

Current Insight into 3D Printing in Solid-State Lithium-Ion Batteries: A Perspective

Srikanth Ponnada,^[a] Demudu Babu Gorle,^[b] Rapaka S Chandra Bose,^[c] Maryam Sadat Kiai,^[d] Meghali Devi,^[e] Chikkili Venkateswara Raju,^[f] Nilgun Baydogan,^[g] Karuna Kar Nanda,^[b, h] Frank Marken,^[i] and Rakesh K Sharma^{*[a]}

Compared to the state-of-art lithium-ion batteries, the all-solid-state batteries offer improved safety along with high energy and power density. Although considerable research has been conducted, the inherent problems arising from solid electrolytes and the lack of suitable electrolytes hinder their development in practical applications. Furthermore, traditional synthesis routes have drawbacks due to limited control to fabricate the solid electrolytes with desired shape and size, impeding their maximum performance. In recent years, additive manufacturing or three-dimensional (3D) printing techniques have played a vital role in constructing solid-state batteries because of the rational design of functional electrode and electrolyte materials

for batteries with increased performance. 3D printing in batteries may provide a new technology solution for existing challenges and limitations in emerging electronic applications. This process boosts lithium-ion batteries by creating geometry-optimized 3D electrodes. 3D printing offers a range of advantages compared to traditional manufacturing methods, including designing and printing more active and passive components (cathodes, anodes, and electrolytes) of batteries. 3D printing offers desired thickness, shape, precise control, topological optimization of complex structure and composition, and a safe approach for preparing stable solid electrolytes, cost-effective and environmentally friendly.

Introduction

Since the dawn of the Industrial era, an inexpensive and reliable energy supply has been a critical keystone in economic growth and affluence. In recent decades, the energy supply has shifted immensely towards electricity as the primary resource for day-to-day consumption. The electrical energy storage technique can address the intermittent nature of renewable energy sources and allow long-term and seasonal energy shifting, enabling energy usage long after being produced. Rechargeable batteries are ubiquitous and offer efficient storage through electrochemical reactions. Presently, lithium-

ion batteries (LIBs) predominate the battery market and have found recognition in applications including flexible wearable devices, textiles, electric vehicles, and the internet of things (IoTs).^[1-3] 3D printing concept at a large scale is important as a perspective in its commercial development. There is no significant standardization concept about the 3D-printing technique of LIBs for large-scale commercial production. Hence, the companies are trying to derive their own standardization of (3D) printing techniques based on solid-state batteries.

The predilection towards LIBs is attributed to the high energy densities, longer lifespan, and low and falling prices. The electrodes are composed of lithium (Li) intercalation

[a] Dr. S. Ponnada, Dr. R. K Sharma
Sustainable Materials and Catalysis Research Laboratory (SMCRL)
Department of Chemistry
Indian Institute of Technology Jodhpur
Karwad, Jodhpur-342037, India
E-mail: rks@iitj.ac.in

[b] Dr. D. Babu Gorle, Dr. K. Kar Nanda
Materials Research Centre
Indian Institute of Science
Bangalore-560012, India

[c] Dr. R. S Chandra Bose
Centre for Materials for Electronics Technology
Thrisur-680581, Kerala, India

[d] Dr. M. Sadat Kiai
Nano-Science and Nano-Engineering Program, Graduate School of Science, Engineering and Technology
Istanbul Technical University
Istanbul-34469, Turkey

[e] M. Devi
Department of chemistry
National Institute of Technology
Silchar, Cachar, Assam-788010, India

[f] Dr. C. Venkateswara Raju
Research Centre for Photoenergy Harvesting & Conversion Technology (phct)
Department of Energy Materials and Engineering
Dongguk University
Seoul, 04620, Republic of Korea

[g] Dr. N. Baydogan
Energy Institute, Ayazaga Campus
Istanbul Technical University
Maslak, 34467 Istanbul-Turkey

[h] Dr. K. Kar Nanda
Institute of Physics
Bhubaneswar, Odisha-751005, India

[i] Dr. F. Marken
Department of Chemistry
University of Bath
Claverton Down, Bath BA2 7AY, UK

 © 2022 The Authors. *Batteries & Supercaps* published by Wiley-VCH GmbH.
This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

compounds and function as host structures to store electrical energy. The Li-ion shuttles between two electrodes through the electrolyte during charge and discharge cycles, causing oxidation and reduction at the electrodes. In addition to the materials utilized, cell engineering and system integration have a role in determining performance metrics such as specific power, energy density, charge-discharge rates, cycle stability, and overall safety. Although LiBs have made significant progress since their introduction to the market in 1991, several practical challenges must be overcome, especially electric vehicles (EVs).^[1] The capacity mismatch between cathode and anode in the modern LiBs impedes their progress and maximum performance. Li-rich cathodes are dominant for cathode electrodes; in particular, layered oxides are preferred because of their highest capacities ($\geq 250 \text{ mAh g}^{-1}$) and are inexpensive.^[2] However, problems arising from cathodes, such as poor kinetics and inefficient voltage fading, need to be solved. Li metal (3860 mAh g^{-1}) and graphite (372 mAh g^{-1}) have grabbed considerable research attention among the anode materials, but they endure dendrite formation and low columbic efficiency.^[4] In recent years silicon (Si) and silicon oxide (SiO_x) have been studied as anode materials and have nearly five to ten times the energy density compared to graphite.^[5] Over the years, the current collectors and polymer separators have become thinner to accommodate active electrodes with increased volume fractions. Although liquid electrolytes have shown good compatibility with existing cell designs and offer high conductivity and wetting of electrode surfaces,^[6] they suffer from poor ion selectivity, insufficient thermal and electrochemical stabilities, and are sometimes intrinsically dangerous. Solid electrolyte separators are replacing liquid electrolytes to explore new LiB's chemistry. By carefully manipulating the structure of electrodes/electrolytes, the power density and energy density can be increased, while the battery life can be extended. As a result, meeting current demands will necessitate an effective synthesis strategy and a thorough understanding of the structure-composition-property-performance relationship.

3D printing refers to the additive manufacturing technique, which involves layer-by-layer materials deposition to produce

3D shapes monitored from the computer-aided design (CAD),^[7–10] shown in Figure 1. Since its inception in the late 20th century, 3D printing has been developed into various techniques, with many unique frameworks emerging in recent years. The American Society for Testing and Materials (ASTM) categorizes 3D printing techniques into seven groups,^[11] i.e., 1) material extrusion (direct ink writing (DIW) and fused deposition modelling (FDM)); 2) material jetting (inkjet printing); 3) binder jetting; 4) powder bed fusion (selective laser sintering and selective laser melting); 5) directed energy deposition; 6) vat photopolymerization (stereolithography (SLA)); 7) sheet lamination.^[12] Figure 2 shows a few important 3D techniques. The method and the precursor materials employed define the size of 3D printed products (millimeter to beyond meter scale) and their properties (geometry, rigidity, pore size, and shape). 3D printing offers flexibility to produce diverse, complex nanostructures efficiently, fast prototyping, inexpensive, and explore structure-property relationships over a wide range of length scales.^[13,14]

To date, numerous synthesis techniques have been investigated for energy storage applications; however, 3D printing offers many benefits and opportunities comparatively.^[15–17] 3D printing technologies, such as electrodes produced from inks, 3D printed graphene electrodes, and 3D printed ceramic-polymer electrolytes, are becoming increasingly popular in the battery industry.^[18,19] Recent simulations by Trembacki et al. demonstrated that 3D battery designs outperform 2D battery designs by $3.7\times$ – $6.9\times$ at the maximum power density simulated.^[20] The advantages of 3D printing include 1) designing and preparing active and passive components (cathodes, anodes, and separators) of LiBs with desired thickness and shape, 2) precise control and topological optimization of complex structure and composition, 3) safe approach for preparing stable solid electrolytes, cost-effective, and environmentally friendly.^[15,21] For example, an all-component 3D printed LiB made of graphene oxide inks with lithium iron phosphate (LFP) cathode, lithium titanium oxide (LTO) anode, and polymer composite electrolyte was prepared by extrusion-based printing.^[22] When tested for half-cell performance, the cathode and anode displayed specific capacities nearly equal to

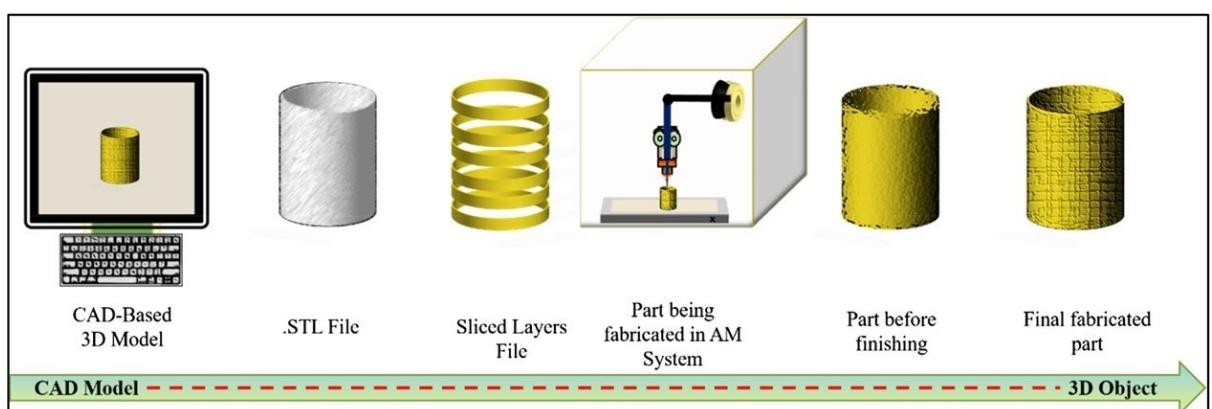


Figure 1. Overview of the process involved in the design and fabrication of 3D objects. Reproduced with permission from Ref. [10]. Copyright (2018) The Author(s). Published by Informa UK Limited.

