale fabrication of all-solid-state batteries', Device. https://doi.org/10.1016/j.device.2024.100468

Link to publication on Research at Birmingham portal

General rights
Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

• Users may freely distribute the URL that is used to identify this publication.
• Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
• Users may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
• Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy
While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.
Spraying Li$_6$PS$_5$Cl and silver-carbon multilayers to facilitate large-scale fabrication of all-solid-state batteries

Authors
Christopher Doerrer, Michael Metzler, Guillaume Matthews, ..., Peter G. Bruce, Mauro Pasta, Patrick S. Grant

Correspondence
chris.doerrer@utoronto.ca (C.D.), patrick.grant@materials.ox.ac.uk (P.S.G.)

In brief
This paper presents a scalable layer-by-layer spray printing approach for manufacturing solid-state battery components including the separator, cathode, and anode. The authors also discuss the benefits and opportunities of creating different structural designs by spray printing for improved battery performance.

Highlights
- Spray-printed sulfide separators, composite cathode, and an Ag-C layer
- Dense, 10-μm sprayed sulfide separators with a conductivity of 1 mS cm$^{-1}$
- Platform for exploring new electrode/electrolyte designs and interlayers
- Ag-C layer improves anode-free cycling due to Li-Ag formation at Ag particles
Spraying Li$_6$PS$_5$Cl and silver-carbon multilayers to facilitate large-scale fabrication of all-solid-state batteries

Christopher Doerrer,1,3,5,* Michael Metzler,1 Guillaume Matthews,1,2 Junfu Bu,1 Dominic Spencer-Jolly,1,4 Peter G. Bruce,1,2 Mauro Pasta,1,2 and Patrick S. Grant1,2,*

1Department of Materials, University of Oxford, Oxford OX1 3PH, UK
2The Faraday Institution, Quad One, Becquerel Avenue, Harwell Campus, Didcot OX11 0RA, UK
3Department of Mechanical and Industrial Engineering, University of Toronto, 5 King’s College Road, Toronto M5S 3G8, ON, Canada
4School of Metallurgy and Materials, University of Birmingham, Elms Road, Birmingham B15 2SE, UK
5Lead contact
*Correspondence: chris.doerrer@utoronto.ca (C.D.), patrick.grant@materials.ox.ac.uk (P.S.G.)

https://doi.org/10.1016/j.device.2024.100468

SUMMARY

In recent years, solid-state battery (SSB) performance has steadily improved with the use of sulfide solid electrolytes (SEs). However, most research has focused on small (diameter <10 mm), thick (separator >500 μm) pellet-type cells that use non-scalable manufacturing routes and yield a low cell energy density. Technical applications require thinner and larger sheet-type cells made by scalable techniques. We examine the applicability of a scalable layer-by-layer process for manufacturing SSBs and demonstrate functional examples for each battery component. Spraying in combination with layer densification results in thin and highly dense coatings, which are desired for high energy density and long-lasting SSBs. This work expands on existing manufacturing routes and demonstrates the potential of spray printing to create tailored structures through the layer-by-layer approach for improved battery performance.

INTRODUCTION

All-solid-state batteries (SSBs) can achieve higher energy densities and a higher level of safety than conventional Li-ion batteries (LIBs), with potential use in electric vehicles and other transport sectors and portable consumer electronics.1,2 Inorganic solid electrolytes (SEs) such as oxides and sulfides with a high Li-ion conductivity of 1–10 mS cm$^{-1}$ that is comparable with conventional liquid electrolytes have been critical for SSB development.3–5 From a cell fabrication point of view, oxide-based SSBs are difficult to realize because the high stiffness and high melting point of oxide particles require elevated temperature processing, usually to promote sintering, to achieve acceptable density and intimate solid-solid contacts.6 Sulfide-based SSBs offer plastic deformation and consolidation at room or slightly elevated temperature (<300 °C) and readily achievable pressures (~100 MPa).7 A low manufacturing temperature is preferred from an energy consumption perspective and for composite cathodes to avoid interdiffusion or side reactions between the SE, the cathode active material (CAM), and carbon additives.

Sulfide-based SSBs have been demonstrated with improving performance in both rate and cyclability.8,9–12 Best-performing SSBs are usually constructed as uniaxially cold-pressed pellet-type cells, which have low process scalability, and often use...
an impractical SE separator thickness as high as 1 mm, resulting in a low overall cell energy density. There remains a need for scalable techniques for industrial production of practical sheet-type SSBs with reduced SE separator thickness (<100 µm) and larger cell area (e.g., DIN A5 size: 148 × 210 mm²) while preserving the most attractive performance aspects of pellet-type cells.

The production of sulfide-based SSBs with high energy density at large scale faces several challenges. The instability of sulfides in the presence of water vapor requires operation in a low dew point dry room or inert atmosphere to prevent the formation of toxic H₂S.¹³,¹⁴ The addition of a polymeric binder to the SE and cathode is required to provide mechanical stability and to ensure adhesion to the current collector. Unfortunately, a high binder fraction impedes Li-ion and electron movement. Both dry- and wet-chemical approaches have been investigated for sheet-type SSB production.¹⁵⁻¹⁷ Whereas dry processes based on polytetrafluoroethylene (PTFE) often showed encouraging performance by creating networks of SE particles and thin polymer fibrils, it is still unclear whether the approach can be cost-effective and produce cells at large scale.¹⁸⁻²¹ Wet-chemical approaches for SSB fabrication mainly rely on derivatives of slurry casting, which is a coating technique where a paste-like slurry is spread on a substrate foil using a doctor blade coater. While slurry casting is productive for the fabrication of conventional LIBs, it may not allow for optimal usage of the slurry constituents in components for SSBs. Electrodes for SSBs, for example, do not rely on liquid electrolyte permeation through the pores; instead, the SE must be included in a multi-particle slurry, with the position of the particles determining the quality of ionic percolation. Local particle arrangement is critical for maximizing their function, and particle migration or sedimentation during manufacture in the coating must be avoided.

