Three-dimensional printing of high-mass loading electrodes for energy storage applications

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Abstract
Nanostructured materials afford a promising potential for many energy storage applications because of their extraordinary electrochemical properties. However, the remarkable electrochemical energy storage performance could only be harvested at a relatively low mass-loading via the traditional electrode fabrication process, and the scale of these materials into commercial-level mass-loading remains a daunting challenge because the ion diffusion kinetics deteriorates rapidly along with the increased thickness of the electrodes. Very recently, three-dimensional (3D) printing, a promising additive manufacturing technology, has been considered as an emerging method to address the aforementioned issues where the 3D printed electrodes could possess elaborately regulated architectures and rationally organized porosity. As a result, the outstanding electrochemical performance has been widely observed in energy storage devices made of 3D printed electrodes of high-mass loading. In this review, we systemically introduce the basic working principles of various 3D printing technologies and their practical applications to manufacture high-mass loading electrodes for energy storage devices. Challenges and perspectives in 3D printing technologies for the construction of electrodes at the current stage are also outlined, aiming to offer some useful opinions for further development for this prosperous field.

KEYWORDS
3D printing, electrode structures, energy storage devices, high-mass loading, thick electrodes

1 | INTRODUCTION

To optimize our energy structure and reduce the dependence on nonrenewable fossil fuels, our society is accelerating its electrification. In this context, electrochemical energy storage systems play an indispensable role in deploying clean transportation, modern information technology, and so forth. In the past decades, high-energy lithium-ion batteries (LIBs) and high-power supercapacitors (SCs) have aroused tremendous interest from...
both scientific and industrial communities, leading to the explosive development of these energy storage systems. The recent booming of the Internet of Things, 5G communication technology, artificial intelligence, smart electronic devices, and so forth, imposes increasing requirements on energy storage devices that drive continuous interest in overhauling these systems. After years’ intensive exploration, the performance of many electrode materials has approached their theory limits through rational regulation of their nanostructures, providing excellent possibilities to boost the practical performances of LIBs and SCs. Nevertheless, the extraordinary electrochemical performance of these nanostructured electrode materials is mainly harvested at relatively low-mass loadings (<1 mg cm\(^{-2}\)). In the real electrochemical devices, a large number of auxiliary components are needed and a low mass loading of active species could only offer very limited energy density. Therefore, in order to pave the way to producing practically workable energy storage devices, high-mass loading (>1 mg cm\(^{-2}\)) electrodes are indispensable. However, an electrode consisting of active materials, polymer binders, and conductive additives operates using coupled dynamics and thick electrodes with high-mass loadings usually complicate these processes because of the tortuous diffusion paths and randomly distributed undesired interfaces.

A viable strategy to address the aforementioned issues is to rational construction of electrode architectures with elaborately organized pores of different scales and tailored interfaces. Nevertheless, the commercially available blade-casting technology fails to fulfill these requirements due to the lack of control during the assembly of different components into an electrode architecture. In this regard, a myriad of emerging manufacturing technologies have been widely explored, such as slurry coating, infiltration, magnetic-assisted oriented assembly, wood- or ice-templating, flow-directing assembly, and so forth. Multiple preparation steps or complicated chemical reactions are inevitable in the aforementioned processes. In addition, flexible design and manufacture of electrodes with elaborate structures is difficult to achieve. By contrast, three-dimensional (3D) printing techniques exhibit more practicability for offering a flexible, efficient, and economical maneuver to fabricate high-mass loading electrodes and/or energy storage devices. As a result, 3D printing is highly tunable and offers excellent flexibility in precisely controlling the geometrical shape, thickness, and porosity of the printed electrodes. 3D printing can realize the device construction during the manufacture of electrodes, reducing the subsequent procedure of device assembly and packaging. 3D printing is environmental-friendly and cost-efficient as the unique electrode construction process can largely prevent the waste of the raw materials.

Because of these unique merits, 3D printing has been widely used to construct high-mass loading electrodes for robust energy storage recently. As a result, a timely summary of the recent progress is of paramount importance to draw continuous attention to this emerging field. After a brief discussion of the categories of 3D printing
technologies and their working principles, we focus on their special role in elaborately regulating the architecture of electrodes with high-mass loading for high-performance rechargeable batteries and SCs. Then, the pressing challenges of 3D printing technologies for energy storage applications and the outlook of the possible directions in the near future are summarized, aiming to prompt the further development of this prosperous field.

