Printed electronics to accelerate solid-state battery development

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Abstract

The transition from conventional liquid electrolyte Li-ion batteries towards solid-state systems requires a paradigm shift on how these batteries are fabricated and how the R&D process can be augmented in order to fulfil the ever-increasing demand for reliable and high-performance energy storage systems. This work briefly looks over the main aspects of printed electronics and its potential to accelerate the development of solid-state batteries. It emphasizes the main challenges related to the fabrication of solid-state batteries and how printed electronics can address them in a timely and affordable manner. Importantly, the proposed printed electronics methods and solutions highlight the ability for immediate upscaling to mass production as well as downscaling for rapid prototyping and custom designing.

Regardless of the application, batteries are ubiquitous - starting from portable devices, smartphones, and laptops, through electric vehicles of various sizes, ending at large energy storage systems to support smart grid and renewable energy generators [1]. This multitude of applications create an ever-growing demand for capable, energy-efficient, safe, sustainable, well-performing battery systems, and suitable fabrication methods. Moreover, for more dedicated applications, the battery fabrication technologies are expected to provide an additional capability of tailoring the batteries, i.e., specific shapes and dimensions, flexibility, compatibility with extremely fast charging-discharging, or extreme temperatures [2]. Nowadays, the sustainability aspect concerning batteries throughout their lifetime has also become important in selecting battery vendors, favoring solutions that are more environmentally friendly at every step of the battery lifetime, starting from production, through its usage, and ending at recycling [3]. Expectedly, customers anticipate that the battery will fulfill all the technical requirements and will be offered at an affordable price. Although state-of-the-art Li-ion liquid electrolyte batteries offer satisfactory performance (for now), the researchers and manufacturers spend tremendous efforts on the development of next-generation batteries to fulfill the ever-growing customer demand and overcome the limitations imposed by liquid electrolyte-based energy storage systems [4].

One of the very promising approaches that addresses the aforementioned needs is the replacement of liquid electrolyte with its solid-state substitute. In this approach, the ionic liquid-soaked separator located between the cathode and anode is replaced with a solid layer of material with high ionic conductivity. Table 1 offers a comparison of solid-state and liquid electrolytes with emphasis on their main advantages and disadvantages/limitations [5].

In addition to the advantages mentioned in table 1, the researchers highlight that solid-state electrolytes offer compatibility with high-potential cathodes (>4.2 V), higher energy density than conventional liquid electrolyte batteries, and improved safety (low flammability) at low costs [6, 7]. All these benefits and advantages of Solid-State Batteries (SSBs) attracted numerous research institutes and private enterprises towards further R&D efforts. This trend is especially visible in the Electric Vehicle (EV) arena, where several large automotive companies with EV aspirations, such as Toyota, VW, BMW, Ford, Mercedes-Benz, and General Motors have already made major investments in the companies involved in the SSBs development (QuantumScape, Solid...
Power, and Factorial Energy). At the same time, enterprises recognize the challenges and aim to achieve full commercial SSBs deployment in the second half of the decade.

Despite the great potential and strong involvement of resourceful companies, the current SSBs suffer from several drawbacks such as poor selection and stability of suitable high ionic conductivity solid electrolytes, undesired interfacial resistances, and internal and interfacial nano- and microscale degeneration of the materials, to name a few [8–10]. Another challenge of SSBs is related to fabrication methods, material compatibility, and interactions during processing and layers formation [11, 12]. All these factors and undesired interactions jeopardize the electrochemical performance of the SSBs and require further development and optimization. Importantly, strong collaborative research efforts of scientists and engineers are needed to develop SSBs systems with state-of-the-art materials and architectures that offer superior performance but also are easy in processing and fabrication. Figure 1 represents a pouch SSBs architecture with three printed layers: cathode, solid-state electrolyte, and anode.