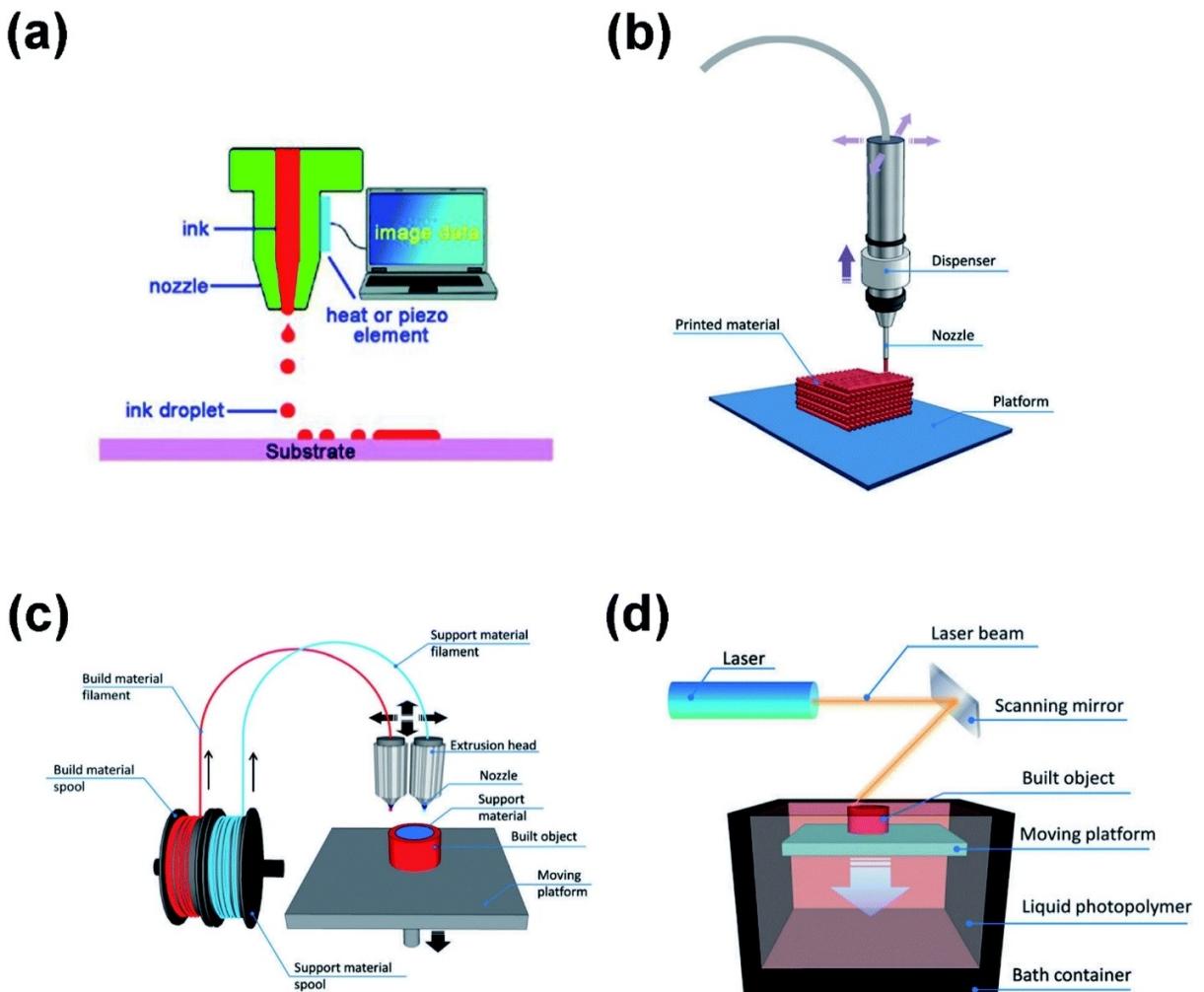


Figure 2. Scheme of a) inkjet printing, b) direct ink writing, c) fused deposition modelling and d) stereolithography. Reproduced with permission from Ref. [11]. Copyright (2021) Royal Society of Chemistry.

their theoretical capacities. In contrast, the full cell displays better initial charge and discharge capacities with good cyclic stability. Printed Li salt as a scaffold was fabricated to incorporate Li-based alloy as LiB anode material.^[23] Saturated Li salt electrolyte contributed to the solid electrolyte interphase (SEI) formation at the anode surface and maintained the structural integrity. Moreover, a dendrite-free lithium anode was obtained with ultralong cycling time, low overpotential, and good stripping and plating ability. 3D printing technology presents opportunities not limited to electrode and electrolyte materials but also enables the continuous fabrication of fully 3D-printed LiBs.

Most studies have focused on the fundamental 3D printing guidelines for preparing electrode and electrolyte materials to enhance their electrochemical performances.^[7,12,15,24–28] Although excellent reviews have been reported, no study explores the large-scale synthesis and market for 3D printing for their use in commercial applications. This review highlights the present challenges posed by electrode and electrolyte materials that hinder the high performance of LiBs and address the issues from the perspective of various 3D printing

approaches. Figure 3 shows the schematic illustration of the types of fabrication involved in LiB 3D printing.

Challenges in Li-Ion Batteries

Energy and cycle life

LiBs have enabled the constant development of electrical energy storage and superseded other rechargeable technologies.^[29] LiBs display almost zero memory effect compared to other battery chemistry, where partial charge/discharge will not cause low capacity. Due to unmatched high specific energy and energy density, they are integrated into microchips, smart textiles, electronics, and EVs and are now pervading grid storage.^[30] Energy densities are not significant for grid storage, but volumetric energy densities are frequently more important for electric vehicles and portable devices. The high energy density of LiBs is due to nonaqueous electrolytes that allow for increased operating voltages (~4 V) compared to systems that use aqueous electrolytes (<2 V). Present-day LiBs

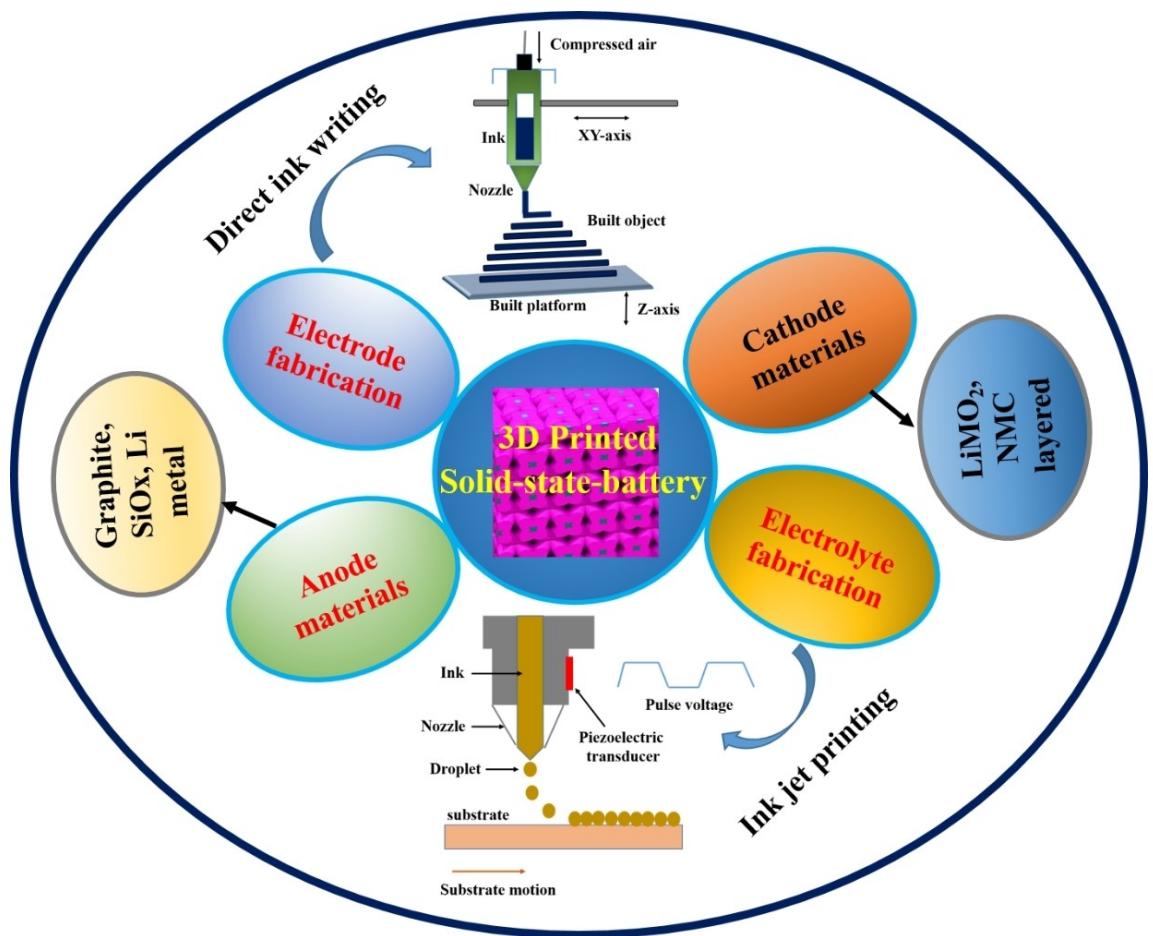


Figure 3. Schematic illustration of types of fabrication involved in 3D printed solid-state battery.