In this paper, we introduce a scalable layer-by-layer spray printing approach for sulfide-based SSB fabrication. The layer-by-layer deposition process includes the drying of each thinly deposited layer of a dilute slurry to restrict binder or particle migration to the particle length scale. The drying process prevents the intermixing of particles from adjacent layers across the coating thickness and provides greater design freedom compared with other fabrication techniques. Layer-by-layer spray printing has improved the performance of LIB and oxide-based SSB electrodes by designing the local electrode microstructure to better match the local electrochemical environment.²²⁻²⁸ We adapted the spray printing process to operate in a fully inert atmosphere suitable for reactive sulfides. Large-area (10 × 10 cm²) sulfide SE separators with high ionic conductivity of 1 mS cm⁻¹ are produced with a thickness of 10 µm, which is among the thinnest reported.¹⁹ For the sulfide electrolyte, both suspensions and solutions are investigated, and their effect on microstructure, crystallinity, and ionic conductivity on SE coatings has been investigated. A spray-printed sulfide-based SSB cathode is demonstrated with 63% capacity retention after 800 cycles. Finally, the spray process is demonstrated for the sequential production of a multi-layer nanoparticulate Ag-C layer for a Li-metal-free anode followed by subsequent sulfide SE separator coating.²⁹,³⁰ We show how spray printing can facilitate both the individual elements of an SSB and their convenient integration. There exist many benefits and opportunities of layer-by-layer spray processing for the fabrication of sulfide-based SSB cell components, such as the separator, cathode, and anode.

RESULTS

A layer-by-layer, large-area spray printing process was explored for the manufacture of a thin argyrodite Li₆PS₅Cl (LPSCl) SE separator, a composite cathode, and an anode-free Ag-C interlayer. In the following sections, we will describe the spray process, followed by a discussion of each sprayed battery component.

The spray deposition tool is equipped with four individual spray nozzles and a movable hotplate that operates in an Ar atmosphere. The principle of the spray process is shown in Figure 1A. It involves pumping a feedstock suspension/solution at a controlled rate to a nozzle operating with Ar gas where it is atomized into a fine spray of droplets that are directed and deposited over a heated metallic foil. On deposition of the droplets, the liquid evaporates almost instantly, as illustrated by the mass flow (m) of the solvent directed from the coating to the surrounding atmosphere resulting from the high heat flow (q). The hotplate is scanned in the x-y plane at a constant spray height (z) by a computer-controlled gantry to cover uniformly an area of 25 × 25 cm², and the whole apparatus is operated automatically inside an Ar-filled glovebox. The spray process was supplemented by an integrated inspection vision system and a non-contact laser displacement height sensor that allowed for in-process quality control and dimensional monitoring. The magnified view in Figure 1B shows schematically an example of a sprayed coating with a typical binder distribution and a high porosity (30%–50%).
Additional information on the spray deposition tool can be found in Note S1.

Spray printing of thin sulfide solid electrolyte separators

Coating fabrication

The spray process introduced in Figure 1 was used to manufacture thin LPSCI SE separators, aiming to retain the high intrinsic ionic conductivity of LPSCI, for direct use in SSBs. The aforementioned high reactivity of sulfides limits the choice of solvents, which must also be carefully matched with a compatible binder (e.g., nitrile butadiene rubber binder with xylene solvent) for successful slurry formation. However, non-polar solvents such as xylene disperse sulfide particulates and dissolve binders, more polar solvents, e.g., ethanol or isopropanol (IPA), can dissolve sulfides, which are then reprecipitated during drying. Reprecipitated sulfide, however, may be only semi-crystalline and have reduced ionic conductivity. Nonetheless, the solution/reprecipitation approach can be beneficial in creating micron-scale structural features independent of the initial particle size, intimate contact between the CAM and the sulfide SE in composite cathodes, or infiltrating conventional porous LIB electrodes where relatively low volume fractions of SE might be used to promote Li-ion percolation.

Two LPSCI-based suspension/solutions were investigated to spray LPSCI SE coatings as shown in Figure 2A: (1) IPA to dissolve and reprecipitate LPSCI and (2) ethyl acetate (EA) to suspend LPSCI particulate and dissolve 5 vol% polyvinylidene fluoride (PVDF). Mixtures (1) and (2) are referred to as IPA/LPSCI and EA/LPSCI and were chosen as exemplary systems to study an LPSCI-based solution and suspension, respectively. Since IPA and EA have comparable boiling points of 82.3 °C and 77.1 °C, similar process parameters such as substrate temperature could be used to isolate the influence of the suspension/solution while reducing the effects of other variables.

The spray printing process allows for a high flexibility in relation to the spray area and substrate shape, and typical spray-printed LPSCI-based SE coatings on different substrates are shown in Figure 2B. Ionic conductivity tests were conducted by SE deposition directly onto stainless-steel discs, typically comprising 5–20 sprayed layers depending on the concentration of the suspension and the target thickness.

