

Manufacturing Scale-Up of Anodeless Solid-State Lithium Thin-Film Batteries for High Volumetric Energy Density Applications

Diyi Cheng, Khanh Tran, Shoba Rao, Zhongchun Wang, Richard van der Linde, Shahid Pirzada, Hui Yang, Alex Yan, Arvind Kamath,* and Ying Shirley Meng*



Cite This: *ACS Energy Lett.* 2023, 8, 4768–4774



Read Online

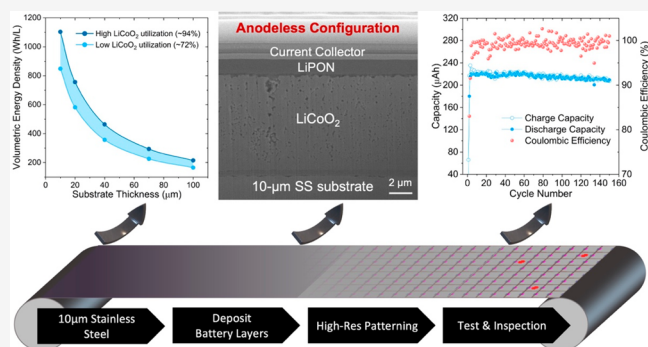
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: Compact, rechargeable batteries in the capacity range of 1–100 mAh are targeted for form-factor-constrained wearables and other high-performance electronic devices, which have core requirements including high volumetric energy density (VED), fast charging, safety, surface-mount technology (SMT) compatibility, and long cycle life. To maximize the VED, anodeless solid-state lithium thin-film batteries (TFBs) fabricated by using a roll-to-roll process on an ultrathin stainless-steel substrate (10–75 μm in thickness) have been developed. A high-device-density dry-process patterning flow defines customizable battery device dimensions while generating negligible waste. The entire fabrication operation is performed in a conventional, humidity-controlled cleanroom, eliminating the need for a costly dry-room environment and allowing for simplified, lower-cost manufacturing. Such scale-up using an anodeless architecture also enables a thermal-budget-compatible packaging and metallization scheme targeted at industry-compatible SMT processes. Further manufacturability improvements, such as the use of high-speed tests, add to the overall range of elements necessary for mass production.



Lithium battery technology has undergone rapid development in the past decades since the discovery of layered oxide cathode materials in the 1970s, and now lithium batteries serve as power sources for various applications ranging from portable devices to electric vehicles and stationary energy storage systems.^{1–3} In the present lithium battery catalogue, all-solid-state batteries (ASSBs) provide improved safety and energy density over their liquid-electrolyte-containing counterparts, and therefore they have garnered increased attention and research efforts in the past years.^{4,5} Sharing a similar formulation concept, a solid-state lithium thin-film battery (TFB) is one type of ASSBs that utilizes a solid-state electrolyte and active electrode thin films produced via vacuum deposition techniques such as sputtering, atomic layer deposition, etc. TFBs were pioneered by Oak Ridge National Laboratory in 1992,^{6,7} where J. B. Bates et al. produced a thin-film solid-state electrolyte (SSE) named lithium phosphorus oxynitride (LiPON) by substituting 5–8% of the O with N in Li₃PO₄ via radio frequency (RF) sputtering in a nitrogen atmosphere.⁶

LiPON then rapidly drew research attention in the ASSB field. TFBs typically consist of a layered architecture with well-

defined interface cell geometry, which serves as an ideal platform for fundamental research on interfaces and electrochemical behaviors within the system;^{8,9} More importantly, LiPON exhibits exemplary cyclability with a vast choice of electrode materials, i.e., LiCoO₂,¹⁰ LiMn₂O₄,¹⁰ Li-Ni_{0.5}Mn_{1.5}O₄,¹¹ Li₄Ti₅O₁₂,¹² Si,^{13,14} and Li metal,^{10–12} etc. TFBs employing lithium phosphorus oxynitride (LiPON) as solid electrolyte have demonstrated remarkable high-voltage compatibility (up to 5 V) and high capacity retention over thousands of cycles with low rates of self-discharge.^{11,15}

Given the promise of LiPON materials in battery applications, many people sensed the opportunity to commercialize LiPON-based TFBs. Right after the birth of LiPON, the first TFB patent was issued in 1994, and the TFB

Received: September 1, 2023

Revised: October 11, 2023

Accepted: October 12, 2023

Published: October 20, 2023



was commercially licensed.¹⁶ In the following years, several others joined the effort to commercialize LiPON.^{17,18} Although the market has seen promising LiPON-based products during the rapid-development time frame, the products remain confined to niche applications.^{19,20} Key limitations include the thin nature of the cathode material in TFBs and the single-layer cell configuration, which limit the energy stored in such devices to mainly small-capacity applications. In addition, the small-area form factors primarily use thick, rigid substrates (e.g., silicon or glass) that largely limit the versatility and VED of the resulting cells.

Although the market has seen promising lithium phosphorus oxynitride-based products during the rapid-development time frame, the products remain confined to niche applications.