are constrained by cells with volumetric energy density ($< 650 \text{ Wh L}^{-1}$) and gravimetric energy density ($< 250 \text{ Wh kg}^{-1}$). Maximizing the energy density is achieved by increasing the cell voltage or/and charge storage capacity (Li^+ insertion/extraction into/from the electrode). Cell voltage can be increased only by increasing the operating voltage of the cathode since the anode is already operating at a voltage close to that of Li/Li^+ . In contrast, charge storage capacity can be improved by increasing the number of crystallographic sites for ion intercalation. Conversion-type reactions are more studied compared to insertion reactions because they are not limited by sites available for insertion/extraction of Li. It is also generally accepted that the weight and volume of the inactive components should be kept to a minimum to enhance energy yield. However, some inert materials or the minimal amounts of them are necessary to match the safety and performance. Besides that, it is frequently overlooked that the electrode porosity and the electrolyte inside the pores must be taken into account, as they will affect the specific energies and energy densities. Therefore, several strategies are studied to improve the energy density, such as decreasing pore size, calendaring electrodes, optimizing the electrode composition, and increasing the mass loading. A recent article presented a plot demonstrating all the improvements in specific energy

due to cell/electrode optimization and engineering advancements in materials capacity (Figure 4a).^[1] However, the rate of increment accomplished by the above methods has been decelerating in recent years. Therefore, there is huge interest in driving energy density's future improvement to $\sim 500 \text{ Wh kg}^{-1}$ and $> 1000 \text{ Wh L}^{-1}$.

Cost

LiBs are front runners in addressing the long-term goal of achieving a low carbon-free future. Although their widespread application is still comparatively narrow, potential cost reduction and enhanced performance can eventually determine their utilization. Hence cost prognosis has gained tremendous interest, and many researchers are developing new models to understand the cost change in LiBs.^[31] Over the last three decades, the cost of LiBs has dramatically declined due to improvements in manufacture scale cell and materials optimizations (Figure 4b).^[31,32] Recently, in 2020, an exhaustive analysis showed that since the first commercialization in 1991, the real cost of Li-ion cells has fallen by 97% when measured by their energy capacity.^[32]

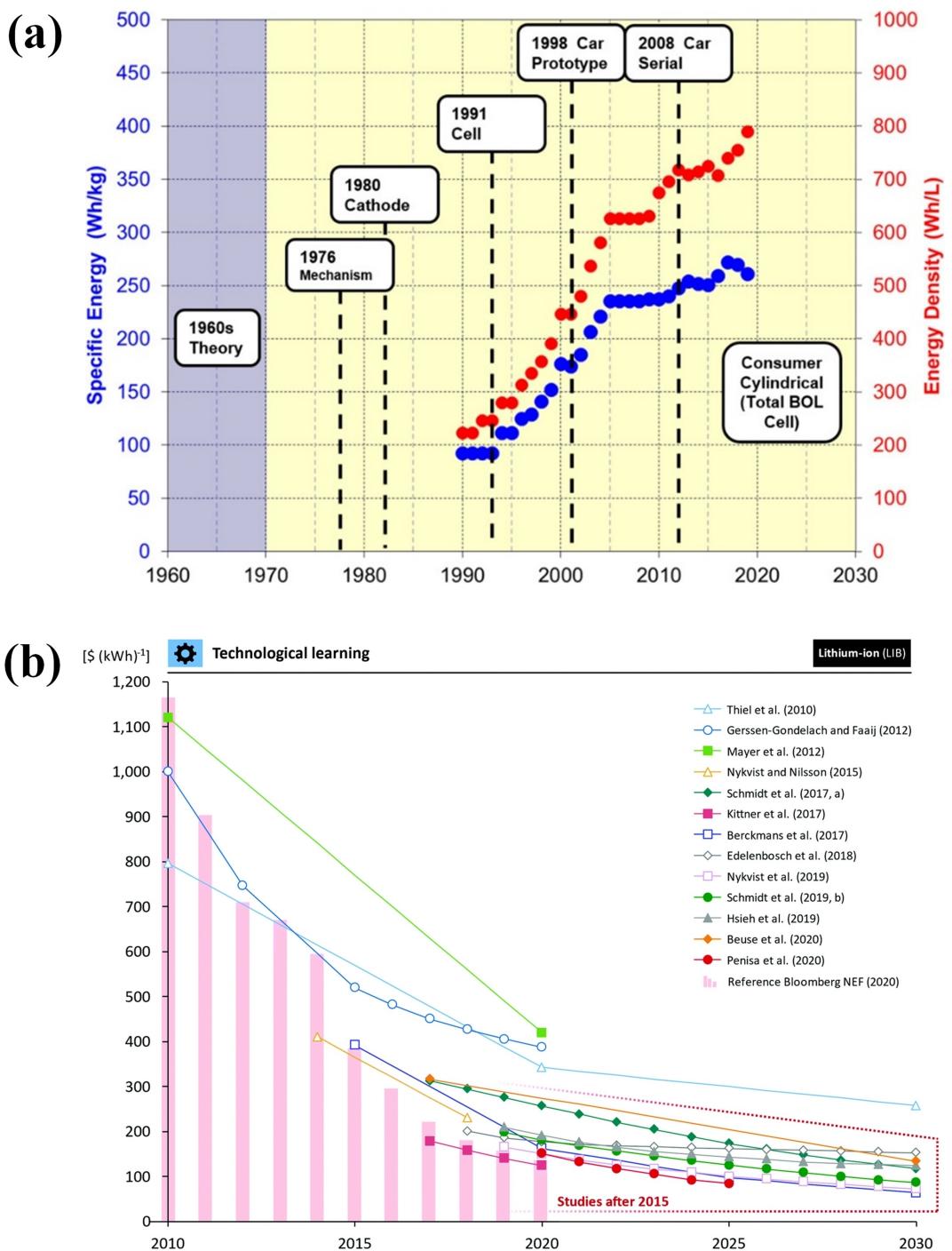


Figure 4. Trends and challenges in LiBs over the years. a) Graphical representation of improvements in energy density in LiBs. Reproduced with permission from Ref. [1]. Copyright (2021) American Chemical Society. b) Graphical representation of cost decline and forecasted values of LiBs using technological learning methods. Image reproduced with permission from Ref. [31]. Copyright (2021) Royal Society of Chemistry.

Considering the decline in cost over the years, there is still an opportunity to reduce the price further. Opportunities for cost reductions in LiBs can be found across their entire value chain, for example, production improvements, materials breakthroughs, performance upgrades, and closing value addition loop.^[1,2,4–7,12–14] Manufacturing processes can help a great deal with cost-cutting since the manufacturing process of the cathode (calcination) and anode (graphitization) requires high-

temperature batch processes.^[33] Reducing or removing additives, binders, and solvents during the cell assembly process can further reduce costs. Reducing thermal management regulations by expanding the thermal operating window can also decrease costs.^[34] Adding safety features can significantly reduce engineering costs by minimizing different levels of engineering requirements.^[34,35] Innovation in electrode materials by exploring novel materials composition and synthesis

methods is another possibility to lower the cost. The formation of SEI requires a large volume for staging and may take up to weeks; simplifying the overall process would greatly benefit.^[36] Lastly, reducing cost opportunity must be evaluated depending on the ability to bring down costs per-kWh and consider supply and distribution effects to validate the outcome, requiring the development of models and simulation tools.

Safety

In addition to energy density and cost, LiBs must satisfy certain safety measures specific to individual applications. Although various performance aspects of LiBs have improved with a decline in cost, safety concerns in both consumer and stationary storage, including aircraft and automobile industry, still pose major concerns.^[37] Among the various components, state-of-the-art electrolytes are most susceptible to LiBs. Although electrochemically inert, electrolytes are made of volatile and flammable organic solvents, Li salts, and additives, and their safe operating temperature is below 80 °C.^[38] Separators, which are just 10–30 μm thick, break the direct contact between electrode and electrolyte. However, their thermal shrinkage or meltdown can be hazardous. So, developing non-flammable, shear thickening electrolytes with ceramic coated separators with unique functions like fire retardant or warning can considerably cease the fire early. Since cathodes undergo phase transformation and oxygen release in overcharging state, they have a significant impact on the thermal stability of LiBs.^[39] Often, they are accompanied by heat evolution and oxidation of electrolyte and separator that can lead to the irrepressible thermal runaway. The formation of Li dendrite on the surface of the anode is a common issue that can break the contact between active materials.