Coating morphology

Scanning electron microscope (SEM) images of pristine LPSCI powder shown in Figure 2C are compared with as-sprayed IPA/LPSCI and EA/LPSCI coatings in Figures 2D and 2E, respectively. In the EA/LPSCI coating, the LPSCI particulate was preserved throughout the spraying process, whereas the IPA/LPSCI coating comprised large-scale, non-particulate features, suggesting that the feedstock particulate had dissolved and then reprecipitated as a semi-integral coating, as intended. There was a significantly higher pore fraction in the EA/LPSCI coating, estimated at >30 vol %, as shown in the cross-sections in Figure S1. Conversely, precipitated IPA/LPSCI coatings had a relative density of >90% but with micro-cracks that formed during drying and likely were exacerbated by the absence of an elastic binder. Cracking in IPA/LPSCI coatings likely occurred during rapid solvent evaporation and fast reprecipitation of LPSCI on the substrate, followed by thermal contraction on cooling to room temperature. As-sprayed IPA/LPSCI and EA/LPSCI coatings had an average surface roughness (Ra) of 2.3 μm and 3.4 μm, respectively.

The average roughness for the IPA/LPSCI and EA/LPSCI coating decreased to 0.1 μm and 0.2 μm, respectively, by uniaxial densification at room temperature and 500 MPa, as shown in Figures S1 and S2. For comparison, a 700-μm-thick LPSCI SE pellet was made by pressing identical pristine powder in a tungsten carbide die-set at 500 MPa typical of laboratory studies, and it had an average roughness of 0.7 μm. Based on the SEM cross-sections shown in Figure S1, the relative densities of the pellet, IPA/LPSCI, and EA/LPSCI coatings were estimated by applying a gray-level threshold (more details in the experimental procedures section) as 96%, 98%, and 99%, respectively. The relative density of the pellet was consistent with previous results; however, a relative density of >98% is generally recommended for a practical cycle life in sulfide-based SE separators. Residual pores in the pressed pellet were mainly at the SE particle-particle interface. The relatively high density of the IPA/LPSCI coating was because the reprecipitated SE was more continuous and film-like than particulate in structure. Pore filling by binder in the EA/LPSCI coating enabled an even higher density with almost no residual porosity, as shown in the cross-sectional SEM image in Figure S3. Corresponding energy-dispersive X-ray spectroscopy (EDX) maps (Figure S3) showed the binder (due to the F signal) was located between the sulfide particles. However, increasing the binder fraction to 10 wt% resulted in PVDF-rich regions on the coating surface, as shown in Figure S4, which can be expected to impede Li-ion movement, suggesting that 5 wt% represents a good balance between inter-particle and current collector adhesion and maintaining ionic percolation.

Ionic conductivity and crystal structure

The sprayed coating and pellet ionic conductivity was determined by electrochemical impedance spectroscopy (EIS) using two stainless-steel blocking electrodes and the equivalent circuit shown in Figure S5. Measurements were taken at a variety of uniaxial pressures up to 500 MPa. Lower pressures resulted in higher resistances and lower ionic conductivity, as shown in Figure S6. The Nyquist plot in Figure 2F shows the EIS response of the sprayed coatings alongside the SE pellet, with the corresponding ionic conductivities and resistances shown in Figure 2G. The sprayed coatings had ionic conductivities of 1.08 mS cm⁻¹ and 0.10 mS cm⁻¹ for EA and IPA, respectively, lower than the cold-pressed pristine powder conductivity of 2.15 mS cm⁻¹. This arose because of the chemical degradation of the sulfide by the organic solvent and the influence of the ionically insulating binder in the EA sulfide coating. Despite the lower ionic conductivity, the resistance was significantly lower than the pellet because of the decreased thickness of the sprayed coatings. Heat treatment may increase the ionic conductivity of precipitated sulfide SEs made from a solution process, so a 30-μm-thick IPA/LPSCI coating was annealed at 300 °C. As expected, the conductivity increased to 0.39 mS cm⁻¹, with the corresponding Nyquist plot shown in Figure S7. The morphology of the annealed coating is shown in Figure S8 with no indication of any structural change compared with the as-sprayed coating. In general, there was consistent coating-to-coating thickness and ionic conductivity, suggesting good control over the key spray printing process parameters.
To analyze any effect of the spray process on the interaction between solvent and LPSCI, the crystal structure was investigated by X-ray diffraction (XRD). Figure 2H compares the XRD spectra of the sprayed coatings with the pristine powder. EA/LPSCI showed high crystallinity similarly to the pristine powder, whereas IPA/LPSCI showed much lower intensity and broader peaks indicating lower crystallinity. This suggested that the conductivity decrease of EA/LPSCI was predominantly caused by the addition of non-conducting binder rather than reduced crystallinity, and it is consistent with previous reports. In the case of IPA/LPSCI, the lower crystallinity explained the lower ionic conductivity because there were fewer low-resistance ionic
pathways for Li ions. Annealed IPA/LPSCl showed increased crystallinity, consistent with the increase in ionic conductivity. However, the XRD data suggested that the crystallinity was lower than pristine powder, with residual LiCl and Li2S impurities that are known to be comparatively poor ionic conductors. Due to the absence of a polymer binder in the IPA/LPSCl coating, it was assumed that the ionic conductivity decrease arose from irreversible side reactions during the IPA/LPSCl exposure.