Meanwhile, other research efforts have attempted to increase the yield of LiPON synthesis in order to make it compatible with bulk-scale ASSBs. Muñoz et al. obtained LiPON glass via ammonolysis in a tube furnace after heat treatment from 600 to 750 °C. However, the ionic conductivity of LiPON glass was lower by 2–4 orders of magnitude compared with its thin-film analogue.²¹ Alternative methods such as plasma-torch-assisted synthesis²² and ball-milling²³ were able to produce LiPON in large batches, but these processes also suffer from issues like high interfacial impedance between particles and altered LiPON properties.

Fresh attention was placed on LiPON with the comeback of Li metal anodes in the battery field around the late 2010s.^{24–32} Considering the superior electrochemical stability of LiPON against Li metal anodes shown by Dudney et al. in 2015,¹¹ LiPON has great potential for use in Li metal batteries as either a SSE or a protective coating layer. Fresh insights gained on the interfacial chemistry between Li metal and LiPON also shed light on interface engineering in bulk Li metal batteries.^{9,33,34} LiPON-based TFBs gained popularity with an

Compact electrochemical energy storage components that can be integrated to power an electronic system for the life of the device are increasingly needed at the commercial scale.

anodeless configuration that could largely increase the cell energy density.

Concurrently, the miniaturization of electronics has been a trending direction due to the advancements in wearable, hearable, and implantable technologies. Compact electrochemical energy storage components that can be integrated to power an electronic system for the life of the device are increasingly needed at the commercial scale.³⁵ LiPON-based TFBs present a solution, as they offer significantly higher energy density and provide form factor flexibility due to their modifiable cell dimensions. However, the current TFB market requires technology and manufacturing breakthroughs on a large scale to meet a higher volumetric energy density (VED). Most commercial batteries using thin-film technology have been restricted to low capacity, low VED niche applications primarily due to substrate choice. Common substrate materials for TFB fabrication include alumina, silicon, sapphire, mica, etc., which are typically thick, rigid, electrically insulating, brittle, and expensive. These features lead to low VED and a limited area form factor that limits such TFBs to niche applications with capacities in the range around 250 μAh , unsuitable for mAh-class applications.

Figure 1A plots the VED of TFBs with various cell configurations and materials. (Detailed parameters used for calculations are listed in Table S1.) In the depicted three cases, lithium metal serves as the anode material since it provides the highest capacity and high cell voltage; LiPON serves as the solid-state electrolyte, for its excellent stability and cyclability against varying electrode materials; and lithium cobalt oxide (LiCoO₂) is chosen as the cathode material because of its fairly high electrode potential against the Li anode, high capacity,

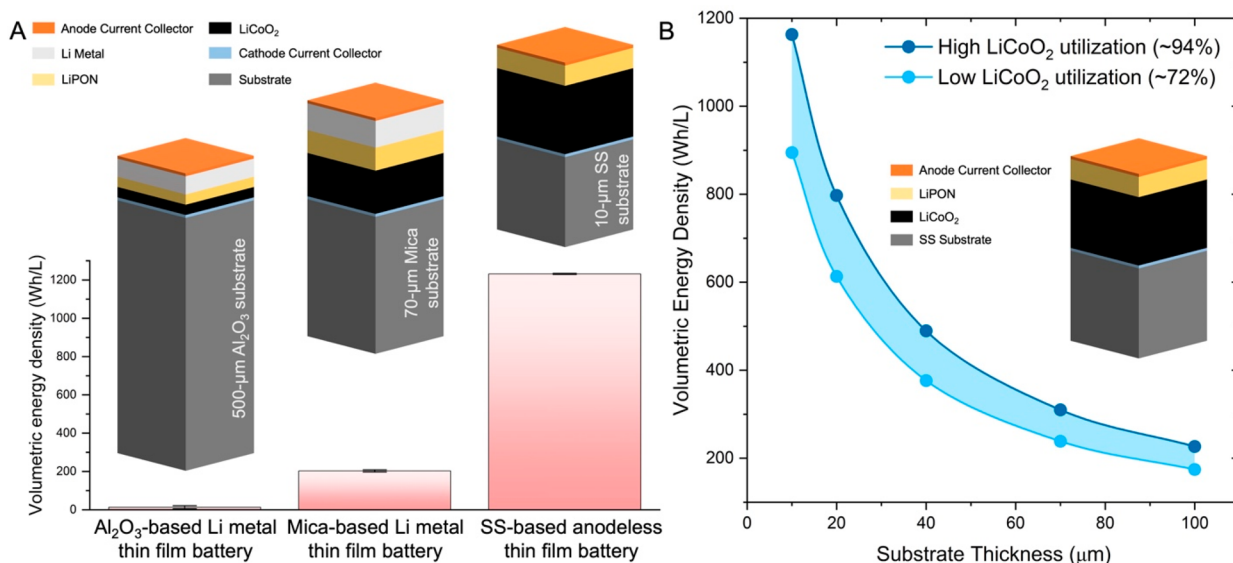


Figure 1. (A) Schematics of Li metal thin-film batteries with different cell architectures and corresponding VEDs. (B) VEDs of SS-based anodeless thin-film battery with varying SS thicknesses.