2 | 3D PRINTING TECHNOLOGIES

3D printing was first developed by Sachs et al. at Massachusetts Institute of Technology in the early 1990s, and the prototype was a powder-based manufacturing approach. At the initial stage, the research attention mainly focused on metals and ceramics as the precursors for the rapid production of diverse metal and ceramic architectures. Then, 3D printing has found extended applications in a wide spectrum of emerging fields including biology, medicine, automotive, aerospace, engineering, energy storage, and so forth, which employ diverse precursors. According to American Society for Testing and Materials (ASTM), 3D printing mainly includes the following 7 categories: (1) Material extrusion (ME), (2) Binder jetting (BJ), (3) Material jetting (MJ), (4) Powder bed fusion (PBF), (5) VAT photopolymerization (VAT-P), (6) Sheet lamination (SL), (7) Direct energy deposition (DED). These different 3D printing technologies are schematically depicted in Figure 2. Among them, the most commonly used 3D printing technologies for constructing electrodes/devices are direct ink writing (belonging to ME), fused deposition modeling (belonging to ME), stereolithography (belonging to VAT-P), and selective laser sintering (belonging to PBF). Therefore, we restrict our discussion to them in the following sections to emphasize their unique merits for facilitating energy storage applications. More details about the other 3D printing technologies can be inquired in articles specialized in 3D printing.

2.1 | Direct ink writing

Direct ink writing (DIW) is a typical type of ME processes, which can build arbitrary structures in a layer-by-layer manner by spraying inks with a nozzle. The accuracy and resolution of the printed structures depend on the rheological properties of printing inks and the resolution of the equipment. The prerequisite for DIW process is to endow printing inks with ideal rheological behavior. In general, the

![FIGURE 2](image-url)
printing inks should meet the following requirements. First, the inks should be non-Newtonian fluid. In other words, the apparent viscosity of the printing inks should decrease with the increasing shear forces inside the nozzles. In addition, the inks should possess certain self-supporting property to avoid the flow and deformation of fabricated structures when the extruding process stops. A wealth of additives are highly effective to modulate the rheological properties of printing inks. In an example, Compton and Lewis reported an epoxy-resin based printing ink with nano-clay platelets and dimethyl methyl phosphonate (DMMP) as additives. Specifically, nano-clay platelets could endow both shear yield stress and shear-thinning behaviors to the inks while DMMP is capable of lowering the initial viscosity of epoxy resins for improved solids loading. Besides, milled carbon fibers and silicon carbide whiskers with high-aspect-ratio were also filled in the epoxy resins to enhance the mechanical properties. Because of the tailored properties, this epoxy resins-based printing ink enabled the production of printed structures with elaborately designed morphology (Figure 3(A) left). Meanwhile, the fibers with high-aspect-ratio would distribute along the printing direction, which helps to enhance the mechanical properties of the printed architecture (Figure 3(A) right). In another attempt, Zhu and his collaborators fabricated electrodes for SCs via a DIW process using graphene oxide suspension containing graphene nanoplatelets and hydrophilic fumed silica as additives. Because of the essentially improved viscosity, storage modulus, and yield stress, the ink offered ideal rheological behavior for 3D printing, allowing the controlled construction of the 3D hierarchical graphene aerogels SCs electrodes with periodic macropores. Because of the elaborately regulated structures, the 3D printed electrodes can allow fast ion diffusion even with an ultrahigh thickness. Therefore, the SCs based on the printed electrode deliver a higher power density and energy density.

Despite these successes, there are still some drawbacks needed to be addressed for further extending the utilization of the DIW technology for energy storage. One concern is that most of the additives of printing inks are insulated that would inevitably deteriorate the electrical conductivity, thus influencing the electrochemical performance of the printed electrodes. As a result, an additive removing process is usually needed after the DIW process, which will complicate the electrode fabrication. In this context, printing inks free of additives are highly demanded. Gratson and Lewis formulated the printing inks by employing poly(acrylic acid) (PAA) sodium salt and poly(ethylenimine) (PEI) as anionic polyelectrolyte and cationic polyelectrolyte, respectively. The phase behaviors and rheological properties of the inks can be easily controlled by changing the relative content of PAA and PEI. By adjusting the chemical compositions of inks and deposition reservoirs, the polyelectrolyte composite exhibited the desired rheological property, which can quickly congeal during the printing process. Moreover, the choices of polyelectrolytes may be rationally expended to other polyelectrolyte systems, such as those based on
biologically, optically, or electrically active polyelectrolytes. In addition, MXenes, the atom-thick transitional metal carbides/nitrides, are also the widely used additive-free active materials because of the metallic conductivity and solution processability.\textsuperscript{57} In summary, the endowment of printing inks with optimum rheological behaviors is always indispensable for a DIW process.