A spray-printed composite cathode
SSB cathodes comprise active material, SE, and electron conductive material. Additionally, elastic binders are required for sufficient current collector adhesion, for flexibility and ability to be handled during manufacture. Figure 3A shows schematically the spray printing concept for a composite cathode, from formation of the cathode itself, through to final assembly into a functional cell. Following this scheme, first, a 30-μm-thick composite cathode was spray-printed from a LPSCl, LiNi0.83Mn0.06Co0.11O2 (NMC), and carbon black (CB) suspension, which was dispersed and mixed with the relatively better performing PVDF/EA mixture from the previous section. Here, a slightly lower binder content of 3 wt % was used in the SE separator to reduce resistance to Li-ion and electron percolation. However, even smaller amounts of binder <3 wt % led to insufficient adhesion of the particle layers to the substrate. Second, an EA/LPSCl layer was then spray-printed directly onto the newly formed composite cathode to form in situ the SE separator. The cathode and SE separator layers were then densified jointly to an estimated relative density of 95% and 99%, respectively, using a uniaxial pressure of 500 MPa at room temperature. Densification aimed to promote solid-solid contact at the individual SE-CAM particulate interfaces within the cathode, and the SE membrane-composite cathode interface. Finally, cell assembly was completed by adding a 50-μm-thick Li foil as the anode and then a steel foil “upper” current collector. Details about the anode preparation can be found in Note S2. The SEM image and corresponding Al, Ni, and S EDX maps in Figure 3B show the multi-layer assembly, distinguishing the Al current collector (Al EDX map), the composite cathode (Ni EDX map from the NMC), and the percolating electrolyte pathways and thin sulfide (S EDX map) SE separator.

Short circuits due to densification and accelerated Li dendrite penetration of the separator were an occasional feature of the more complex spray-printed multi-layer arrangements (with more details in Note S3). To avoid these short circuits and to investigate the intrinsic performance of the sprayed cathode alone, cells with a 700-μm-thick SE separator were also fabricated for electrochemical investigation in a custom-made cell setup. These 5-mm-diameter cells comprising a sprayed cathode, thick
SE separator, and Li were cycled at a relatively low uniaxial stack pressure of 2.5 MPa in a polyether ether ketone (PEEK) mold under protective atmosphere. The cathodes reproducibly delivered a discharge capacity of 157 mA h g⁻¹ at 30°C and 0.1 mA cm⁻² (0.08 C), suggesting a CAM utilization of 75%, as shown in Figure S9 (assuming a theoretical capacity of 210 mA h g⁻¹ at room temperature). To increase CAM utilization, the cycling temperature was increased to 80°C, which increased capacity by a further 60 mA h g⁻¹, as shown in Figure S9. The CAM utilization was close to 100% at 80°C assuming a theoretical capacity of 220 mA h g⁻¹ at 80°C. Figure 3C shows the effect of increasing C-rates at 80°C, with capacity decreased by 26% between 0.08 C and 0.6 C. Figure 3D shows that the sprayed cathode after 800 cycles at 0.6 C had a retained capacity of 63%.

A spray-printed Ag-C layer for an anode-free cell design

Fabrication and performance of the Ag-C layer

In order to minimize cost and maximize gravimetric and volumetric performance at the cell scale, there should be little to no excess Li in an SSB anode. One way to achieve this is to assemble the cell without a pre-existing Li anode and instead to form the Li anode by plating in situ from a Li-rich cathode on the first charge cycle. Such an approach avoids the considerable difficulties in forming a thin Li metal anode from a highly reactive Li solid (foil), liquid, or vapor.

To facilitate the uniform nucleation and growth of metallic Li at the anode on the first and subsequent cycles, a particulate interlayer, e.g., Ag-C, between the current collector and the SE separator has been shown to be beneficial. The interlayer enables higher current density compared with direct plating on a metal current collector due to more homogeneous Li plating, which also helps to mitigate Li dendrite formation. The functional benefits of an Ag-C coating are discussed in this section along with a suggested spraying sequence that facilitates its manufacture and allows for subsequent deposition of SE separator coatings.

Figure 4A shows schematically the fabrication process of an anode-free high-energy-density SSB using spray printing. Ag nanoparticles and graphite particles were dispersed in IPA/N-methyl-2-pyrrolidone (NMP) with 10 wt % PVDF and sprayed

Please cite this article in press as: Doerrer et al., Spraying Li₆PS₅Cl and silver-carbon multilayers to facilitate large-scale fabrication of all-solid-state batteries, Device (2024), https://doi.org/10.1016/j.device.2024.100468

Device 2, 100468, August 16, 2024

OPEN ACCESS
on a stainless-steel foil that formed the anodic current collector. The Ag-C coating thickness was ~5 μm, slightly thinner than previously reported carbon layers made by screen printing and blade coating.\textsuperscript{30,52} A LPSCI SE separator was then spray-printed on top of the Ag-C layer as described above using a second spray nozzle. Subsequently, an NMC-based composite cathode, prepared separately by a solvent-free, dry-processing approach, was pressed on the SE separator using a uniaxial pressure of 500 MPa.\textsuperscript{13} A dry-processed cathode was preferred in this case because it was considered important to minimize the cathode binder fraction in order to reduce impedance at the CAM/SE interlayer interface. The dry process successfully allowed the binder fraction to be reduced to 1 wt % of polytetrafluoroethylene (PTFE), rather than >2 wt % associated with slurry cast composite SSB cathodes and SE separators.\textsuperscript{30} Due to the fibrillar nature of PTFE, there is less coverage of the CAM/SE interface, in contrast to slurry casting where the binder tends to reprecipitate as a layer on the CAM and SE particles.\textsuperscript{53} Figure S10A shows a plan-view SEM image of the upper free surface of the dry-processed cathode showing ~50-nm-thick PTFE fibrils that formed during dry shear processing, anchored to the NMC particles, and forming a 3D mesh, or web, that provided electrode mechanical stabilization. PTFE fibrils were confirmed by the fluorine EDX map shown in Figure S10B, which allowed for differentiation between fibrils and the CNFs.