Furthermore, the dendrite can pierce through the polymer separator leading to an internal short circuit and thermal runaway. Although this issue has been mitigated in modern LiBs, dendrite deposition is still observed at the edges of graphite anodes.^[40] Many techniques are studied to address the issues outlined above; however, it is highly unlikely that a single approach can resolve them. Achieving these targets requires exploring novel materials and employing innovative fabrication techniques.

Material challenges

Present LiBs is composed of lithium transition metal oxide cathode and graphite anodes that operate reversibly through the intercalation of Li ions. The capacity of intercalation electrode type is constrained by the chemical bonding of the host structures, reaching its theoretical limits. Hence, alloying or a conversion mechanism with a high ratio of Li-ion to host atom is explored for next-generation batteries.

Anodes

Graphite anodes dominate the modern commercial LiBs;^[41–43] however, they are limited by insufficient capacity (Figure 5a). An operating voltage near Li/Li⁺ can cause Li plating, leading to additional safety risks. Therefore, replacing graphite with Si or Li could be a potential alternative. Si or Si oxide (SiO_x) can show a five- or ten-fold higher theoretical capacity.^[5] The high-capacity stems from alloying mechanisms, where Si can host up to 4.4 Li-ions (forming Li_{4.4}Si). But SiO_x is associated with the detrimental formation of inorganics like Li₄SiO₄ and Li₂O, leading to substantial first cycle irreversibility loss.^[44] Also, the formation of a stable SEI is difficult during cycling processes because of continuous large volume expansion/contraction. Numerous nanostructured designs have been studied over the years to improve their performances. Li metal as an anode is an excellent choice because of its low electrochemical potential and high theoretical capacity, but significant constraints must be overcome. Li dendrite formation is a primary cause of thermal runaway and explosive caused by internal short circuits (Figure 5a).^[42]

Recently, 3D printing of cellulose nanofiber (CNF) was investigated to produce Li anodes (c-CNf/Li) with a high aspect ratio. The porous structure of CNF stabilizes Li and inhibits the dendrite by reducing the local current density and increasing the ion accessibility.^[45] The CNF scaffold for the Li metal anode performed well with a low overpotential of 50 mV and extremely stable cycling for 300 cycles at a high current density of 5 mA cm⁻². Strong mechanical strength of the cellulose nanofibers stabilizes the anode throughout the freeze-drying and Li melting diffusion processes. The porous aerogel induced high ion accessibility makes it an ideal Li host that mitigates Li dendrite formation.^[46]

Electrolyte

Liquid solutions comprising Li salts in aprotic organic solvents (Li-hexafluorophosphate in ethylene carbonate-dimethyl carbonate) are commonly used as electrolytes in LiBs (Figure 5b).^[42] The presence of moisture can cause instability of Li salts, and organic solvents are flammable, making the electrolytes a severe threat to the safety of LiBs, so various liquid, polymeric and solid-based electrolytes are studied. Polymer electrodes exhibit outstanding features such as ease of processing, good resistance toward mechanical deformation, shock and vibration, and low flammability.^[47] They also present better interfacial contact at electrode-electrolyte surfaces and better compatibility than inorganic solid electrolytes. However, polymer electrolytes exhibit relatively low ionic conductivity at room temperature and only attain favorable values at temperatures above 70–80 °C.^[42,47] Gel polymer electrolytes are based on a combination of polymer and liquid electrolytes.^[48] The polymer matrix ensures mechanical stability and safety while the liquid component achieves ionic conductivity. Solid electrolytes offer many benefits in all-solid-state LiBs, such as improved safety, broader operating voltages, and high energy

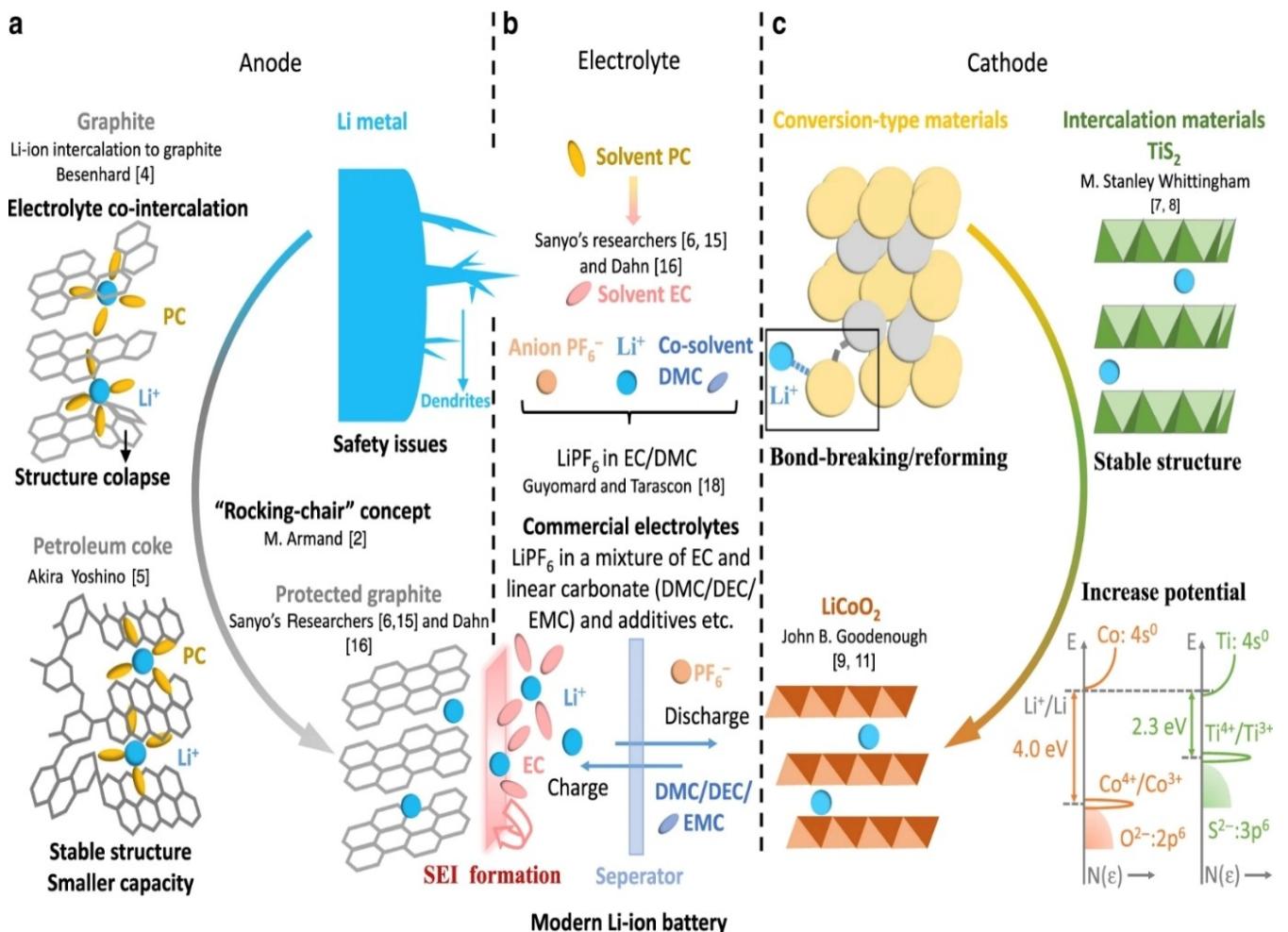


Figure 5. Modern day LIBs and evolution of active material components. a) Anode materials such as graphite, petroleum coke and Li metal. b) Electrolyte materials composed of. c) Various cathode chemistries and materials such as intercalation, conversion and LiCoO_2 . Image reproduced with permission from Ref. [42]. Copyright (2020) The Author(s). Published by Nature Publishing Groups.

density for a wide range of applications.^[49] Obtaining a uniform interface and minimizing the contact resistance at electrode and electrolyte surfaces remains a major drawback in solid-state electrolytes.^[6]

The gel electrolyte may achieve high ionic conductivity ($4.3 \times 10^{-3} \text{ S cm}^{-1}$ at ambient temperature, 80% liquid-electrolyte content). The gels are free standing and easy to handle but since durability is a challenge, all-solid, polymer-based electrolytes are preferred. The hardened electrolyte gel retains its structure and good lithium-ion conductivity after exposure to UV radiation, leading to solid state 3D-printed LIBs.^[50]

Cathodes

Cathodes that operate at higher voltages and have higher capacities are becoming more popular for increasing energy density (Figure 5c)^[42,51] Among the layered spinel and olivine oxide cathodes, the layered class demonstrates a high practical capacity of about 180 Ah kg^{-1} . All three classes of oxides have certain advantages and disadvantages over one another.