Researchers proposed a variety of solid-state electrolyte materials that provide sufficient ionic conductivity [13]. These materials and composites can be grouped into the following categories: oxides, polymers, sulfides, halides, and hydrides, offering room temperature ionic conductivity in a range of $10^{-2} - 10^{-4}$ S·cm$^{-1}$, which is comparable to organic liquid electrolytes (ethylene carbonate and dimethyl carbonate)–$10^{-2}$ S·cm$^{-1}$ [14–18]. The subsequent challenges related to undesired solid-solid interfacial interactions can be addressed by interface engineering through surface modifications, material composition optimization, interfacial structure design, and novel in situ characterization methods that provide in-depth information about the interface behavior during battery cycling (charging and discharging) [19, 20].

| Table 1. Main advantages and disadvantages of solid-state and liquid electrolytes in Li-ion batteries [5]. |
|---|---|
| **Solid electrolyte** | **Disadvantages** |
| 1. Excellent chemical and physical stability | 1. Reduced contact area with electrodes |
| 2. Perform well as a thin film ($\approx 1 \mu$m) | 2. Interface stress due to charging and discharging |
| 3. Ionic conductivity only (excludes electron) Transference number $= 1$ | 3. Lower ionic conductivity than liquids |
| **Liquid electrolyte** | 1. May rely on the formation of Solid Electrolyte Interface (SEI) layer |
| 2. Can accommodate volume expansion at the electrode during cycling | 3. Both ionic and electronic conduction. Transference number typically 0.5 |
| 3. High ionic conductivity | |

![Figure 1. Architecture of pouch SSBs with printed solid electrolyte and electrodes.](image-url)
The aforementioned challenges and solutions need to be considered while selecting and developing a suitable fabrication method and eventual upscaling efforts [21]. Further, a good understanding of the fabrication processing, occurring phenomena, and its requirements will allow early-stage problem detection and resolving. It is essential because many promising solid-electrolyte materials demonstrate high ionic conductivity in laboratory conditions, but when combined with additives and implemented into battery cell structure, the final battery performance is below expectations.

Printed electronics has proven to be a suitable method for the fabrication of battery electrodes and has a high potential to embrace the recent SSBs developments and accelerate the popularization and commercialization of fully printed SSBs [22]. Printed electronics is a set of various printing methods that use functionalized inks/slurries and controlled material deposition to create electronic devices, for instance, batteries [23, 24].

The most common industrial battery coating method - slot die coating—rather than printing techniques, belongs to a category of coating techniques in which the slurry is transferred through a slot gap onto a moving substrate. Although slot die coating is designed for coating uniform thin films at flat substrates and high-throughput fabrication, it is not suitable for more complex multilayer battery architectures [25]. In addition to flexibility, selectivity, and vast materials compatibility, printed electronics is a unique fabrication method that generates a negligible amount of material waste, making it a well-suited candidate for becoming one of the future’s sustainable fabrication technologies. Inkjet-, spray- and screen-printing are the most common systems used in the research and development of printed electronic components and systems because they offer high adaptability and the most promising up- and down-scaling (prototyping) capabilities [26]. The effortless up- and down-scaling of battery fabrication enables production of an entire spectrum of solid-state batteries of different sizes and shapes, according to the product requirements. Printed electronics is also one of the fabrication technologies that can fulfill the needs of battery applications by providing production capacity to deliver billions of battery components and architectures at nominal costs. Recently, 3D printing gained the interest of the research community as a suitable battery manufacturing method [27]. While 3D printing allows printing of high-quality batteries, usage of 3D printing for mass-production of batteries remains a significant challenge due to difficulties in upscaling the process. Thanks to recent advancements in developing solid-electrolyte materials, all functional layers (cathode, solid electrolyte, and anode) can be printed layer by layer (figure 2) [28].

In printed batteries, the printing process can be split into three phases where cathode, solid-electrolyte, and anode are printed consequently on each other. Regardless of the layer, the active material and additives are dissolved/dispersed/suspended in a solvent (i.e., N-Methyl-2-pyrrolidone (NMP), water, Dimethyl sulfoxide (DMSO), Dimethylformamide (DMF), etc), creating an ink/slurry that is used during the printing process. The solvent in the printing process mainly serves as a material carrier. However, the solvent is also expected to appropriately dissolve the additives and have negligible influence on the physicochemical properties of the active material during and after the printing process [29]. Often the active material in the ink/slurry is accompanied with additives (surfactants, co-solvents, binders, etc). Surfactants additions, such as isopropanol, 1-butanol, 1-pentanol, or Capstone FS 3100 aim to reduce the surface tension of the inks and consequently improve the wetting and material distribution on the surface [30]. Co-solvents serve a dual role in ink formulation—they modify the surface tension of the inks and influence the drying process due to a variation in the boiling points of the introduced solvents [31]. Binders, such as Polyvinylidene Fluoride (PVDF), Polyvinylpyrrolidone (PVP), Styrene Butadiene Rubber (SBR) play a crucial role in battery fabrication. While during printing and drying, they improve the homogeneity of the inks/slurries and adhesion between the active material particles and layers beneath, during battery operation, they compensate the battery active material lattice expansion and contraction.