To investigate Li deposition during plating, pristine and cycled SEM images of the Ag-C layer are compared in Figures 4B and 4C. Figure 4B shows an SEM cross-section image of the pristine sprayed Ag-C layer and the SE separator with corresponding Ag, C, and S EDX maps showing differentiation between the layers and intimate interlayer contact. Figure 4C shows the small Ag particles in a C-rich as-sprayed Ag-C layer. After a charge of 0.25 mA h cm\textsuperscript{-2} was passed, a new sphere-like phase developed and always linked to prior Ag particles. It is beyond the scope of the current work to unpick the detailed processes occurring in the Ag-C layer, which have been the focus of other publications.\textsuperscript{30,52} Based on previous work, the new spherical phase is very likely Li\textsubscript{2}Ag\textsubscript{y}, possibly with some metallic Li also. At 2 mA h cm\textsuperscript{-2}, the new phase was significantly coarser and more widespread. Once the cell was discharged, the overall Ag-C layer morphology became similar again to the pristine coating. It is likely that at low charge rates, toward the thermodynamic limit, the C in the Ag-C layer can become fully lithiated, and a lithium-rich Li\textsubscript{2}Ag\textsubscript{y} is formed at the Ag particles. At higher charge rates, the rate of formation of the Li\textsubscript{2}Ag\textsubscript{y} alloy may be kinetically limited, and all of lithiated carbon, Li\textsubscript{2}Ag\textsubscript{y}, and Li metal may be present.\textsuperscript{30} To demonstrate the effectiveness of the sprayed Ag-C, the electrochemical effect on Li plating of an Ag-C coating on stainless-steel foil was compared with a blank stainless-steel foil in Figures 4D and 4E. The charging profile in Figure 4D vs. a Li\textsuperscript{+}/Li counter electrode showed that for the stainless-steel foil only, there was a higher Li plating nucleation overpotential and faster cell failure when compared with the Ag-C coating. In contrast, the Ag-C coating was able to sustain a current density of 2 mA cm\textsuperscript{-2} for at least 5 mA h cm\textsuperscript{-2} at 60 °C.

Performance of a full cell

The electrochemical performance of the sprayed Ag-C layer was further investigated in a full cell using the configuration in Figure 4A. To avoid short circuits after cell assembly due to the low thickness of the sprayed separator coatings (which would require more sophisticated cell assembly with low tolerances during positioning and stacking; Note S3) an easier to handle 700-μm-thick SE separator was used. Figure 4E shows the first charge and discharge curves at a current density of 0.2 mA cm\textsuperscript{-2} and 30 °C. Cells with the Ag-C coating showed a first cycle Coulombic efficiency (CE) of 78% and a discharge capacity of 190 mA h g\textsuperscript{-1}, representing a CAM utilization of 90%. Cells with a stainless-steel foil again showed early cell failure during charge consistent with the observations in Figure 4D at 60 °C. The shoulder-like shape in the discharge curve was ascribed to the delithiation of the graphite particles in the Ag-C layer, as observed previously.\textsuperscript{52} Despite the encouraging data after one cycle, cell failure occurred at the beginning of the second charge, as shown in Figure S11. This behavior was consistent with the literature where a similar graphite layer achieved a first cycle CE of 67% at 60 °C and cell failure was at the beginning of the second charge due to short circuit.\textsuperscript{52} The higher first CE achieved herein might be ascribed to the lower current density (0.2 mA cm\textsuperscript{-2} compared to 0.5 mA cm\textsuperscript{-2}). Cell failure in the second cycle is believed to have occurred due to Li dendrite penetration through the SE separator. Li dendrites grow from inhomogeneous Li deposition at the anode during charge, even with an Ag-C layer, and are accelerated by any through-thickness cracks. This condition can arise due to the following: limited Li transport across the Ag-C layer, leading to undesirable Li deposition at the SE rather than “behind” the Ag-C and on the current collector, and volume changes across the cell during the first cycle, leading to a loss of physical contact of the SE with the Ag-C layer, or there were residual manufacturing defects, such as cracks, within the SE that promoted easy dendrite propagation. Having obtained a first cycle proof of principle here, further work now focuses on layer optimization, including different carbon selections to optimize homogeneous Li plating and stripping.

Using the performance data from Figure 4E, we evaluated the influence of decreasing the SE thickness from 50 μm to 5 μm on the cell energy density per unit volume and per unit mass as shown in Figure 4F, assuming the same composite cathode loading and thickness (15 mg cm\textsuperscript{-2}, 70 μm) with the Ag-C layer, to give increases of 44% to 1,059 W h L\textsuperscript{-1} and 23% to 301 W h kg\textsuperscript{-1}, respectively. Since the separator does not actively contribute to the stored energy in a battery, it is desirable to minimize its mass or volume fraction. Thin separators also reduce raw material costs and improve cycling performance due to shorter Li-ion pathways.\textsuperscript{30} Figure 4F emphasizes the positive effect of reducing separator/membrane thickness, noting that spray printing has already been demonstrated successfully for ~5-μm-thick inorganic separators in conventional LIBs.\textsuperscript{28}