The main advantages of the DIW process lie in the relatively broad choices of raw materials, including colloids, nanoparticles, organic materials and so forth. Besides, it can be directly printed on almost any surfaces. Therefore, DIW technology exhibits a strong possibility for energy storage applications. However, the endowment of the printing inks with desired rheological behaviors is complicated, which may increase the cost of manufacturing and limit the choices of raw materials.

### 2.2 Fused deposition modeling

Fused deposition modeling (FDM) represents another promising type of ME technology, which is one of the most popular 3D printing technology in both academia and industry. The schematic diagram of FDM is shown in Figure 3(B). The extrusion heads are heated to melt the thermoplastic materials, which will solidify once being extruded from the extrusion heads. During the printing process, two extrusion heads usually work together synergistically. One is used to extrude thermoplastic materials, the other is applied to extrude temporary supporting substrates when fabricating porous objects.\textsuperscript{52,58} Then, the temporary supporting substrates are removed by manual stripping or dissolving in aqueous solutions after the printing processes.\textsuperscript{59-61}

During the FDM process, the printing materials must be fluid at elevated temperatures and be able to transfer heat efficiently. Thermoplastics including polymers, polymer matrix composites, polymer ceramic composites, nanocomposites, and fiber-reinforced composites are commonly used for the FDM process.\textsuperscript{62}

Up to now, polymers are essential in the FDM process because of their appropriate melting temperatures. The common polymers in the FDM process include polylactic acid (PLA), polymethyl methacrylate (PMMA), polyamide (PA), polypropylene (PP), polycarbonate (PC), and acrylonitrile-butadiene-styrene (ABS).\textsuperscript{63-68} Maurel et al. printed graphite-PLA-based composite filaments to assemble anodes for LIBs by the FDM process. Such printed electrodes could offer a specific capacity of 200 mAh g\textsuperscript{−1} at 18.6 mA g\textsuperscript{−1} (C/20) after 6 cycles and 140 mAh g\textsuperscript{−1} at 37.3 mA g\textsuperscript{−1} (C/10).\textsuperscript{69} FDM process is energy-efficient with negligible precursor waste and has been considered as a promising technology to develop commercial 3D-printed energy storage devices.\textsuperscript{70} However, the low printing resolution, the poor electrical conductivity of plastic filaments, and limited choices of the raw materials represent the bottlenecks for FDM.

### 2.3 Stereolithography

Stereolithography (SLA) is another form of 3D printing process that belongs to the VAT photo-polymerization technology. The precondition of using SLA technology to fabricate objective models is to precisely control the solidification of liquid resins through a photo polymerization process. The exposure of the printed resin under a digital light projector or laser beam driven by a computer would contribute to a solidified casual pattern in the resin. After relocating the platform, another layer of resin could be printed and solidified at the desired position. By repeating the printing, solidification, and relocation for designed times, the three-dimensional products with desired morphologies would be obtained after washing-off the unsolidified resins.\textsuperscript{53,71,72} Figure 3(C) shows two types of SLA devices where their differences lie in the build orientation and the method of illumination.

For a successful photo crosslink, the photocurable moieties in printing materials are of essential significance. Low-molecule-weight polyacrylate or epoxy macromers were first developed for the SLA process, which could generate a glass-like network during crosslinking and polymerization induced by light. Chen et al. exploited a UV-cured poly(ethylene oxide)-based gel polymer electrolyte which showed a high ionic conductivity at room temperature ($4.8 \times 10^{-3}$ S cm\textsuperscript{−1}) and could directly be coated on the electrodes of LIBs without the use of a separator.\textsuperscript{73} In the past decades, some new polymers have been exploited as printing materials. For example, Zehbe et al. designed a photoreactive resin made of methacrylated oligomers, methacrylated monomers, and photoinitiators to be modulated with ionic liquids as printing materials.\textsuperscript{74} The ionic conductivity of the as-prepared ionogel electrolyte reached $7.0 \times 10^{-4}$ S cm\textsuperscript{−1} at room temperature and $3.4 \times 10^{-3}$ S cm\textsuperscript{−1} at 90°C. Moreover, the ionogel electrolyte exhibited enhanced thermal and mechanical stability, which could be used in batteries or fuel cells.