Contrary to general LiMO_2 layered oxides, Li-rich $\text{Li}_{1+x}(\text{Ni}_{1-y},\text{Mn}_y)\text{Co}_{2-x}\text{O}_2$ (NMC) layered oxide undergoes the oxidation of transition metal ions first followed by oxidation oxide ions with oxygen evolution when charged for the first time. Li-rich and Mn-rich oxides (LMR-NMC) have an unusually high specific capacity of up to 300 mAh g^{-1} at a marginally lower voltage than typical NMC.^[33] However, slightly Mn-rich LMR-NMC layered oxides suffer from layered to the spinel phase transition, which causes continuous voltage leak, poor rate capability, and life cycle. Moreover, they also endure unpredictable SEI formation with the dissolution of transition metals.^[29] Alternatively, the 3D $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4@\text{C}$ nanocrystal cathodes produce greater energy density and higher operating voltage than pure LiFePO_4 . Coin cells with 3D $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4@\text{C}$ nanocrystal have a superior capacity of $108.45 \text{ mAh g}^{-1}$ at 100 C with a reversible capacity of $150.21 \text{ mAh g}^{-1}$ at 10 C after 1000 cycles. Electrode width and thickness can be adjusted by modifying printing speed and changing the printer nozzle and consequent pressure.^[52]

The price of Co has plummeted over the past decade and has increased sharply in recent years.^[33] Although the Li supply

is not in danger, Li prices have recently risen steadily due to the growing demand of the battery market, which currently consumes 40% of the total supply. In this regard, Ni-rich cathodes and Co-free has grabbed research attention to improve the capacity.^[53] Ni-rich cathodes have three significant drawbacks in the cycle, thermal and air instability. Fully 3D printed LIBs with thick, biphasic semisolid electrodes have been investigated recently with significant areal capacity. These electrodes consist of well-distributed, active electrode particles (LFP or LTO) and conductive carbon particles, creating an electrolyte percolation network in a lithium-based solution. For higher performance, an appropriate carbon network is required in biphasic electrode inks to overcome the resistive character of most electrochemically active Li-ion compounds. Also, these electrode inks must have a viscoelastic response for direct ink writing.^[54]

3D Printed Solid-State Li-Ion Batteries' Performance Metrics for Mitigating the Challenges

3D printing is increasingly employed in manufacturing batteries as its intrinsic additive fabrication feature assists economic efficiency through minimal waste production. Owing to its deposit on-demand aspect, 3D printing enables the fabrication of almost every part of LiB with diverse materials, ranging from macroscale to nanoscale, with well-controlled geometry and precise layer by layer deposition without any templates.^[55,56] This section discusses the functionality of 3D printing in LIBs at a component level.

Electrode fabrication

Conventional processes like sol-gel methods, electron beam evaporation, chemical vapor deposition, spin-coating, electrostatic-spray deposition, and pulsed laser deposition are employed to fabricate thin films.^[57–59] Apart from being complex and expensive, these methods involve high-temperature post-treatments, which leads to side reactions between thin films and the substrate. These undesired side reactions cause cracking and peeling of the thin films from the substrate, thereby reducing the efficiency of the LiB.

Jiang and coworkers reported the fabrication of SnO₂ thin film anodes and LiCoO₂ thin film cathodes using inkjet printing for rechargeable LIBs.^[60] The fabrication of the SnO₂ electrodes involved milling for uniform nano-SnO₂ dispersion, which caused slight structure damage resulting in poorer electrochemical efficiency. To elucidate this challenge, a dispersion of nano-LiCoO₂, carbon black, CMC solution, and monoethanolamine in a commercial surfactant solution was used as the ink. Later, Li₄Ti₅O₁₂ and LiMn₂O₄ thin films were fabricated as anode and cathode for LIBs following similar methods. This simple modification with inkjet printing of the electrodes offers excellent discharge capacity and cyclic stability. Replacing the conventional carbon black with surface-modified carbon in ink for inkjet printing of the LiCoO₂ based thin film displayed

superior electrochemical properties due to better electrical contact between the surface-modified carbon material and the active LiCoO₂ material. Another study reported the substitution of Al current collector with CNT paper to prepare LiFePO₄ thin film by inkjet printing for improved electrochemical efficacy, owing to better contact between CNT paper and LiFePO₄ active material.

3D printing by fused deposition modeling is successfully employed in conventional slurry casting electrode fabrication methods, which usually eliminate tiresome post-treatments. Graphene-based poly-lactic acid filament (G/PLA) composites with different ratios of active materials were formulated with this method for efficient LIBs. 3D printing promises immense advancements in manufacturing patterned electrodes in sandwich-type LIBs for faster ion diffusion and higher active material load. Li₄Ti₅O₁₂ and LiCoO₂ electrodes with micro-dot patterns were constructed by inkjet printing using a capillary glass nozzle that is difficult to fabricate with conventional processes. The Li₄Ti₅O₁₂ electrode displayed a sharp redox peak at 1.5 V. In contrast, the LiCoO₂ electrode achieved reversible electrochemical performance in the range 3.8–4.2 V. A direct ink writing (DIW) technique was employed to fabricate 3D patterned Li₄Ti₅O₁₂ electrodes. Individual lines were printed employing the direct ink writing (DIW) technique using several nozzles to fabricate 3D patterned Li₄Ti₅O₁₂ electrodes with improved capacity retention than flat electrodes. The DIW technique was used to construct planners and 3D patterned LiMn₂O₄ cathode with carbon black, poly(vinylidene fluoride), and N-methyl-2-pyrrolidone.^[61] The resulting cell demonstrated excellent specific capacity and rate capability compared to regular flat electrodes. Recently, several complex structures like zigzag lines, mosquito coils, spiral rectangles, circle grids, and periodic micro lattices have been developed in 3D printing of electrodes for modulated electrochemical properties.^[12]

To print high aspect ratio electrode architectures, optimization of composition and rheology of each ink is key. This ensures reliable flow through fine deposition nozzles by enhancing the adhesion and structural strength to withstand drying and sintering without delamination or distortion.^[62]

3D printing allows the fabrication of electrodes with unique configurations such as 1D fibers, 2D papers, and 3D frameworks for LIBs used in wearables. Wang et al. studied 3D printed fibers for energy storage in wearables with LiFePO₄ cathode and Li₄Ti₅O₁₂ anode employing the DIW technique.^[63] Long and durable LiFePO₄ electrode fibers with 23 cm in length and 200 μm in diameter were constructed with this method, which inferred excellent mechanical strength and flexibility of the printed electrodes.

Electrolyte fabrication

Usually, the injection of the solid-state electrolyte in lithium-ion micro batteries (LIMB) involves an expensive and complex physical vapor deposition method that resembles common active metal deposition. Delannoy et al. explored LIMB construction with porous electrodes and fabricated the solid-state

electrolyte with inkjet printing using the silica-based chemical solution as ink. Here, the inkjet-printed electrolyte displayed similar electrochemical performance to the fabricated physical vapor deposition (PVD). As electrolytes are generally impregnated after electrode fabrication, the external shape of electrolytes is dictated by the configuration of the electrodes. Chen et al. fabricated a zigzag-shaped gel polymer electrolyte with stereolithography, which enabled improved contact between the electrodes and electrolytes, reducing carrier diffusion paths.^[64] This work validated the extraordinary potential of 3D printing in the fabrication of solid electrolytes with customized shapes along with conventional ones.

The mechanical properties of gel polymer electrolytes and ceramic electrolytes are the most noticeable distinction. Ceramics have high elastic moduli, making them more suited for rigid battery designs. The polymers have low elastic moduli, which makes them helpful for developing flexible battery designs. Polymers are also often less difficult to process than ceramics, which lowers the overall cost of manufacture. On the other hand, Ceramics are more suitable for use in high-temperature or other harsh conditions than polymer.^[65] Polymer electrolytes provide advantages over ceramics in terms of processibility and flexibility while also retaining the advantages of solid electrolytes, such as dimensional stability and safety and the ability to prevent lithium dendrite formation. In some polymer electrolytes, lithium salts are solvated by the polymer chains, while in others, a solvent is added to form a polymer gel.^[66] In general, the former is mechanically stronger, allowing for the formation of a free-standing film. Unlike polymer gels, which require mechanical support from other battery components, polymer gels have higher conductivities. The conduction mechanism in polymer gels is similar to that in liquid electrolytes. However, a gel has the advantages of greater safety and shape flexibility over a liquid electrolyte.

Functional layer deposition over electrodes

Proper thermal management is crucial for the safe operation of LIBs, as all its components are highly combustible. DIW deposition of multi-walled carbon nanotube (MWCNT) coated thermal responsive polyethylene (PE) microspheres over the LiFePO₄ electrodes was investigated to eliminate this issue.^[67] The MWCNT facilitates rapid heat diffusion through the PE microspheres, thus shutting down the battery immediately. The instantaneous shutdown ability of the functional layer was verified with a cell with PE-MWCNT printed LiFePO₄ cathode with a graphite anode, LiPF₆ ethylene carbonate/dimethyl carbonate electrolyte, and a separator. A shut down was obtained at 113 °C with 1 mg PE-MWCNT within 1 min. 3D printing ensures facile and precise printing of the functional layer over the electrodes with improved electrochemical efficiency than cells with no functional layer.