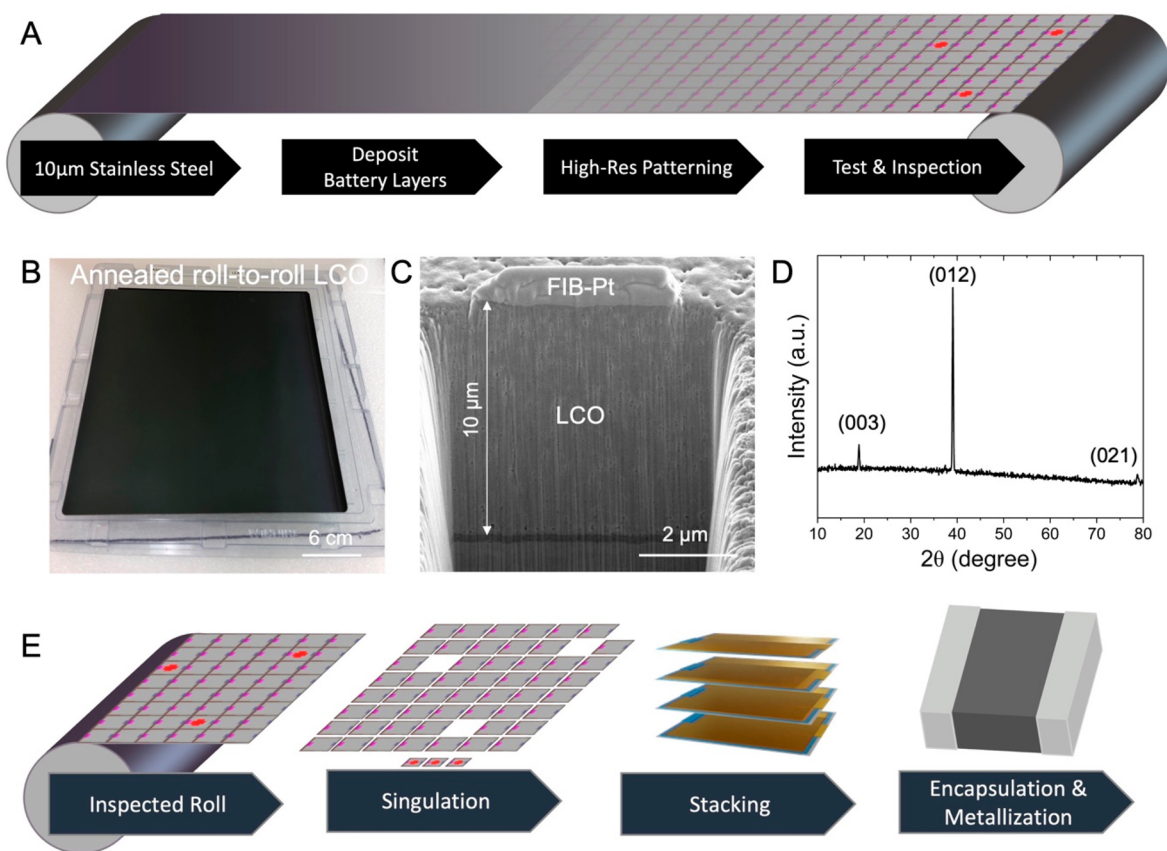


Figure 2. (A) Schematic of the high-throughput roll-to-roll deposition. (B) Photo of an annealed roll-to-roll LCO sheet. (C) Cross-sectional FIB/SEM image of an annealed roll-to-roll LCO. (D) XRD result collected on a LCO sheet. (E) Schematic of the dry-process manufacturing flow.

and good cycling stability. For lab-scale development, the LiCoO_2 thickness is usually targeted around $4 \mu\text{m}$ and a common material such as alumina (Al_2O_3) is used as the substrate, which combined give a relatively low VED due to the low cathode loading and high substrate volume.¹⁵ In some commercially available TFB products, the cathode thickness is targeted at $7\text{--}10 \mu\text{m}$.³⁶ Nevertheless, due to the use of mica-based substrate that is over tens of micrometers thick, the cell's VED is limited to below 200 Wh/L , not to mention the additional wasted volume on packaging materials. To boost the VED significantly, two approaches are key.

The first is to employ an anodeless configuration, where a Li metal anode is not deposited during cell fabrication but instead formed in situ during the first charge cycle. Several merits come with this approach. No Li metal deposition is needed during manufacturing, which simplifies the manufacturing environment and process flow, avoiding potential air exposure during subsequent operations. The absence of a Li metal anode enables a reflow soldering process while attaching onto printed circuit boards (PCBs), as the typical temperature of reflow soldering ($235 \text{ }^\circ\text{C}$) would otherwise lead to Li metal melting.³⁵ As there is no extra lithium source, anodeless TFBs do not have the concern of over discharging during battery operation that can cause irreversible cathode material degradation.¹⁵

The second key for boosting the VED is to use an ultrathin substrate and reduce the packaging material volume to minimize the inactive volumetric component at the product level. Note that a high utilization of thin-film cathode capacity requires high-temperature annealing of the cathode during or

post deposition.³⁷ Therefore, a thin, high-temperature-compatible, and low-cost substrate is needed, such as stainless steel (SS). As such, the third cell configuration in Figure 1A employs an anodeless design on a thin SS substrate ($10 \mu\text{m}$ thick), which can yield an unpackaged VED up to 1232 Wh/L when a $10\text{-}\mu\text{m}$ -thick LiCoO_2 is used. Thin SS substrate is not only crucial for improving the VED but also has merits for manufacturing, as it is electrically conductive, flexible, and less costly than the substrates typically used for TFB manufacture. Figure 1B further demonstrates the impact of substrate thickness on the VED of TFBs. As SS substrate thickness increases from 10 to $100 \mu\text{m}$, the corresponding VED drops from 1163 to 227 Wh/L when the cathode utilization is around 94% , emphasizing the importance of using thin substrates with high cathode utilization efficiency.