**Figure 2.** (a) Printable ink formulation for different layers of solid-state batteries. (b) After the ink formulation, the solution is used to either screen, inkjet, or spray print the battery layer. (c) First printed layer (cathode) of multilayer printing process. (d) Solid-state Li-ion battery architecture consisting of printed cathode, solid electrolyte, anode, and two metallic current collectors.
Table 2. Comparison of ink properties and printable functional features of different printing techniques: screen, gravure, flexography, inkjet, EHD (electrohydrodynamic), and aerosol/spray [36].

| Printing techniques | Ink viscosity [cP] | Layer thickness [nm] | Resolution [μm] | Line width [μm] | Printing speed [mm s]⁻¹ | Alignment accuracy [μm] |
|---------------------|-------------------|----------------------|-----------------|----------------|----------------------|----------------------|
| Screen              | 30 – 12 000       | 1500–50000           | 100             | 40             | 50–300               | ±10                  |
| Gravure             | 100–12 000        | 10–400               | 2               | 35             | 5–1000               | ±10                  |
| Flexography         | 2–500             | 5–50                 | 1               | 3              | 200–830              | ±10                  |
| Inkjet              | 1–30              | 100–500              | 2               | 2–8            | 1.25–7000            | ±2                   |
| EHD                 | 1–10 000          | 20–180               | 2               | 2              | 0.2–8               | ±1                   |
| Aerosol/Spray       | 1–2000            | 300–50000            | 20              | 50–150         | 0.1–500              | ±5                   |

movements [32]. The binder-added flexibility also reduces tensions within the layers and at the layers’ interfaces during fabrication (roll-to-roll process) and battery operation. Another group of materials that can be considered as active materials are the additives that do not affect the printing process but play an important role in battery operation, such as carbon black utilized to improve electronic conductivity within the electrodes.

While most of the active materials in the battery layers are in powder form, particle size is one of the critical factors that need to be taken into account during the printing process development. For instance, different cathode chemistry materials (LiMn₂O₄ (LMO), LiFePO₄ (LFP), LiCoO₂ (LCO), LiNiCoAlO₂ (NCA), LiNiCoMnO₂ (NMC), etc) are composed of particles of various sizes, starting from tens of nanometers ending at several micrometers [33]. Similarly, solid-state electrolyte active materials (oxides, polymers, sulfides, halides, and hydrides) are composed of various size particles ranging from nano to micrometers. As for anode active material, graphite with particle sizes ranging from 10 to 20 μm is the most commonly used material but alternatives are under development - silicon nanoparticles (<150 nm). Moreover, before and after printing, different treatments (plasma and UV) can be applied to improve wettability, enhance interfacial contact, or remove impurities before printing the next layer [34].

Various printing methods have different requirements regarding the ink formulation (particle size, viscosity, boiling point, surface tension, polarity, concentration, etc) [31, 35]. From the battery point of view, screen-printing and spray-coating are the most suitable due to their flexibility and ability to print inks of various viscosities and loaded with micrometer-sized particles (table 2). These methods offer relatively high printing speeds that are crucial for upscaling efforts. Also, essential from the perspective of developing energy- and time-efficient fabrication processes is the ability to print inks heavy-loaded with active materials (high viscosity). However, screen-printing belongs to contact-printing methods, introducing some restrictions and limitations such as the necessity for flat substrates, the inability to print on pressure-sensitive layers, and more troublesome design alterations. At the same time, spray-coating is a non-contact printing method deprived of screen-printing’s limitations. The most important limitation of spray-coating is a relatively large line width, which is however, sufficient for battery applications. While inkjet printing allows high printing accuracy and theoretical zero material waste, it is often slower than the aforementioned methods, and requires low viscosity inks, composed of relatively small particles (≤100 nm). With increasing particle size, material load, and viscosity, the risk of inkjet nozzle clogging is rising significantly. Nonetheless, for custom architectures or high precision applications (mini- and micro-batteries) inkjet printing can be a viable option, especially for printing solid electrolytes (nanoparticles).