One 3D printing technology cannot meet the manufacturing of all battery materials. Higher power and energy densities are obtained by using interdigitated, and 3D printed structures compared to conventional structures. Higher electrochemical

performances can be attributed to higher loading active materials, larger footprint area, and shorter ion transport routes.^[11,68,69] Solid polymer electrolyte (SPE) is prepared by stereolithography (SLA) 3D printing for liquid-free all-solid-state lithium metal batteries (ASSLMBs).^[70] A 3D Archimedean spiral structured SPE shortens the transport of the Li-ion pathway from the electrolyte to the electrode and improves the mass loading of active materials by reinforcing the interfacial adhesion property and high specific surface area of the 3D structure, in comparison with structure-free SPE (Figure 6a). A Battery with this electrolyte was demonstrated with reduced interfacial impedance and a high specific capacity of 128 mAh g⁻¹ after 250 cycles compared to the structure-free SPE with only 32 mAh g⁻¹. Various 3D printable Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ (LATP)-based inks are developed through the direct ink writing (DIW) technique with arbitrary shapes (L, T and +) and higher conductivities (up to 4.24 × 10⁻⁴ S cm⁻¹) and are used to construct ceramic and hybrid solid-state electrolytes (Figure 6b).^[71] The LATP-based electrolytes can be directly printed on LiFePO₄ cathodes by using this printing technique for solid-state batteries, which performed a high discharge capacity of 150 mAh g⁻¹ at 0.5 C. Cheng et al. elevated-temperature DIW technique to fabricate hybrid solid-state electrolytes without any additional procedure, consisting of solid poly(vinylidene fluoride-hexafluoropropylene) matrices and a Li-ion conducting ionic-liquid.^[42] This temperature dependent printing technique prevented the loss of structural integrity.

Discussion

3D printing in solid-state LIBs has started to gain popularity for the fabrication of next-generation energy storage devices with improved energy density, safety, and superior control and precision in manufacturing. Achieving and sustaining an intimate solid-solid contact in the interface between electrodes and solid electrolytes in all-solid-state LIBs is challenging. Advanced characterization techniques are used to analyze interfacial behaviors in LIBs with time and atomic-scale resolution, as rational design of the electrodes-electrolyte interface is critically dependent on an atomic level understanding of ionic interactions and nanoscale phenomena. The solid electrode-electrolyte interface depends on the lattice structure, electronic band structure, and chemical electrochemical and thermal stability. Potential distribution and interface stability mechanisms in LIBs are studied with quantitative electron holography (EH) and EELS. The changes in redox behavior of Li through charging and discharging and thereby the changes in electronic band structures and other kinetic factors in the interface are evident with this analysis.^[72] AFM study also provides important information about space charge layer detection and potential distribution at the interface cross-section.^[73] Spectroscopic, spectrometric, and diffractometric techniques like XAS, XPS, NMR, and XRD facilitate in-situ investigation of interface behavior.^[74]

LIBs have three primary components: cathode, anode, and solid electrolyte. During charging, the Li⁺ are migrated from

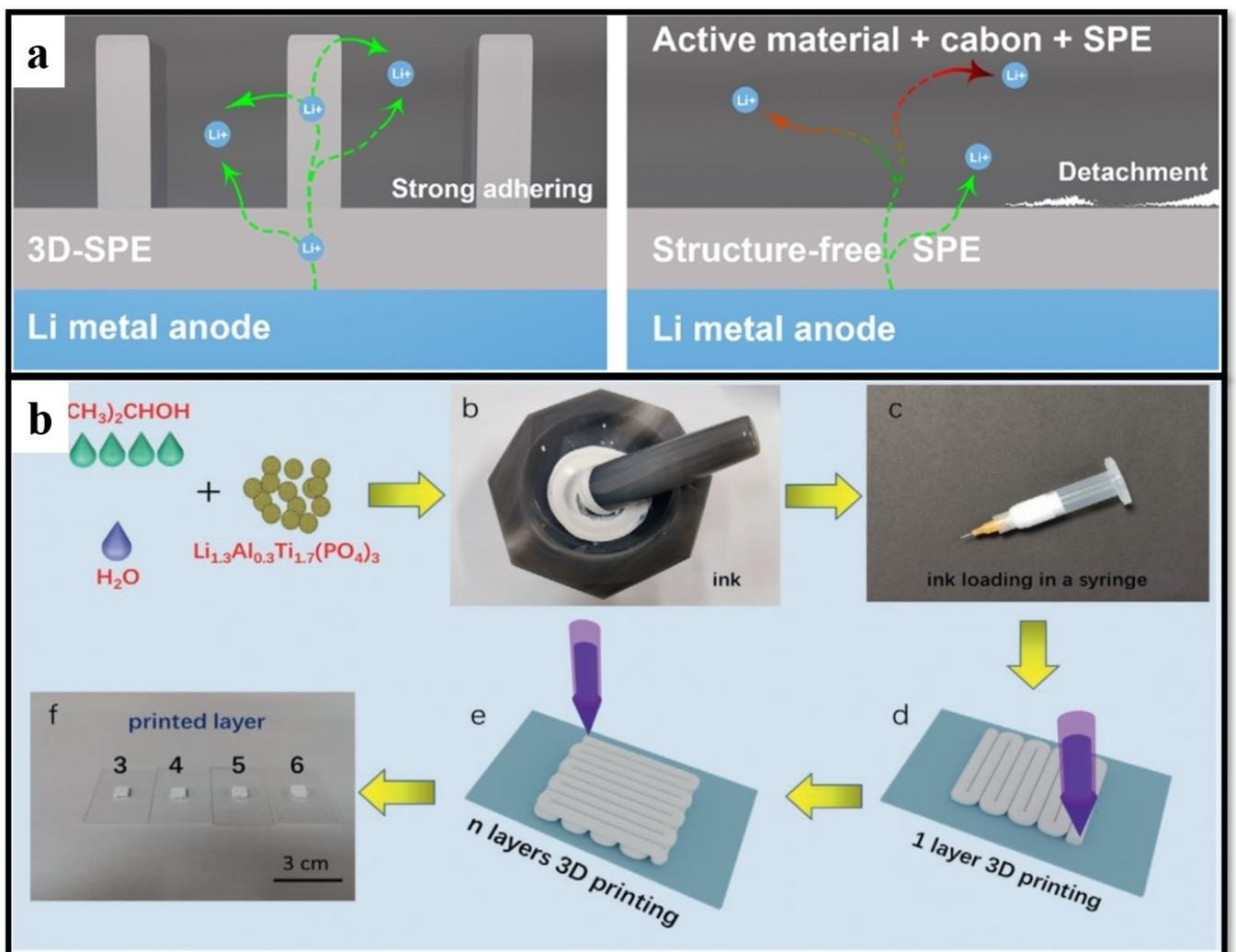


Figure 6. a) Schematic illustration of all-solid-state Li metal battery with SLA 3D printing SPE and structure-free SPE. Image adapted with permission from Ref. [69]. Copyright (2020) American Chemical Society. b) Schematic of DIW printing procedure of LATP ceramic solid-state electrolytes. Image adapted with permission from Ref. [70]. Copyright (2021) Wiley-VCH GmbH.

the cathode to the anode via the solid electrolyte along with e⁻ transfer from the cathode to the anode via the external circuit. During discharging, Li⁺ and e⁻ migrate in the opposite direction. Instability in the interface may arise from both redox and non-redox origins. Solid polymer-based electrolyte is promising for easy fabrication, low cost, and excellent compatibility with lithium salts. However, the interface contact and stability can be improved by using solid polymer electrolyte containing poly(ethylene oxide) and extra stable lithium salt to offer homogeneity, compact morphology, and high electrochemical and thermal stability.^[75] High voltage interface stability is promoted by copolymerization, branching and cross-linking to improve the oxidative capacity of the electrolyte.^[76–78] Switching poly(ethylene oxide) for anti-oxidative polymers such as poly(vinylene carbonate) for better interfacial compatibility with Li anode and high voltage LiCoO₂ cathode is also explored.^[79] Again, gel polymer electrolytes and solid composite offer cohesive properties of solids and diffusion properties of liquids.^[80] FDM is commonly used to precisely fabricate

polymer electrolytes in LIBs, and gel polymer electrolytes are used as a resin for micro-stereolithography to construct 3D architecture in LIBs electrolytes.^[81,64] Interface buffer layer is normally added between the cathode and solid oxide or sulfide electrolytes to mitigate interface interdiffusion.^[82,83] Apart from these, surface modification of the electrodes by effective coating offers an effective way to mitigate interface degradation and offer super interfacial wettability to improve overall electrochemical performance.^[84,85]

One of the main advantages of the 3D printing technique is the micro-manufacturing of several complex and sophisticated structures in electrodes like zigzag lines, mosquito coils, spiral rectangles, circle grids, periodic micro lattices, etc., with precision and control for modulated electrochemical properties^[12] ensures improvement in the precise fabrication of all the components of solid-state LIBs, which results in intimate solid-solid contact in the interface of electrodes and solid electrolytes and overall enhanced electrochemical performance. Also, 3D printing techniques could suggest batteries directly

integrated with other parts of wearable devices that ensure an embedded small and light architecture. This change paves the way for a new wave of wearable technology.^[86]

Conclusion and Outlook

3D printing enables excellent design flexibility and tangible strategy to produce complex, difficult structures through traditional synthetic processes. Using 3D printing technology, LiBs or even an entire device can be fabricated with ease, low cost, and great accuracy because of their free patterning ability. Despite these advantages, 3D printing did not get momentum among the different printing techniques to fabricate LiBs. DIW is the most commonly reported and benefits from printing a broad spectrum of materials from high shear thinning colloids to high viscous polymers. However, printing inks must have high rheological behavior that can be tailored by controlling concentration, composition, and particle size. In comparison, inkjet printing operates on low viscosity polymers having low surface tension. This method is mainly utilized to prepare thin films by droplet deposition for high resolution. FDM is another widely adopted printing process that simultaneously deposits different materials through different nozzles. Although good quality planar electrodes are developed, this method is limited by using thermoplastics at high temperatures. SLA is the oldest, most efficient, low-cost, and layer-by-layer deposition method, mainly used for preparing solid electrolytes. Since this process involves curing each layer with UV light, polymers are mixed with photo-sensitive polymers for most practical applications. Raw materials used in FDA and SLA techniques, such as photo-sensitive and thermoplastics, participate in reactions adversely affecting electrochemical performances.