DISCUSSION

The spray process can be applied to all principal components of an SSB, such as the SE separator, cathode, and anode. Figures 5A–5C show exemplary unique structures based on the methodology described in previous sections, while Figure 5D illustrates potential design concepts to be explored.
Spray printing is particularly attractive for thin (<50 μm) SE layers between the anode and cathode, which are difficult to produce by other techniques. Relatively large areas can be achieved easily, and the SE thickness can be controlled, e.g., by the number of sprayed layers. This is shown in Figure 5A where EA/LPSCl was sprayed on a composite cathode and subsequently densified with a composite anode. The SE separator is highlighted in the S, P, and Cl EDX maps with a thickness as low as ~10 μm. Coating one of the electrodes with a relatively thin SE separator could also have the additional advantage of eliminating the need for subsequent separate lamination steps. Previous investigations at the Li-SE interface during Li plating showed that crack formation in the SE propagated ahead of a Li dendrite, suggesting a higher mechanical integrity (e.g., toughness) is needed. Therefore, such dry crack formation might be counteracted by the integration of tougher, crack-blocking layers that could be sprayed between thin layers of the SE.

Another opportunity lies in using the layered approach enabled by spray deposition to use different SE materials in a single separator, e.g., a two-layered SE separator that combines two materials with a different oxidative and reductive stability to span a large cell voltage and therefore to increase cell energy density. A data-driven perspective estimated that the discovery of an effective SE separator that combines stability against high voltage and Li metal is one order of magnitude less likely compared with a system of two different SEs. The challenge of meeting SE requirements with one material is highlighted by recent interest in halide SEs that offer better stability with high-voltage CAMs but poor stability in contact with a Li metal anode. The combination of two SE types in a pellet-type SSB with a layered halide/sulfide SE separator showed encouraging cycling with relatively low capacity degradation. A two-layer SE separator may be challenging to fabricate with conventional methods such as slurry casting, but the work here suggests that such an arrangement might be realized rather simply by a setup of multiple nozzles that are connected to different spray suspensions to coat a composite cathode, for instance, first with a thin halide SE layer followed by a sulfide SE coating.

The almost instantaneous drying of each layer “freezes” its composition and avoids any re-suspension (by ensuring the liquid flow rate does not exceed the drying capacity of the heated substrate). In this way, additional spatial compositional control is possible, and limited intermixing of discrete layers is ensured. Figure 5B demonstrates spray printing’s ability to create a unique multilayered structure made of alternating coatings of CAM, IPA/LPSCl, and CB (densified after spraying) allowing for heterogeneous designs to be explored. The sequential deposition offers the opportunity for single-step fabrication simply by switching between feedstock suspensions and solutions. Performance improvements might be achieved by tuning the cathode architecture using the greater design freedom of the spray printing process that allows for the manufacture of graded structures of CAM particle size or binder. Optimized LIB electrodes with electrolyte or binder gradients and multilayered patterning of different active materials have been demonstrated to improve the rate performance particularly for short charging times. This could be useful to mitigate low binder concentrations at the electrode-current collector interface occurring for instance in slurry cast LIB electrodes during solvent evaporation in >10-m-long drying ovens, which leads to decreased adhesion and delamination. Due to the instant drying of deposited suspensions in spray printing, unwanted particle movement or binder migration is prevented.

Figure 5. Sprayed multilayers and future design concepts
(A) SEM cross-sections (i) and (ii) with corresponding EDX maps of multilayered sulfide solid electrolyte separators between a composite cathode and composite anode. (B) An SEM cross-section of alternating layers of CAM, IPA/LPSCl, and carbon black. (C) An SEM cross-section of a dual interlayer made of a C and Ag-C coating. (D) Summary of the benefits and opportunities of spray-printed layers for sheet-type solid-state batteries with examples given for the solid electrolyte separator, cathode, and anode.

Spray printing is particularly attractive for thin (<50 μm) SE layers between the anode and cathode, which are difficult to produce by other techniques. Relatively large areas can be achieved easily, and the SE thickness can be controlled, e.g., by the number of sprayed layers. This is shown in Figure 5A where EA/LPSCl was sprayed on a composite cathode and subsequently densified with a composite anode. The SE separator is highlighted in the S, P, and Cl EDX maps with a thickness as low as ~10 μm. Coating one of the electrodes with a relatively thin SE separator could also have the additional advantage of eliminating the need for subsequent separate lamination steps. Previous investigations at the Li-SE interface during Li plating showed that crack formation in the SE propagated ahead of a Li dendrite, suggesting a higher mechanical integrity (e.g., toughness) is needed. Therefore, such dry crack formation might be counteracted by the integration of tougher, crack-blocking layers that could be sprayed between thin layers of the SE.

Another opportunity lies in using the layered approach enabled by spray deposition to use different SE materials in a single separator, e.g., a two-layered SE separator that combines two materials with a different oxidative and reductive stability to span a large cell voltage and therefore to increase cell energy density. A data-driven perspective estimated that the discovery of an effective SE separator that combines stability against high voltage and Li metal is one order of magnitude less likely compared with a system of two different SEs. The challenge of meeting SE requirements with one material is highlighted by recent interest in halide SEs that offer better stability with high-voltage CAMs but poor stability in contact with a Li metal anode. The combination of two SE types in a pellet-type SSB with a layered halide/sulfide SE separator showed encouraging cycling with relatively low capacity degradation. A two-layer SE separator may be challenging to fabricate with conventional methods such as slurry casting, but the work here suggests that such an arrangement might be realized rather simply by a setup of multiple nozzles that are connected to different spray suspensions to coat a composite cathode, for instance, first with a thin halide SE layer followed by a sulfide SE coating.