One of the main advantages of printing technologies is the ability to create multi-stack architectures throughout the controlled material deposition. Naturally, the interfacial interactions of various solvents and materials need thorough investigation, but the flexibility and high compatibility of the printing methods with several solid-state electrolyte materials and proven ability to print the electrodes provide encouragement and positive reinforcement for further research [23, 37].

The selection of materials and appropriate printing methods are extremely complex and require a holistic bottom-up approach where all three development phases (ink/slurry formulation, printing and drying, and battery operation) are equally taken into account. This challenge requires strong collaborative efforts between scientists and engineers to ensure that laboratory-scale promising solid-state electrolyte materials can be successfully used to formulate stable inks/slurries and printed without compromising the performance of the final product—SSBs. Our highlights will help to increase the visibility of printing technologies among battery researchers and enable further developments towards more capable, sustainable, and environmentally friendly batteries.
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Data availability statement

No new data were created or analysed in this study.

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References

[1] Shekhar A R, Parekh M H and Pol V G 2022 Worldwide ubiquitous utilization of lithium-ion batteries: what we have done, are doing, and could do safely once they are dead J. Power Sources 523 231015
[2] Toor A, Wen A, Maksimovic F, Gaikwad A M, Pister K S J and Arias A C 2021 Stencil-printed Lithium-ion micro batteries for IoT applications Nano Energy 82 105866
[3] Duhnen S et al 2020 Toward green battery cells: perspective on materials and technologies Small Methods 4 2000039
[4] Sun Y K 2020 Promising all-solid-state batteries for future electric vehicles ACS Energy Lett. 5 321–3
[5] Bekaeft E, Buanic M, Lassi U, Llordés A and Salminen J 2017 Electrolytes for Li- and Na-Ion batteries: concepts, candidates, and the role of nanotechnology Emerg. Nanotechnologies Recharg. Energy Storage Syst. 1st (Amsterdam: Elsevier) pp 1–43
[6] Manthiram A, Yu X and Wang S 2017 Lithium battery chemistries enabled by solid-state electrolytes Nat. Rev. Mater. 24 21–16
[7] Janek J and Zeier W G 2016 A solid future for battery development Nat. Energy 19 11–4
[8] Moliyaniy P and Witter R 2020 CaF2 solid-state electrolytes prepared by vapor pressure exposure and solid synthesis for defect and ionic conductivity tuning Mater. Des. Process. Commun. 2 076
[9] Sun Y, Guan P, Liu Y, Xu H, Li S and Chu D 2018 Recent progress in lithium lanthanum titanate electrolyte towards all-solid-state lithium ion secondary battery Crit. Rev. Solid State Mater. Sci. 44 265–82
[10] Chen A, Qu C, Shi Y and Shi F 2020 Manufacturing strategies for solid electrolyte in batteries Front. Energy Res. 8 226
[11] Lee J, Lee T, Char K, Kim K J and Choi J W 2021 Issues and advances in scaling up sulphide-based all-solid-state batteries Acc. Chem. Res. 54 3390–402
[12] Hao F, Han F, Liang Y, Wang C and Yao Y 2018 Architectural design and fabrication approaches for solid-state batteries MRS Bull. 43 75–81
[13] Zhao Q, Staln S, Zhao C Z and Archer L A 2020 Designing solid-state electrolytes for safe, energy-dense batteries Nat. Rev. Mater. 5 229–52
[14] Zhao N, Khokhar W, Bi Z, Shi C, Guo X, Fan L Z and Nan C W 2019 Solid garnet batteries Joule 3 1190–9
[15] Vijayakumar M, Inaguma Y, Meshiko W, Crosnier-Lopez M P and Bohnke C 2004 Synthesis of fine powders of Li3+xLa2-xTiO3 perovskite by a polymerizable precursor method Chem. Mater. 16 2719–24
[16] Lau J et al 2018 Solid state electrolytes for lithium battery applications Adv. Energy Mater. 8 1800933
[17] Li X, Liang J, Yang X, Adair K R, Wang C, Zhao F and Sun X 2020 Progress and perspectives on halide lithium conductors for all-solid-state lithium batteries Energ. Environ. Sci. 13 1429–61
[18] Kim S, Oguchi H, Toyama N, Sato T, Takagi S, Koyama N, Kawamura J and Orimo S I 2019 A complex hydride lithium superionic conductor for high-energy-density all-solid-state lithium metal batteries Nat. Commun. 10 1–9
[19] Sun C, Ruan Y, Zha W, Li W, Cai M and Wen Z 2020 Recent advances in anodic interface engineering for solid-state lithium-metal batteries Mater. Horiz. 7 1667–1696
[20] Xiao Y, Wang Y, Bo S H, Kim J C, Miara L J and Ceder G 2019 Understanding interface stability in solid-state batteries Nat. Rev. Mater. 5 105–26
[21] Singer C, Schnell J and Reinhart G 2021 Scalable processing routes for the production of all-solid-state batteries—modeling interdependencies of product and process Energy Technol. 9 2000665
[22] Gonzalves R, Dias P, Hilliou L, Costa P, Silva M M, Costa C M, Corovolta-Galván S and Lancers-Méndez S 2021 Optimized printed cathode electrodes for high performance batteries Energy Technol. 9 2000805
[23] Costa C M, Gonzalves R and Lancers-Méndez S 2020 Recent advances and future challenges in printed batteries Energy Storage Mater. 28 216–34
[24] Deiner L J, Jenkins T, Powell A, Howell T and Rottmayer M 2019 High capacity rate capable aerosol jet printed li-ion battery cathode Adv. Eng. Mater. 21 180128
[25] Hawley W B and Li J 2019 Electrode manufacturing for lithium-ion batteries—analysis of current and next generation processing J. Energy Storage 5 100862
[26] Apilu P, Hiltunen J, Valimäki M, Heiniläo S, Sliz R and Hast J 2015 Roll-to-roll gravure printing of organic photovoltaic modules - Insulation of processing defects by an interfacial layer Prog. Photovoltaics Res. Appl. 23 918–28
[27] Gao X et al 2019 Toward a remarkable Li-S battery via 3D printing Nano Energy 56 595–603
[28] Kim S H, Choi K H, Cho S J, Yoo J, Lee S S and Lee S Y 2018 Flexible/shape-variatile, bipolar all-solid-state lithium-ion batteries prepared by multistage printing Energy Environ. Sci. 11 321–30
[29] Sliz R, Valikangas J, Vilmis P, Hu T, Lassi U and Fabritius T 2021 Replacement of NMP solvent for more sustainable, high-capacity, printed Li-ion battery cathodes 2021 IEEE 16th Nanotechnology Materials and Devices Conference (NMDC) (IEEE) 1–5