As such, we demonstrate a successful employment of the anodeless configuration in a TFB where a thin SS substrate is used. The combination of thick LCO cathode ($10 \mu\text{m}$ in thickness) and thin substrate is able to deliver a much-improved VED. Beyond the battery performance, a roll-to-roll deposition strategy and single-step patterning process are applied which greatly increase the manufacturability on thin substrates. The operation is performed in a standard clean room under normal humidity control without any wet chemical used or generated, further reducing the production cost while minimizing waste and environmental impact. Subsequent high-speed parallel cell parametric electrical measurement is employed to quantify the battery's characteristics prior to subsequent cell stacking operations. Such

products have great potential for market applications in the Internet of Things (IoT), hearables, and wearables, where the need for battery capacity is in the range of 1–100 mAh but is form-factor and space constrained.

In typical TFB fabrication, as most of the substrates are made of rigid, thick materials, a roll-to-roll manufacturing process is not feasible. For ultrathin and flexible substrates, a manufacturing flow was developed, as depicted in Figure 2. Figure 2A shows the general procedure for efficient TFB manufacturing. After deposition, high-resolution patterning is applied to define and isolate the individual cells from each other for subsequent battery parametric measurements and inspection. With deposition and annealing parameters well-tuned, this roll-to-roll process produces a high-quality LCO cathode, as shown in Figure 2B. Cross-section examination by focused ion beam scanning electron microscopy (FIB/SEM) in Figure 2C illustrates a dense 10- μm -thick LCO cathode film with a minimal number of voids observed. The LCO cathode film further manifests a preferred (012) crystal orientation based on X-ray diffraction (XRD) results in Figure 2D, which facilitates lithium-ion transport, especially when a thick LCO cathode is utilized. Figure 2E shows the subsequent workflow after the impedance inspection, where cells are singulated from the sheet and go through a stacking process, including encapsulation and metallization, to form the final product. Owing to the anodeless nature of such TFBs, cell handling after singulation takes place in a normal cleanroom environment, with no dry room needed, which further brings down the production cost.

The schematic in Figure 3A illustrates the high-resolution patterning process required for high-throughput production.

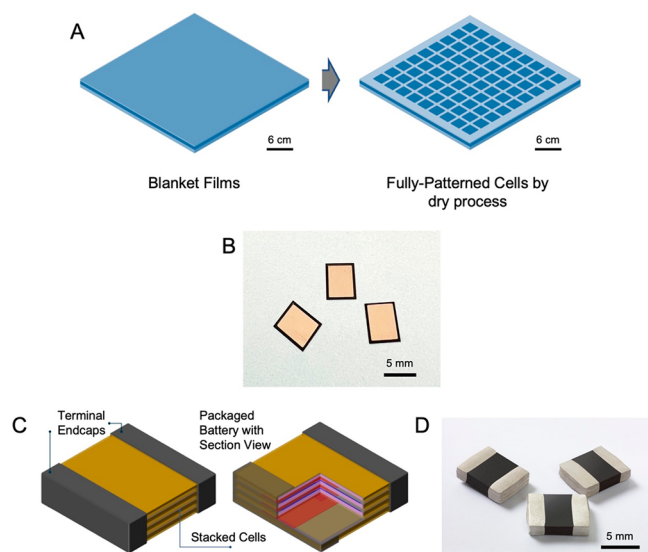


Figure 3. (A) Schematic of the dry-process cell patterning and singulation. (B) Photo of the singulated cells. (C) Schematic of the stacked cells with a cross-sectional view. (D) Photo of the stacked cells.

The battery sheet after deposition is patterned, resulting in the electrical isolation of each cell with defined dimensions. Unlike previously reported procedures where wet acidic and basic chemicals are typically used for patterning,³⁵ the patterning process developed in this work is performed under dry conditions. Figure 3B displays a photo of singulated patterned

cells. The cells show uniform dimensions, as targeted by the patterning process. Based on the dimensional footprint requirements, such a patterning process can accurately tune the form factors of the final product. The single-cell units are assembled to build stacked multilayers, as shown in Figure 3C. Stacked cells connected in parallel share the same pair of terminals for electrochemical cycling while remaining isolated from each other by insulating packaging films between the layers. Such a packaging process is the enabler for producing stacked cells (Figure 3D) with various capacity ranges to meet different application needs. Due to the adjustable dimensions of the single-cell base unit, the stacked cell can fit in a variety of product dimensions, as required.