Compared with ME technology (such as DIW and FDW), SLA can truly design the printed objectives of almost arbitrary shapes. Very recently, a graphene-based photocurable resin has drawn increasing attention as the printed objectives could be endowed with the excellent electrical conductivity and mechanical stress, which offered new afflatus for the construction of high-performance energy storage device using the SLA.
Nevertheless, suitable resins are quite rare which largely restricts the real application of the SLA process in the field of energy storage.

2.4 | Selective laser sintering

Selective laser sintering technology (SLS) is commonly known as selective laser melting (SLM), which is a powder bed fusion process. As reflected in Figure 3(D), a laser beam is used to melt and fuse the selected parts. After lasering, the platform is relocated for the deposition of another layer of printing material, which will undergo laser irradiation at the desired position. After repeating the aforementioned steps, the desired architectures would be created after removing the un-lased regions. The SLS process generally carries out in an inert atmosphere to protect the printed materials from oxidation during the lasering. The architecture created via this process is mainly affected by the hatch spacing, layer thickness, laser power, and scanning speed.

The printing materials in the SLS process can be metal, polymer, ceramic, and composites. The main advantage of the SLS is the rich choices of printing materials compared with other 3D printing technologies, which provides excellent opportunities to fabricate 3D-printed electrodes for energy storage devices in a highly efficient way. Sha et al. synthesized free-standing 3D graphene foams (3D-GFs) of arbitrary shapes by lasering the mixed power of Ni and sucrose through the SLS process. This 3D-GFs obtained from the SLS process exhibit a low density (~1.5×10⁻² g cm⁻³), high porosity (~99.3%), high electrical conductivity (about 8.7 S cm⁻¹), and high damping capacity (~0.06), which showed huge potential in fields including energy storage, sound absorption, damping materials, and so forth. In addition, the laser irradiation could induce intrinsic defects in materials that could essentially enhance the performance of the printed structures for energy storage applications. However, the relatively low printing resolution, high cost, and complicated operation largely hinder the real applications of the SLS technology at the current stage.

3 | 3D PRINTING OF HIGH-MASS LOADING ELECTRODES

3.1 | Rechargeable batteries

Rechargeable batteries dominate the current market of electrochemical energy systems. Among them, LIBs represent the most appealing one and exhibit a wide range of applications including electrical vehicles, consumer electronics, information technologies, and so forth. Recently, a myriad of emerging technologies, such as Li-S batteries, metal-air batteries, and so on appear with worldwide attentions. The bulk-phase involved ion-diffusion process within the electrode materials renders the batteries with high-energy densities but deteriorated power capability. Although the nanostructured electrode materials offer essentially reduced diffusion path for ions within the electrode materials, the improved performance is mainly harvested at low-mass loading which cannot satisfy the requirements of many current and emerged applications. As a result, the designed construction of thick electrode without deteriorating the performance of nanostructured materials plays a pivotal role. 3D printing technology has afforded the capability of scaling the outstanding performance of nanostructured electrode materials into ultrathick electrodes. Practically, the 3D printed thick electrodes are built through either of the following procedures: (1) a 3D porous framework is constructed for active species loading; (2) the active materials are formulated into printing inks to directly fabricate thick electrodes of arbitrary shapes. Because of the rationally designed architectures with elaborately organized pores and penetrated networks for charge transfer, the electron and ion transfer within the electrode are largely reconciled.