[30] Kommeren S, Coenen M J J, Eggenhuisen T M, Slaats T M W L, Gorter H and Groen P 2018 Combining solvents and surfactants for inkjet printing PEDOT:PSS on P3HT/PCBM in organic solar cells Org. Electron. 61 282–8

[31] Sliz R, Lejay M, Fan J Z, Choi M J M J, Kinge S, Hoogland S, Fabritius T, Pelayo García de Arquer F and Sargent E H 2019 Stable colloidal quantum dot inks enable inkjet-printed high-sensitivity infrared photodetectors ACS Nano 13 11988–95

[32] Li T, Yuan X-Z, Zhang L, Song D, Shi K and Bock C 2019 Degradation mechanisms and mitigation strategies of nickel-rich NMC-based lithium-ion Batteries Electrochem. Energy Rev. 3 43–80

[33] Yabuuchi N, Kubota K, Aoki Y and Komaba S 2016 Understanding particle-size-dependent electrochemical properties of Li, MnO2-based positive electrode materials for rechargeable lithium batteries J. Phys. Chem. C 120 875–85

[34] Sliz R, Suzuki Y, Nathan A, Myllyla R and Jabbour G 2012 Organic solvent wetting properties of UV and plasma treated ZnO nanorods: printed electronics approach Org. Photovoltaics XIII 8477 84771G

[35] Sliz R, Huttunen O-H, Jansson E, Kemppainen J, Schroderus J, Kurkinen M and Fabritius T 2020 Reliability of R2R-printed, flexible electrodes for e-clothing applications npj Flex. Electron 4 1–9

[36] Garlapati S K, Divya M, Breitung B, Kreuk R, Hahn H and Dasgupta S 2018 Printed electronics based on inorganic semiconductors: from processes and materials to devices Adv. Mater. 30 1707600

[37] Ping W, Wang C, Wang R, Dong Q, Lin Z, Brozena A H, Dai J, Lao J and Hu L 2020 Printable, high-performance solid-state electrolyte films Sci. Adv. 6 8641–59