Along with the mass production of singulated cells, a production-grade electrochemical test methodology is needed for high-speed parallel-site testing. A customized roll-to-roll-compatible test setup is used to perform electrochemical measurements, including open-circuit voltage (OCV), electrochemical impedance spectroscopy (EIS), etc., at the sheet level. After measurement, the OCV or impedance values are extracted and plotted in accordance with the physical location of individual cells to form a heat map, as the OCV mapping illustrates in Figure 4A. Based on the OCV and impedance values, single cells are binned (similar to semiconductor testing) in order to predict battery performance and quality. Figure 4B displays a typical EIS curve of a single cell, showing a low cell impedance. The singulated cell can then be transferred to a battery cycler for electrochemical sample testing. Figure 4C demonstrates the cycling performance of a singulated cell. The highest areal capacity from the LCO thin-film cathode is ~ 0.69 mAh/cm² in theory when 10- μm -thick LCO is used. In practical cells the cathode utilization is around 80–95%, which corresponds to an areal capacity of 0.55–0.66 mAh/cm². The capacity retention reaches approximately 95% after 150 cycles. As shown in Figure 4D, the singulated and multilayer stacks are cycled with an industry-compatible potentiostatic charging and a galvanostatic discharging step. By multilayer stacking, the accessible discharge capacity achieves mAh with all the layers connected in parallel and functional. The test methodology classifies the quality of singulated cells in large batches with EIS-based process control.

In summary, a manufacturing process flow that incorporates roll-to-roll production on ultrathin stainless steel in dry-process manufacturing is demonstrated with an anodeless cell architecture. Customized form factors with ultrathin packaging deliver industry-leading electrochemical performance and VED for space-constrained product formats. Methodologies such as high-throughput patterning, high-speed electrochemical testing, and multilayer stacked packaging are critical toward commercializing high-VED TFBs with considerably flexible form factors and long cycle life.

Methodologies such as high-throughput patterning, high-speed electrochemical testing, and multilayer stacked packaging are critical toward commercializing high volumetric energy density thin-film batteries with considerably flexible form factors and long cycle life.

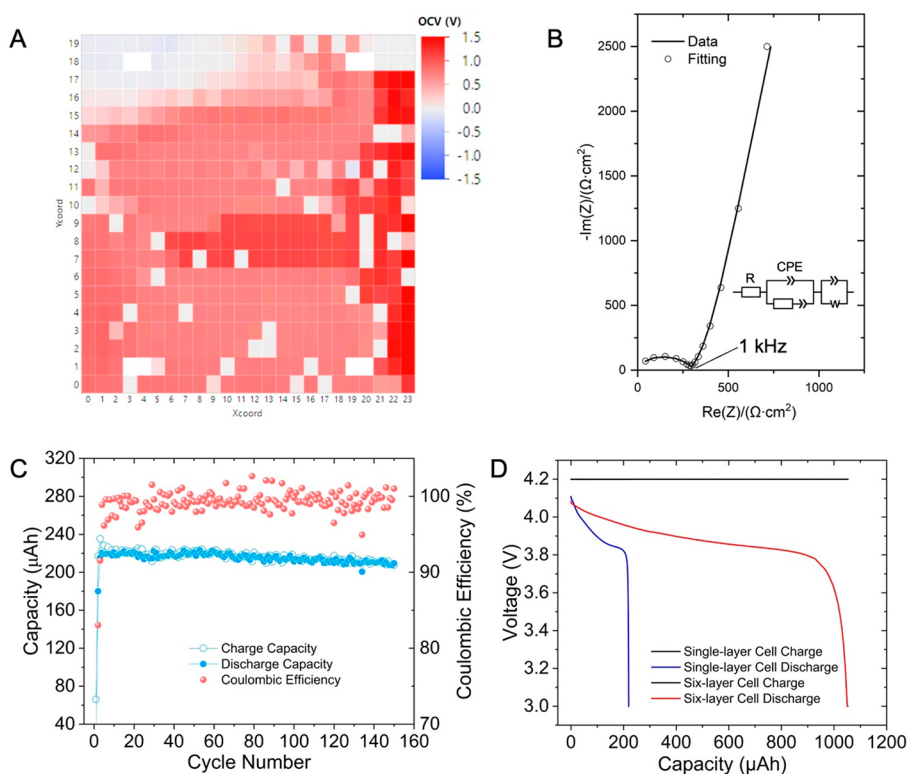


Figure 4. (A) Open-circuit-voltage heat map generated based on high-throughput electrochemical measurement. (B) EIS plot of a full cell showing the low cell impedance. (C) Cycling performance of an anodeless full cell. (D) Voltage curves of the single-layer cell and multilayer mAh-class cell.

To this end, several aspects can be considered for future development of high-VED TFBS. First, as VED is expected to see a large increase with thinner substrates, exploring new options of suitable substrates and reduced substrate thicknesses offers potential ways to further boost the VED of TFBS, in addition to reducing the thickness of inactive packaging materials. The second aspect is to produce TFBS with higher cell capacity by increasing the cathode thickness and using higher-capacity cathode materials, both of which are challenging, especially when the cycle life needs to be on par with the currently available 10- μm -thick LCO cathode. The third aspect pertains to the continual improvement of the long-term cyclability of anodeless TFBS, which could suffer issues such as void formation between the current collector and LiPON, mechanical inelastic deformation of the current collector during repeated cycling, etc. These issues call for solutions that could incorporate seeding layers at the current collector/electrolyte interface and the use of innovative stress engineering when packaging the stack.