Although significant advancements are made in the 3D printing of LiBs, there still exist constraints that hinder their large-scale application. For example, electrodes prepared from conventional methods have superior mechanical properties to 3D printed techniques, associated with the anisotropic nature arising from layered deposition and high residual stress between the layers, and can be tackled by using composite materials. Rational design of porous nanostructures can lead to rapid ion transport kinetics; however, it is difficult to achieve hierachal porous architectures via 3D printing at the nano-scale. Electrochemically active materials that can enhance the capacity of LiBs are limited. Therefore, novel active materials that can be infused with printing inks must be studied. Present 3D printers that are commercially available do not offer great versatility to produce desired properties. As a result, 3D printers with an optimized operating mechanism specifically to print LiB's electrodes and their components are required. The above challenges can be solved shortly. It is possible to accomplish high precision and economics with a wide range of raw materials and robust 3D printing techniques for LiBs.

Acknowledgements

All authors would like to acknowledge Indian Institute of Technology Jodhpur-India; Centre for Materials for Electronics Technology-Thrissur-India; Indian Institute of Science-Bangalore-India; University of Bath-U.K; Institute of Physics-Bhubaneswar-India; and Istanbul Technical University-Turkey, for resource and technical support of this work. Also, D.B.G. and S.P. are grateful to the University Grants Commission-Government of India for providing Dr. D.S. Kothari Postdoctoral Fellowship financial support to D.B.G. And R.K.S. and S.P. are grateful to SERB-CRG-India (CRG/2020/002163).

Conflict of Interest

The authors declare no conflict of interest.

Keywords: 3D printing · anode · cathode · electrolyte · lithium-ion battery · solid-state battery

- [1] A. Masias, J. Marcicki, W. A. Paxton, *ACS Energy Lett.* **2021**, *6*, 621.
- [2] W. He, W. Guo, H. Wu, L. Lin, Q. Liu, X. Han, Q. Xie, P. Liu, H. Zheng, L. Wang, X. Yu, D. Peng, *Adv. Mater.* **2021**, *33*, 2005937.
- [3] M. Li, J. Lu, Z. Chen, K. Amine, *Adv. Mater.* **2018**, *30*, 1800561.
- [4] H. Cheng, J. G. Shapter, Y. Li, G. Gao, *J. Energy Chem.* **2021**, *57*, 451.
- [5] C. P. Grey, D. S. Hall, *Nat. Commun.* **2020**, *11*, 6279.
- [6] A. Manthiram, X. Yu, S. Wang, *Nat. Rev. Mater.* **2017**, *2*, 16103.
- [7] C. Zhu, T. Liu, F. Qian, W. Chen, S. Chandrasekaran, B. Yao, Y. Song, E. B. Duoss, J. D. Kuntz, C. M. Spadaccini, M. A. Worsley, Y. Li, *Nano Today* **2017**, *15*, 107.
- [8] T. D. Ngo, A. Kashani, G. Imbalzano, K. T. Q. Nguyen, D. Hui, *Compos. B. Eng.* **2018**, *143*, 172.
- [9] T. Chu, S. Park, K. Fu, *Carbon Energy* **2021**, *3*, 424.
- [10] A. S. K. Kiran, J. B. Velur, S. Merum, A. V. Radhamani, M. Doble, T. S. Sampath Kumar, S. Ramakrishna, *Nanocomposites* **2018**, *4*, 190.
- [11] M. Pei, H. Shi, F. Yao, S. Liang, Z. Xu, X. Pei, S. Wang, Y. Hu, *J. Mater. Chem. A* **2021**, *9*, 25237.
- [12] Y. Yang, W. Yuan, X. Zhang, Y. Yuan, C. Wang, Y. Ye, Y. Huang, Z. Qiu, Y. Tang, *Appl. Energy* **2020**, *257*, 114002.
- [13] D. W. McOwen, S. Xu, Y. Gong, Y. Wen, G. L. Godbey, J. E. Gritton, T. R. Hamann, J. Dai, G. T. Hitz, L. Hu, E. D. Wachsman, *Adv. Mater.* **2018**, *30*, 1707132.
- [14] K. Shen, H. Mei, B. Li, J. Ding, S. Yang, *Adv. Energy Mater.* **2018**, *8*, 1701527.
- [15] S. Zhou, I. Usman, Y. Wang, A. Pan, *Energy Storage Mater.* **2021**, *38*, 141.
- [16] A. Maurel, S. Grugeon, B. Fleutot, M. Courty, K. Prashantha, H. Tortajada, M. Armand, S. Panier, L. Dupont, *Sci. Rep.* **2019**, *9*, 18031.
- [17] A. Chen, C. Qu, Y. Shi, F. Shi, *Front. Energy Res.* **2020**, *8*, 571440.
- [18] C. Reyes, R. Somogyi, S. Niu, M. A. Cruz, F. Yang, M. J. Catenacci, C. P. Rhodes, B. J. Wiley, *ACS Appl. Energ. Mater.* **2018**, *1*, 5268.
- [19] J. F. Valera-Jiménez, J. C. Pérez-Flores, M. Castro-García, J. Canales-Vázquez, *Appl. Mater. Res.* **2021**, *25*, 101243.
- [20] B. Trembacki, E. Duoss, G. Oxberry, M. Stadermann, J. Murthy, *J. Electrochem. Soc.* **2019**, *166*, A923.
- [21] H. T. Sun, J. Zhu, D. Baumann, L. Peng, Y. Xu, I. Shakir, Y. Huang, X. Duan, *Nat. Rev. Mater.* **2019**, *4*, 45.
- [22] K. Fu, Y. Wang, C. Yan, Y. Yao, Y. Chen, J. Dai, S. Lacey, Y. Wang, J. Wan, T. Li, Z. Wang, Y. Xu, L. Hu, *Adv. Mater.* **2016**, *28*, 2587.
- [23] K. Shen, Z. Cao, Y. Shi, Y. Zhang, B. Li, S. Yang, *Energy Storage Mater.* **2021**, *35*, 108.
- [24] M. P. Browne, E. Redondo, M. Pumera, *Chem. Rev.* **2020**, *120*, 2783.
- [25] L. J. Deiner, C. A. G. Bezerra, T. G. Howell, A. S. Powell, *Adv. Eng. Mater.* **2019**, *21*, 1900737.
- [26] P. Chang, H. Mei, S. Zhou, K. G. Dassios, L. Cheng, *J. Mater. Chem. A* **2019**, *7*, 4230.