The almost instantaneous drying of each layer “freezes” its composition and avoids any re-suspension (by ensuring the liquid flow rate does not exceed the drying capacity of the heated substrate). In this way, additional spatial compositional control is possible, and limited intermixing of discrete layers is ensured. Figure 5B demonstrates spray printing’s ability to create a unique multilayered structure made of alternating coatings of CAM, IPA/LPSCl, and CB (densified after spraying) allowing for heterogeneous designs to be explored. The sequential deposition offers the opportunity for single-step fabrication simply by switching between feedstock suspensions and solutions. Performance improvements might be achieved by tuning the cathode architecture using the greater design freedom of the spray printing process that allows for the manufacture of graded structures of CAM particle size or binder. Optimized LIB electrodes with electrolyte or binder gradients and multilayered patterning of different active materials have been demonstrated to improve the rate performance particularly for short charging times. This could be useful to mitigate low binder concentrations at the electrode-current collector interface occurring for instance in slurry cast LIB electrodes during solvent evaporation in >10-m-long drying ovens, which leads to decreased adhesion and delamination. Due to the instant drying of deposited suspensions in spray printing, unwanted particle movement or binder migration is prevented.
The principal differences between SSB and LIB cathodes is that the electrolyte must be added as an additional component to the slurry or suspension, and the deposition process must take place in a protective atmosphere due to the high reactivity of most SEs, e.g., LPSCI with water vapor to form H₂S. Nonetheless, an SE gradient could be achieved by spraying progressively different CAM/SE ratios as the cathode forms. The spray process shown herein operates in an Ar-filled glovebox and offers the possibility to apply greater levels of microstructural control during electrode formation to solid-state electrodes, where arguably the arising performance improvements in electrode dynamics will be particularly valuable, given the lower intrinsic mobility of SEs.

SSBs, especially involving interlayers such as Ag-C particulate explored here, naturally lend themselves to manufacture by an incremental layer-by-layer approach. For example, Figure 5C demonstrates a dual interlayer consisting of Ag-C and C that may promote Li₄Ag₃ formation preferably at the current collector interface.

Surface asperities of as-sprayed coatings, most typically due to agglomeration of particulates in the feedstock suspensions, must be avoided especially if subsequent densification steps cannot be applied. The sprayed coatings here benefited from post-deposition uniaxial compression that increased density and flatness, and this step should be incorporated into the workflow under protective environment on the pathway to realizing the scalability of the spray printing approach. In particular, stacking multiple layers during cell assembly with subsequent pressing will require high-level process development. In general, the workflow for sprayed SSB assembly should minimize whenever possible handling or movement of sub-components to avoid cracking and contamination.

In summary, we presented a scalable layer-by-layer spray printing approach for manufacturing sulfide-based sheet-type SSB formats, including solid electrolyte separators, composite cathodes, and Li-metal-free Ag-C nanoparticulate-mediated anodes. The morphology, ionic conductivity, and crystallinity of sprayed coatings depended on whether a dissolution/reprecipitation or suspension approach was used, and both provided functioning composite cathodes. Best-performing sulfide coatings had a high ionic conductivity of 1 mS cm⁻¹ and were made from an EA Li₆PS₅Cl dispersion. A sulfide-based sprayed cathode cycled for 800 cycles with a capacity retention of 63%. An anode-free cell with a sprayed Ag-C interlayer to facilitate Li metal plating, and with a sprayed SE separator, was realized as a manufacturing proof of concept. Spray printing has been shown as a versatile manufacturing platform that can find applications in increasing the range of realizable SSB designs and offers the potential to fabricate SSB components at large scale.

**EXPERIMENTAL PROCEDURES**

**Resource availability**

**Lead contact**
Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Christopher Doerrer (chris.doerrer@utoronto.ca).

**Materials availability**
This study did not generate new unique reagents.

**Data and code availability**

The data that support the findings of this study are available from the corresponding author upon reasonable request. Full details of experimental procedures can be found in the [supplemental information](#).

**Spray coatings**

**Electrolyte coatings**

IPA/LPSCI: 1 g of commercial LPSCI (MSE Supplies, Pass 325 mesh, synthesized from >99.9% precursor materials) was stirred in 100 mL anhydrous IPA for 1 h. EA/LPSCI: 1 g of commercial LPSCI was suspended in a 100 mL solution of PVDF binder in anhydrous EA binder (prepared 1 day earlier and left under continuous stirring at 80°C) for 1 h and then mixed and sonicated, giving a PVDF/LPSCI weight ratio of 5:95. Substrates were a 12.5-μm-thick stainless-steel foil and 0.5-mm-thick 5- to 15-mm-diameter stainless-steel discs.

**Cathode coatings**

Commercial powders of single crystal NMC (MSE Supplies), LPSCI, and CB (Sigma-Aldrich) at a ratio of 70:27.5:2.5 by weight were suspended in an EA/PVDF solution and then mixed and sonicated, giving a PVDF:cathode weight ratio of 3:97. Substrate was a 15-μm-thick Al foil.