The use of flexible 10- μm -thick stainless-steel substrates offers tremendous new options to product designers in the form of curved and bendable shapes that are mechanically robust. As this technology combines microelectronics manufacturing with battery chemistry, the needs for higher throughput deposition techniques, low defectivity of source materials, high-speed inspection, and test methodology grant rich opportunities for industry and academia to collaborate and enable entirely new generations of end products.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsenerylett.3c01839>.

Table S1, giving detailed parameters used for the volumetric energy density calculations of thin-film batteries with different cell configuration and materials (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Arvind Kamath – Ensurge Micropower, San Jose, California 95134, United States; Email: arvind.kamath@ensurge.com

Ying Shirley Meng – Materials Science and Engineering Program, University of California San Diego, La Jolla, California 92093, United States; Pritzker School of Molecular Engineering, University of Chicago, Chicago, Illinois 60637, United States; orcid.org/0000-0001-8936-8845; Email: shirleymeng@uchicago.edu

Authors

Diyi Cheng – Materials Science and Engineering Program, University of California San Diego, La Jolla, California 92093, United States; orcid.org/0000-0003-1616-9209

Khanh Tran – Ensurge Micropower, San Jose, California 95134, United States

Shoba Rao – Ensurge Micropower, San Jose, California 95134, United States

Zhongchun Wang – Ensurge Micropower, San Jose, California 95134, United States

Richard van der Linde – Ensurge Micropower, San Jose, California 95134, United States

Shahid Pirzada – *Ensurge Micropower, San Jose, California 95134, United States*
Hui Yang – *Ensurge Micropower, San Jose, California 95134, United States*
Alex Yan – *Ensurge Micropower, San Jose, California 95134, United States*

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acseenergylett.3c01839>

Author Contributions

D.C., A.K., and Y.S.M. initiated the manuscript preparation. K.T., S.R., Z.W., R.v.d.L., S.P., H.Y., A.Y., and A.K. conceived the cell architecture, optimized the processing parameters, and performed electrochemical testing at Ensurge Micropower. D.C., A.K., and Y.S.M. co-wrote the manuscript. All the authors participated in the results discussion and commented on the manuscript.

Notes

The authors declare the following competing financial interest(s): Y.S.M. is a member of the technical advisory board for Ensurge Micropower.

Biographies

Diyi Cheng received his Ph.D. in Materials Science and Engineering at University of California San Diego and is currently a postdoctoral researcher at Lawrence Berkeley National Laboratory. His research interests include lithium metal thin-film batteries, advanced electron microscopy, solid–solid interfaces, metal nucleation and in situ characterizations.

Khanh Tran is a technologist in the fields of semiconductor, battery, and photonics. He holds an M.S. in Electrical Engineering from Stanford University.

Shoba Rao received her M.S. in Electrical Engineering from Stanford University. She currently serves as Sr. Director of Manufacturing and Test Engineering at Ensurge Micropower.

Zhongchun Wang received his Ph.D. in Materials Science and Engineering from Shanghai Institute of Ceramics, Chinese Academy of Sciences in China. Currently he works as principal battery engineer at Ensurge Micropower.

Richard van der Linde received his B.S. in Electrical Engineering at Colorado State University, Fort Collins. Currently he serves as the Senior Director of Product Engineering at Ensurge Micropower.

Shahid Pirzada received his Ph.D. in Metallurgical Engineering from University of Idaho, Moscow. Currently he is with Ensurge Micropower.

Hui Yang received her Ph.D. in Chemistry from the Institute of Chemistry, Chinese Academy of Science. Her research focuses on the fundamental understandings of electrochemical reaction mechanisms and developing materials to enable high-energy-density solid-state batteries. Currently she is a staff engineer in Technology Development at Ensurge Micropower.

Alex Yan received his Ph.D. in Applied Physics from Eindhoven University of Technology, The Netherlands. Currently he focuses on developing solid state batteries at Ensurge Micropower.

Arvind Kamath received his Ph.D. in Materials Science and Engineering from the microelectronics program at The University of Texas, Austin. Currently he serves as EVP in Technology Development at Ensurge Micropower.

Ying Shirley Meng is a Professor at the Pritzker School of Molecular Engineering at University of Chicago. Her research focuses primarily

on energy storage materials and systems, including rechargeable batteries for electric vehicles, power sources for Internet of Things, as well as grid-scale storage for deep renewable energy penetration.

ACKNOWLEDGMENTS

D.C. is grateful for the internship training and funding support during that period by Ensurge Micropower. Y.S.M. gratefully acknowledges the partial funding support for the interface characterization via cryogenic electron microscopy from the U.S. Department of Energy, Office of Basic Energy Sciences, under Award Number DE-SC0002357.