- [27] M. Wei, F. Zhang, W. Wang, P. Alexandridis, C. Zhou, G. Wu, *J. Power Sources* **2017**, *354*, 134.
- [28] Y. Zhang, G. Shi, J. Qin, S. E. Lowe, S. Zhang, H. Zhao, Y. L. Zhong, *ACS Appl. Electron. Mater.* **2019**, *1*, 1718.
- [29] T. Kim, W. Song, D. Y. Son, L. K. Ono, Y. Qi, *J. Mater. Chem. A* **2019**, *7*, 2942.
- [30] E. Pomerantseva, F. Bonaccorso, X. Feng, Y. Cui, Y. Gogotsi, *Science* **2019**, *366*, eaan8285.
- [31] L. Mauler, F. Duffner, W. G. Zeier, J. Leker, *Energy Environ. Sci.* **2021**, *14*, 4712.
- [32] M. S. Ziegler, J. E. Trancik, *Energy Environ. Sci.* **2021**, *14*, 1635.
- [33] R. Schmuck, R. Wagner, G. Hörpel, T. Placke, M. Winter, *Nat. Energy* **2018**, *3*, 267.
- [34] Y. Ye, L. Y. Chou, Y. Liu, H. Wang, H. K. Lee, W. Huang, J. Wan, K. Liu, G. Zhou, Y. Yang, A. Yang, X. Xiao, X. Gao, D. T. Boyle, H. Chen, W. Zhang, S. C. Kim, Y. Cui, *Nat. Energy* **2020**, *5*, 786.
- [35] L. Bravo Diaz, X. He, Z. Hu, F. Restuccia, M. Marinescu, J. V. Barreras, Y. Patel, G. Offer, G. Rein, *J. Electrochem. Soc.* **2020**, *167*, 090559.
- [36] D. L. Wood, M. Wood, J. Li, Z. Du, R. E. Ruther, K. A. Hays, N. Muralidharan, L. Geng, C. Mao, I. Belharouak, *Energy Storage Mater.* **2020**, *29*, 254.
- [37] J. Deng, C. Bae, J. Marcicki, A. Masias, T. Miller, *Nat. Energy* **2018**, *3*, 261.
- [38] X. Wu, K. Song, X. Zhang, N. Hu, L. Li, W. Li, L. Zhang, H. Zhang, *Front. Energy Res.* **2019**, *7*, 65.
- [39] X. Liu, D. Ren, H. Hsu, X. Feng, G. L. Xu, M. Zhuang, H. Gao, L. Lu, X. Han, Z. Chu, J. Li, X. He, K. Amine, M. Ouyang, *Joule* **2018**, *2*, 2047.
- [40] K. Liu, Y. Liu, D. Lin, A. Pei, Y. Cui, *Sci. Adv.* **2018**, *4*, eaas9820.
- [41] J. Asenbauer, T. Eisenmann, M. Kuenzel, A. Kazzazi, Z. Chen, D. Bresser, *Sustain. Energy Fuels* **2020**, *4*, 5387.
- [42] J. Xie, Y.-C. Lu, *Nat. Commun.* **2020**, *11*, 2499.
- [43] W. He, C. Chen, J. Jiang, Z. Chen, H. Liao, H. Dou, X. Zhang, *Batteries & Supercaps* **2022**, *5*, e202100258.
- [44] K. Kitada, O. Pecher, P. C. M. M. Magusin, M. F. Groh, R. S. Weatherup, C. P. Grey, *J. Am. Chem. Soc.* **2019**, *141*, 7014.
- [45] D. Cao, Y. Xing, K. Tantratian, X. Wang, Y. Ma, A. Mukhopadhyay, Z. Cheng, Q. Zhang, Y. Jiao, L. Chen, H. Zhu, *Adv. Mater.* **2019**, *31*, 1807313.
- [46] R. R. Kohlmeyer, A. J. Blake, J.O Hardin, E. A. Carmona, J. Carpene-Núñez, B. Maruyama, J. D. Berrigan, H. Huang, M. F. Durstock, *J. Mater. Chem. A* **2016**, *4*, 16856.
- [47] D. Zhou, D. Shanmukaraj, A. Tkacheva, M. Armand, G. Wang, *Chem.* **2019**, *5*, 2326.
- [48] X. Cheng, J. Pan, Y. Zhao, M. Liao, H. Peng, *Adv. Energy Mater.* **2018**, *8*, 1702184.
- [49] R. Chen, A. M. Nolan, J. Lu, J. Wang, X. Yu, Y. Mo, L. Chen, X. Huang, H. Li, *Joule* **2020**, *4*, 812.
- [50] Y. Gambe, H. Kobayashi, K. Iwase, S. Stauss, I. Honma, *Dalton Trans.* **2021**, *50*, 16504.
- [51] N. Mohamed, N. K. Allam, *RSC Adv.* **2020**, *10*, 21662.
- [52] J. Hu, Y. Jiang, S. Cui, Y. Duan, T. Liu, H. Guo, L. Lin, Y. Lin, J. Zheng, K. Amine, F. Pan, *Adv. Energy Mater.* **2016**, *6*, 1600856.
- [53] A. Manthiram, *Nat. Commun.* **2020**, *11*, 1550.
- [54] T. S. Wei, B. Y. Ahn, J. Grotto, J. A. Lewis, *Adv. Mater.* **2018**, *30*, 1703027.
- [55] M. E. Prendergast, J. A. Burdick, *Adv. Mater.* **2020**, *32*, 190251.
- [56] F. Zhang, M. Wei, V. V. Viswanathan, B. Swart, Y. Shao, G. Wu, C. Zhou, *Nano Energy* **2017**, *40*, 418.
- [57] K. S. Ganesh, P. J. Kumar, O. M. Hussain, *J. Electroanal. Chem.* **2018**, *828*, 71.
- [58] C. Alié, C. Calberg, C. Páez, D. Liquet, D. Eskenazi, B. Heinrichs, N. Job, *J. Power Sources* **2018**, *403*, 173.
- [59] Y. Liu, R. Wei, W. Ding, X. Wang, W. Song, Z. Sheng, J. Dai, C. Liang, X. Zhu, Y. Sun, *Appl. Surf. Sci.* **2019**, *478*, 408.
- [60] Y. Zhao, Q. Zhou, L. Liu, J. Xu, M. Yan, Z. Jiang, *Electrochim. Acta* **2006**, *51*, 2639.
- [61] J. Li, M. C. Leu, R. Panat, J. Park, *Mater. Des.* **2017**, *119*, 417.
- [62] K. Sun, T. S. Wei, B. Y. Ahn, J. Y. Seo, S. J. Dillon, J. A. Lewis, *Adv. Mater.* **2013**, *25*, 4539.
- [63] Y. Wang, C. Chen, H. Xie, T. Gao, Y. Yao, G. Pastel, X. Han, Y. Li, J. Zhao, K. Fu, L. Hu, *Adv. Funct. Mater.* **2017**, *27*, 1703140.
- [64] Q. Chen, R. Xu, Z. He, K. Zhao, L. Pan, *J. Electrochem. Soc.* **2017**, *164*, A1852.
- [65] L. Porz, D. Knez, M. Scherer, S. Ganschow, G. Kothleitner, D. Rettenwander, *Sci. Rep.* **2021**, *11*, 8949.
- [66] J. Castillo, A. Santiago, X. Judez, I. Garbayo, J. A. C. Clemente, M. C. Morant-Miñana, A. Villaverde, J. A. González-Marcos, H. Zhang, M. Armand, C. Li, *Chem. Mater.* **2021**, *33*, 8812.
- [67] Z. X. Huang, G. J. Sim, J. C. Tan, H. Y. Low, H. Y. Yang, *Energy Technol.* **2018**, *6*, 1715.
- [68] M. Cheng, R. Deivanayagam, R. Shahbazian-Yassar, *Batteries & Supercaps* **2020**, *3*, 130.
- [69] Y. He, S. Chen, L. Nie, Z. Sun, X. Wu, W. Liu, *Nano Lett.* **2020**, *20*, 7136.
- [70] Z. Liu, X. Tian, M. Liu, S. Duan, Y. Ren, H. Ma, K. Tang, J. Shi, S. Hou, H. Jin, G. Cao, *Small* **2021**, *17*, 2002866.
- [71] M. Cheng, Y. Jiang, W. Yao, Y. Yuan, R. Deivanayagam, T. Foroozan, Z. Huang, B. Song, R. Rojaee, T. Shokuhfar, Y. Pan, J. Lu, R. Shahbazian-Yassar, *Adv. Mater.* **2018**, *30*, 1800615.
- [72] K. Yamamoto, Y. Iriyama, T. Asaka, T. Hirayama, H. Fujita, C. A. Fisher, K. Nonaka, Y. Sugita, Z. Ogumi, *Angew. Chem. Int. Ed.* **2010**, *49*, 4414.
- [73] J. Y. Liang, X. X. Zeng, X. D. Zhang, P. F. Wang, J. Y. Ma, Y. X. Yin, X. W. Wu, Y. G. Guo, L. J. Wan, *J. Am. Chem. Soc.* **2018**, *140*, 6767.
- [74] K. Nie, Y. Hong, J. Qiu, Q. Li, X. Yu, H. Li, L. Chen, *Front. Chem.* **2018**, *6*, 616.
- [75] Q. Ma, X. Qi, B. Tong, Y. Zheng, W. Feng, J. Nie, Y. S. Hu, H. Li, X. Huang, L. Chen, Z. Zhou, *ACS Appl. Mater. Interfaces* **2016**, *8*, 29705.
- [76] Y. Tong, L. Chen, X. He, Y. Chen, *Electrochim. Acta* **2014**, *118*, 33.
- [77] L. Porcarelli, C. Gerbaldi, F. Bella, J. R. Nair, *Sci. Rep.* **2016**, *6*, 19892.
- [78] A. Wang, H. Xu, Q. Zhou, X. Liu, Z. Li, R. Gao, N. Wu, Y. Guo, H. Li, L. Zhang, *Electrochim. Acta* **2016**, *212*, 372.
- [79] J. Chai, Z. Liu, J. Ma, J. Wang, X. Liu, H. Liu, J. Zhang, G. Cui, L. Chen, *Adv. Sci.* **2017**, *4*, 1600377.
- [80] B. W. Zewde, L. Carbone, S. Greenbaum, J. Hassoun, *Solid State Ionics* **2018**, *317*, 97.
- [81] A. Maurel, M. Armand, S. Grangeon, B. Fleutot, C. Davoisne, H. Tortajada, M. Courty, S. Panier, L. Dupont, *J. Electrochem. Soc.* **2020**, *167*, 070536.
- [82] T. Kato, T. Hamanaka, K. Yamamoto, T. Hirayama, F. Sagane, M. Motoyama, Y. Iriyama, *J. Power Sources* **2014**, *260*, 292.
- [83] J. Haruyama, K. Sodeyama, L. Han, K. Takada, Y. Tateyama, *Chem. Mater.* **2014**, *26*, 4248.
- [84] Z. Lyu, G. J. Lim, R. Guo, Z. Kou, T. Wang, C. Guan, J. Ding, W. Chen, J. Wang, *Adv. Funct. Mater.* **2019**, *29*, 1806658.
- [85] M. Li, J. Wei, L. Ren, Y. Zhao, Z. Shang, D. Zhou, W. Liu, L. Luo, X. Sun, *Cell Rep. Phys. Sci.* **2021**, *2*, 100374.
- [86] S. Praveen, P. Santhoshkumar, Y. C. Joe, C. Senthil, C. W. Lee, *Appl. Mater. Res.* **2020**, *20*, 100688.

Manuscript received: May 17, 2022

Revised manuscript received: May 21, 2022

Version of record online: June 7, 2022