DIW is the most widely employed 3D printing technology to fabricate high-mass loading electrodes for rechargeable batteries, due to the low cost and flexible choices of raw materials. In addition, the well-designed electrode structures can achieve the coexistence of high-mass loadings and high energy densities in energy storage devices. Chen et al. used an ink composed of graphene oxide (GO), SiO₂ nanoparticles, and phenolic resin to print a 3D scaffold for sulfur loading after subsequent heat treatment and hydrofluoric acid etching (Figure 4(A,B)). Such an architecture possesses periodic pores that are interconnected, thus facilitating the electrolyte infiltration (Figures 4(C-E)). Meanwhile, the scaffold consisting of reduced GO (Figures 4(F,G)) renders efficient electron transfer in the thick electrode. Moreover, the hierarchically porous network favors high sulfur loading. Because of these structural merits, the decent electrochemical performance in terms of large specific capacity, excellent rate capability, and long-term stability is offered at a sulfur loading of 10 mg cm⁻² (Figures 4(H–J)).

Energy storage devices with interdigitated electrodes are an appealing power source for many on-chip devices used for information technology. Such a configuration eliminates the use of separator while the two interdigitated electrodes are separated by a narrow gap (Figure 4(K)). As a result, the distance and thickness of the electrodes play an important role in determining their electrochemical performance. Due to the high controllability
of the 3D printing technology, the gap width and the thickness of electrodes can be carefully adjusted. Fu and co-workers employed solid-state gel polymer electrolyte and GO-based composite inks to prepare 3D printed LIBs using the DIW technology, where LiFePO$_4$ (LFP) and Li$_4$Ti$_5$O$_12$ (LTO) were used as the cathode and anode materials, respectively. The digital images of the 3D-printed components are shown in Figure 4(L). SEM images reveal that the active materials are dispersed uniformly in the r-GO matrix and the porous filaments are stacked tightly, which ensures excellent mechanical performance and electrical conductivity of the 3D-printed electrodes (Figure 4(M)). Even at a mass loading of 18 mg cm$^{-2}$, the entire 3D-printed full battery still showed remarkable cycling stability and high initial charge/discharge capacities (Figure 4(N)).

Despite these successes, the strict requirements of the DIW process on printing materials largely prevent its further use in the field of energy storage. Another widely used 3D printing technology to construct thick electrodes
is the FDM process, which imposes less requirements on printing materials if only they are thermoplastic. Maurel and co-workers prepared a PLA/graphite filament by the FDM process, which can be used as the anode of LIBs (Figure 5(A)). To facilitate the printing process, 11 wt% of the plasticizer (PEGDME500) was introduced into the PLA/graphite matrix contributing to an ink with low rigidity and enhanced ductility. As such, quite complex 3D structures could be easily printed (Figure 5(B)). SEM observation reveals that the graphite particles are uniformly distributed in the PLA matrix (Figure 5(C)) and the mass loading of graphite can reach 49.2 wt% of the total mass. When the thickness reached about 250 μm, the printed anode disk shows an outstanding reversible capacity of 200 mAh g⁻¹ at 18.6 mA g⁻¹ (C/20) after six cycles and 140 mAh g⁻¹ at 37.3 mA g⁻¹ (C/10). In another attempt, they further prepared the PLA/LiFePO₄, PLA/graphite filaments, and PLA/SiO₂ filaments, making the cathode, anode, and separator of LIBs through the FDM process. By using the new design, it is possible to fabricate a variety of separator patterns with different infill densities capable of improving the impregnation of the liquid electrolyte and avoiding short-circuits (Figure 5(D)). In addition, multifarious shapes of whole “one-shot” LIBs can be designed and printed (Figure 5(E,F)). Although the reversible capacity of these assembled batteries remained to be improved, the designing idea facilitated by the FDM process opens a new avenue to prepare high-performance rechargeable batteries of arbitrary shapes.

SLA is a type of light-assisted 3D printing techniques, in which a light source is applied to polymerize a photocurable resin and a solid polymeric layer is obtained eventually. Compared with extrusion-based 3D printing techniques, such as FDM mentioned above, truly arbitrary designed structure can be constructed by SLA since this process is not restricted by the toolpath or serial extrusion. Also, a distinct characteristic of SLA lies in its relatively high accuracy. Chen et al. used NaCl as granular support and photosensitive resins as carbon precursors to fabricate cellular carbon microstructures using the SLA technology. In addition, graphite particles could be introduced during the printing process to improve electrical conductivity and mechanical