REFERENCES

- (1) Rao, G. V. S.; Tsang, J. C. Electrolysis method of intercalation of layered transition metal dichalcogenides. *Mater. Res. Bull.* **1974**, *9*, 921–926.
- (2) Goodenough, J. B.; Mizushima, K.; Wiseman, P. J. (UK Atomic Energy Authority). Electrochemical cell and method of making ion conductors for said cell. EP0017400B1, 1976.
- (3) Xu, K. Electrolytes and interphases in Li-ion batteries and beyond. *Chem. Rev.* **2014**, *114*, 11503–11618.
- (4) Tan, D. H. S.; Banerjee, A.; Chen, Z.; Meng, Y. S. From nanoscale interface characterization to sustainable energy storage using all-solid-state batteries. *Nat. Nanotechnol.* **2020**, *15*, 170–180.
- (5) Banerjee, A.; Wang, X.; Fang, C.; Wu, E. A.; Meng, Y. S. Interfaces and Interphases in All-Solid-State Batteries with Inorganic Solid Electrolytes. *Chem. Rev.* **2020**, *120*, 6878–6933.
- (6) Bates, J. B.; Dudney, N. J.; Gruzalski, G. R.; Zuhr, R. A.; Choudhury, A.; Luck, C. F.; Robertson, J. D. Electrical properties of amorphous lithium electrolyte thin films. *Solid State Ionics* **1992**, *53–56*, 647–654.
- (7) Bates, J. B.; Dudney, N. J.; Gruzalski, G. R.; Zuhr, R. A.; Choudhury, A.; Luck, C. F.; Robertson, J. D. Fabrication and characterization of amorphous lithium electrolyte thin films and rechargeable thin-film batteries. *J. Power Sources* **1993**, *43*, 103–110.
- (8) Wang, Z.; Santhanagopalan, D.; Zhang, W.; Wang, F.; Xin, H. L.; He, K.; Li, J.; Dudney, N.; Meng, Y. S. In situ STEM-EELS observation of nanoscale interfacial phenomena in all-solid-state batteries. *Nano Lett.* **2016**, *16*, 3760–3767.
- (9) Cheng, D.; Wynn, T. A.; Wang, X.; Wang, S.; Zhang, M.; Shimizu, R.; Bai, S.; Nguyen, H.; Fang, C.; Kim, M.; et al. Unveiling the Stable Nature of the Solid Electrolyte Interphase between Lithium Metal and Lipon Via Cryogenic Electron Microscopy. *Joule* **2020**, *4*, 2484–2500.
- (10) Dudney, N. J. Solid-state thin-film rechargeable batteries. *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.* **2005**, *116*, 245–249.
- (11) Li, J.; Ma, C.; Chi, M.; Liang, C.; Dudney, N. J. Solid electrolyte: The key for high-voltage lithium batteries. *Adv. Energy Mater.* **2015**, *5* (4), 1401408.
- (12) Put, B.; Mees, M. J.; Hornsved, N.; Hollevoet, S.; Sepúlveda, A.; Vereecken, P. M.; Kessels, W. M. M.; Creatore, M. Plasma-Assisted ALD of LiPO(N) for Solid State Batteries. *J. Electrochem. Soc.* **2019**, *166*, A1239–A1242.
- (13) Li, J.; Dudney, N. J.; Nanda, J.; Liang, C. Artificial solid electrolyte interphase to address the electrochemical degradation of silicon electrodes. *ACS Appl. Mater. Interfaces* **2014**, *6*, 10083–10088.
- (14) Santhanagopalan, D.; Qian, D.; McGilvray, T.; Wang, Z.; Wang, F.; Camino, F.; Graetz, J.; Dudney, N.; Meng, Y. S. Interface limited lithium transport in solid-state batteries. *J. Phys. Chem. Lett.* **2014**, *5*, 298–303.
- (15) Neudecker, B. J.; Dudney, N. J.; Bates, J. B. Lithium-Free[®] Thin-Film Battery with In Situ Plated Li Anode. *J. Electrochem. Soc.* **2000**, *147*, 517.
- (16) Bates, J. B.; Dudney, N. J.; Gruzalski, G. R.; Luck, C. F. Thin Film Battery And Method For Making Same. U.S. Patent US 5,338,6, Aug 16, 1994.

