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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 fulfil 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

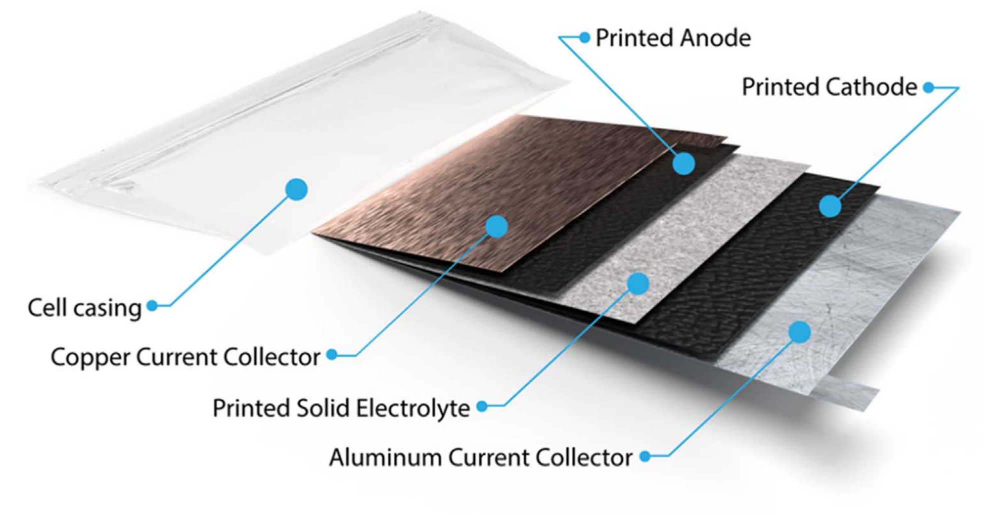

Figure 1. Architecture of pouch SSBs with printed solid electrolyte and electrodes.

Table 1. Main advantages and disadvantages of solid-state and liquid electrolytes in Li-ion batteries [5].

Solid electrolyte	
Advantages	Disadvantages
1. Excellent chemical and physical stability 2. Perform well as a thin film (≈1 μm) 3. Ionic conductivity only (excludes electron) Transference number = 1	1. Reduced contact area with electrodes 2. Interface stress due to charging and discharging 3. Lower ionic conductivity than liquids
Liquid electrolyte	
Advantages	Disadvantages
1. Excellent contact area with the electrode 2. Can accommodate volume expansion at the electrode during cycling 3. High ionic conductivity	1. Poor physical and chemical stability 2. May rely on the formation of Solid Electrolyte Interface (SEI) layer 3. Both ionic and electronic conduction. Transference number typically 0.5

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} $S\cdot cm^{-1}$, which is comparable to organic liquid electrolytes (ethylene carbonate and dimethyl carbonate)–10^{-2} $S\cdot cm^{-1}$ [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].

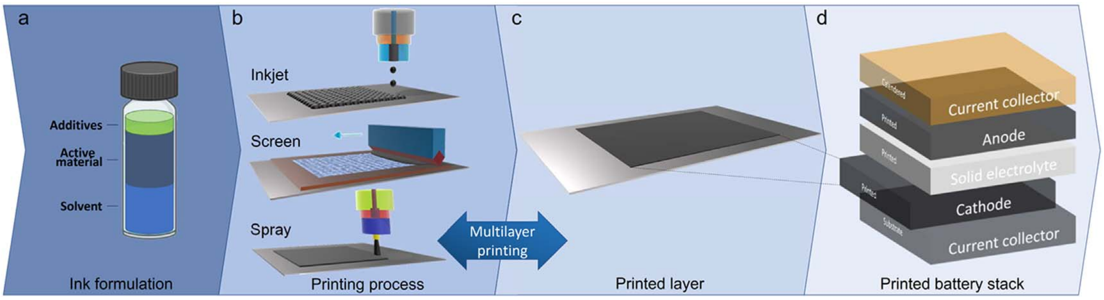

Figure 2. (a) Printable ink formulation for different layers of solid-state batteries. (b) After the ink formulation, the solution is used to either screen, inkjet, or spray print the battery layer. (c) First printed layer (cathode) of multilayer printing process. (d) Solid-state Li-ion battery architecture consisting of printed cathode, solid electrolyte, anode, and two metallic current collectors.

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

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 ($LiMn_2O_4$ (LMO), $LiFePO_4$ (LFP), $LiCoO_2$ (LCO), $LiNiCoAlO_2$ (NCA), $LiNiCoMnO_2$ (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 ($\leqslant$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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