**Ag-C coatings**

A solution of PVDF in a mixture of solvents (97% IPA, 3% NMP by volume) was prepared. Ag nanoparticles and graphite were suspended in this solution in a ratio of 1:3 by weight and then mixed and sonicated, giving a similar PVDF:Ag:carbon ratio as that described by Samsung.29 Substrate was a 12.5-μm-thick stainless-steel foil. The composite interlayer was composed of 22.5 wt % Ag nanoparticles, 67.5 wt % graphite, and 10 wt % PVDF binder.

**Heat treatment**

The IPA/LPSCI coating was annealed at 300°C in a box furnace under an Ar atmosphere (heating/cooling rate: 10°C min⁻¹, holding temperature: 30 min) to increase ionic conductivity and crystallinity.

**Scanning electron microscopy and energy-dispersive X-ray spectroscopy**

Sulfide-based coatings were cross-sectioned by an automated Ar ion polishing system (PECS 2, Gatan) and transferred under vacuum into a Zeiss Merlin scanning electron microscope using an air tight transfer device. Images were taken by the Everhart Thornley and in lens secondary electron detectors. EDX was carried out by an Oxford Instruments X-Max 150 silicon drift detector, and analysis was conducted in AZtec software. The SEM analysis of dry composite cathodes was performed at an accelerating voltage of 3 kV to preserve the delicate features of the microstructure that are beam sensitive. In addition, composite cathodes were coated with approximately 4 nm of platinum with a Leica EM ACE200 coating system in order to avoid charging on the surface and to improve image resolution.

**Electrochemical measurements**

EIS was performed in a Gamry Instruments Interface-1000 potentiostat using a voltage amplitude of 10 mV in the frequency range from 1.6 MHz to 0.1 Hz at stack pressure up to 500 MPa. IPA/LPSCI and EA/LPSCI coatings for EIS were sprayed on 5-mm-diameter steel discs. A sulfide SE pellet for EIS was made of 25 mg powder uniaxially pressed in a PEEK mold (5 mm diameter) at room temperature and 500 MPa. Galvanostatic cycling was performed at a constant current (0.1 mA cm⁻² to 0.8 mA cm⁻²) between 4.3 V and 2.5 V at 30°C, 60°C, and 80°C.

**X-ray diffraction**

XRD measurements were carried out in a Rigaku MiniFlex with Cu Kα₁ radiation inside an Ar-filled glovebox. Patterns were collected from 10° to 70° in 2θ using a step size of 0.01° at room temperature. Characteristic XRD peaks were identified and named by the Materials Project database(53; LPSCI (mp-985592), LiCl (mp-22905), and stainless steel (mp-13, mp-150).

**Cell assembly**

Cells were assembled and cycled in a custom-designed device described in detail in an earlier study.27 All electrochemical tests used a sulfide solid separator of ~0.7 mm and had a diameter of 5 mm. Sprayed cathodes and Ag-C coatings...
were cut from the sprayed sheet using a hollow punch. The manufacture of dry composite electrodes involved two main processes of first powder mixing and then powder consolidation. The cathode mixture was made by mixing sulfide SE, single crystal NMC, and carbon nanofibers in a 40-ml zirconia grinding bowl containing 55 g of 5-mm-diameter zirconia balls in a planetary mill (Fritsch Pulverisette 7) at 140 rpm for 30 min. PTFE (Sigma-Aldrich) was suspended and mixed for another 15 min to give a binder:electrode ratio of 1:99 by weight. Typically, 4 mg of the PTFE cathode powder mixture was then consolidated in a 5-mm WC die-set (Maassen 54KB500M-H) at 250 MPa and subsequently expelled to obtain a free-standing electrode. A sulfide SE pellet made of typically 25 mg powder was pressed in a PEEK mold (5 mm diameter) at 250 MPa. Subsequently, depending on the cell stack, a composite cathode and Ag-C layer were added and uniaxially pressed against LPSCI powder at 500 MPa.

Roughness and relative density

The surface roughness and relative density of as-sprayed and densified coatings as well as a LPSCI pellet were estimated from cross-sectional SEM images shown in Figure S1. Each cross-section was prepared by an Ar-ion etching tool to create a smooth cross-sectional surface. Using a gray-level threshold in ImageJ, the surface roughness was extracted as a function of the length l of the total height of the roughness R was measured as the distance between the minimum and maximum value, while the average roughness R was calculated by

$$R_a = \frac{1}{l} \int_0^l |y|dx$$

Relative densities were estimated in a similar manner using a gray-level threshold to isolate pores in the images.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.device.2024.100468.

ACKNOWLEDGMENTS

The authors are thankful for the financial support of Faraday Institution project award SOLBAT (FIRG022 and FIRG056) and the Henry Royce Institute through the UK Engineering and Physical Science Research Council (EP/R010145) for capital equipment. We are grateful to the David Cockayne Center for Electron Microscopy.

AUTHOR CONTRIBUTIONS

C.D. contributed to all aspects of the research. M.M. helped with spraying, annealing of coatings, EIS, and cell cycling. C.D. and M.M. carried out cross-sectional etching and SEM of sprayed coatings. C.D. performed and analyzed XRD experiments. G.M. carried out SEM/EDX measurements of the dry-processed cathode. D.S.-J. carried out SEM/EDX measurements of the pristine and cycled anode-free layer, supervised by P.G.B. All authors contributed to data analysis and discussion. C.D. wrote the paper. M.M., G.M., J.B., and P.S.G. revised and amended the paper. The project was supervised by M.P. and P.S.G.

DECLARATION OF INTERESTS

The authors declare no competing interests.

Received: February 7, 2024
Revised: February 9, 2024
Accepted: July 1, 2024
Published: July 24, 2024

REFERENCES