- (17) STMicroelectronics, EnFilm™ - rechargeable solid state lithium thin film battery, EFL700A39 Datasheet, June 2014. <https://www.st.com/en/power-management/efl700a39.html>
- (18) Bhardwaj, R. C. Charging techniques for solid-state batteries in portable electronic devices. U.S. Patent US 9,553,4, Jan 24, 2017.
- (19) DigiKey. EFL700A39 EnFilm™ Rechargeable Battery, Jan 13, 2016. <https://www.digikey.com/en/product-highlight/s/stmicroelectronics/efl700a39-enfilm-rechargeable-battery> (accessed Aug 14, 2023).
- (20) Cymbet Corp. EnerChip™ CBC012 Solid State Energy Storage, DS-72-02 Rev C. <https://www.mouser.com/datasheet/2/99/DS-72-02-4421.pdf> (accessed Aug 14, 2023).
- (21) Muñoz, F.; Durán, A.; Pascual, L.; Montagne, L.; Revel, B.; Rodrigues, A. C. M. Increased electrical conductivity of LiPON glasses produced by ammonolysis. *Solid State Ionics* **2008**, *179*, 574–579.
- (22) Westover, A. S.; Kercher, A. K.; Kornbluth, M.; Naguib, M.; Palmer, M. J.; Cullen, D. A.; Dudney, N. J. Plasma Synthesis of Spherical Crystalline and Amorphous Electrolyte Nanopowders for Solid-State Batteries. *ACS Appl. Mater. Interfaces* **2020**, *12*, 11570–11578.
- (23) López-Aranguren, P.; Reynaud, M.; Gluchowski, P.; Bustinza, A.; Galceran, M.; López del Amo, J. M.; Armand, M.; Casas-Cabanas, M. Crystalline LiPON as a Bulk-Type Solid Electrolyte. *ACS Energy Lett.* **2021**, *6*, 445–450.
- (24) Tikekar, M. D.; Choudhury, S.; Tu, Z.; Archer, L. A. Design principles for electrolytes and interfaces for stable lithium-metal batteries. *Nat. Energy* **2016**, *1*, 16114.
- (25) Lin, D.; Liu, Y.; Cui, Y. Reviving the lithium metal anode for high-energy batteries. *Nat. Nanotechnol.* **2017**, *12*, 194–206.
- (26) Han, X.; Gong, Y.; Fu, K.; He, X.; Hitz, G. T.; Dai, J.; Pearse, A.; Liu, B.; Wang, H.; Rubloff, G.; et al. Negating interfacial impedance in garnet-based solid-state Li metal batteries. *Nat. Mater.* **2017**, *16*, 572–579.
- (27) Han, F.; Westover, A. S.; Yue, J.; Fan, X.; Wang, F.; Chi, M.; Leonard, D. N.; Dudney, N. J.; Wang, H.; Wang, C. High electronic conductivity as the origin of lithium dendrite formation within solid electrolytes. *Nat. Energy* **2019**, *4*, 187.
- (28) Yan, K.; Lu, Z.; Lee, H. W.; Xiong, F.; Hsu, P. C.; Li, Y.; Zhao, J.; Chu, S.; Cui, Y. Selective deposition and stable encapsulation of lithium through heterogeneous seeded growth. *Nat. Energy* **2016**, *1*, 16010.
- (29) Liu, J.; Bao, Z.; Cui, Y.; Dufek, E. J.; Goodenough, J. B.; Khalifah, P.; Li, Q.; Liaw, B. Y.; Liu, P.; Manthiram, A.; et al. Pathways for practical high-energy long-cycling lithium metal batteries. *Nat. Energy* **2019**, *4*, 180–186.
- (30) Zachman, M. J.; Tu, Z.; Choudhury, S.; Archer, L. A.; Kourkoutis, L. F. Cryo-STEM mapping of solid-liquid interfaces and dendrites in lithium-metal batteries. *Nature* **2018**, *560*, 345–349.
- (31) Li, Y.; Li, Y.; Pei, A.; Yan, K.; Sun, Y.; Wu, C. L.; Joubert, L. M.; Chin, R.; Koh, A. L.; Yu, Y.; et al. Atomic structure of sensitive battery materials and interfaces revealed by cryo-electron microscopy. *Science* (80-). **2017**, *358*, 506–510.
- (32) Fang, C.; Li, J.; Zhang, M.; Zhang, Y.; Yang, F.; Lee, J. Z.; Lee, M.-H.; Alvarado, J.; Schroeder, M. A.; Yang, Y.; et al. Quantifying inactive lithium in lithium metal batteries. *Nature* **2019**, *572*, 511–515.
- (33) Hood, Z. D.; Chen, X.; Sacci, R. L.; Liu, X.; Veith, G. M.; Mo, Y.; Niu, J.; Dudney, N. J.; Chi, M. Elucidating Interfacial Stability between Lithium Metal Anode and Li Phosphorus Oxynitride via in Situ Electron Microscopy. *Nano Lett.* **2021**, *21*, 151–157.
- (34) Cheng, D.; Wynn, T.; Lu, B.; Marple, M.; Han, B.; Shimizu, R.; Sreenarayanan, B.; Bickel, J.; Hosemann, P.; Yang, Y.; et al. A free-standing lithium phosphorus oxynitride thin film electrolyte promotes uniformly dense lithium metal deposition with no external pressure. *Nat. Nanotechnol.* **2023**, DOI: 10.1038/s41565-023-01478-0.
- (35) Oukassi, S.; Salot, R.; Bazin, A.; Secouard, C.; Chevalier, I.; Poncet, S.; Poulet, S.; Boissel, J. M.; Geffraye, F.; Brun, J. Millimeter scale thin film batteries for integrated high energy density storage. *2019 IEEE International Electron Devices Meeting (IEDM 2019)*, San Francisco, CA, Dec 7–11, 2019; pp 618–621.
- (36) Wang, Z.; Lee, J. Z.; Xin, H. L.; Han, L.; Grillon, N.; Guy-Bouyssou, D.; Bouyssou, E.; Proust, M.; Meng, Y. S. Effects of cathode electrolyte interfacial (CEI) layer on long term cycling of all-solid-state thin-film batteries. *J. Power Sources* **2016**, *324*, 342–348.
- (37) Wang, B.; Bates, J. B.; Hart, F. X.; Sales, B. C.; Zuhr, R. A.; Robertson, J. D. Characterization of Thin-Film Rechargeable Lithium Batteries with Lithium Cobalt Oxide Cathodes. *J. Electrochem. Soc.* **1996**, *143*, 3203.