![A](image1.png) ![B](image2.png) ![C](image3.png) ![D](image4.png) ![E](image5.png) ![F](image6.png)
performance. In contrast to the traditional technology to construct cellular carbon microstructures, SLA offers better controllability on the cell structures and overall morphologies. The cellular carbon microstructures fabricated via the simple SLA and subsequent carbonization process (Figure 6(A)) show excellent mechanical strength (elastic modulus: 23.9 MPa, compressive stress: 0.36 MPa) and outstanding conductivity (0.43 S cm$^{-1}$). Apart from its capability of producing the conductive framework as electrodes, the SLA technology could also be used to fabricate and optimize the gel and/or solid-state electrolytes for rechargeable batteries.$^{73,74,94}$ Traditionally, the electrolyte is introduced via an independent process apart from the electrodes, thus complicating the manufacturing process.$^{95-97}$ In contrast, the SLA can directly print gel and/or solid-state electrolytes on the electrodes, which will not only simplify the fabrication process, but also customize the electrolytes according to practical requirements. The use of solid-state electrolytes will not only provide enhanced safety, but also offer more choices about electrode materials to increase the energy densities of energy storage devices at the same time. In addition, high ions transference numbers, flexible shapes and a wide range of operating temperatures are also the important reasons of exploiting solid-state electrolytes.$^{98-102}$

Alternatively, the SLS features with using a focused laser as the power source for 3D prototyping, allowing the range choice of materials if only thermally fusible.$^{103}$ Furthermore, the SLS is capable of constructing complex 3D structures. The solvent evaporation and sintering post-processing steps are unnecessary in the SLS process, which means that the handling time can be significantly reduced.$^{92}$ These merits make the SLS a remarkable technology for the accurate manufacture of exquisite structures for energy storage devices. Acord et al. prepared 3D NCA (LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$) for LIBs cathodes with SLS process (Figure 6(B)).$^{92}$ The prepared 3D NCA electrodes with high-mass loading exhibited graded microstructure, dual-phase states, and rational porosity, exhibiting huge potential for next-generation LIBs' cathodes. It is worthy to note that the laser irradiation process can also introduce structural defects to electrode materials, precisely manufacture heterostructures and electrode architectures at the same time, providing designing thoughts from several aspects to elaborate high-mass loading electrodes.$^{78}$

To simultaneously combine the advantages of different 3D printing technologies, distinct printing processes could also be rationally combined for improved controllability. Wei and co-workers applied a DIW process to prepare the thick cathode and anode made of LiFePO$_4$ and Li$_4$Ti$_5$O$_{12}$, respectively.$^{93}$ To produce ideal printing inks, active materials (LiFePO$_4$ or Li$_4$Ti$_5$O$_{12}$) and KB carbon particles were added into the lithium bis (trifluoromethane) sulfonamide/propylene carbonate solution. Meanwhile, they also prepared

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**FIGURE 6** A, Digital photo of cellular carbon microstructures. Reproduced with permission.$^{91}$ Copyright 2017, Elsevier. B, Schematic diagram of fabricating 3D NCA with SLS process. Reproduced with permission.$^{92}$ Copyright 2020, Elsevier. C, The sketch map of fully 3D-printed LIBs and printing inks. D, Areal capacity for the fully printed LIBs (left). Areal capacity of full (unpackaged) cells of varying electrode thickness at 0.2 mA cm$^{-2}$ (right). Reproduced with permission.$^{93}$ Copyright 2018, Wiley-VCH
UV-curable composite inks to make packaging and separator for LIBs through an SLA process. The sketch map of fully 3D-printed LIBs and printing inks is shown in Figure 6(C). Such a device exhibits superior areal capacity (4.45 mAh cm\(^{-2}\) at 0.14 mA cm\(^{-2}\)) and the corresponding value of full (unpackaged) cells is 14.5 mAh cm\(^{-2}\) at 0.2 mA cm\(^{-2}\) with electrode thickness up to 1 mm. (Figure 6(D)).

### 3.2 Supercapacitors

SCs, owing to their rapid charging and discharging, have been applied in many areas where high power densities are needed\(^{104-107}\). Generally, SCs can be divided into electrical double-layer capacitors (EDLCs) and pseudo-capacitors\(^{108-110}\). EDLCs store the charges by electrostatically adsorbing electrolyte ions on the surface of active
materials, for example porous carbon. The pseudo-capacitors utilize the fast and reversible redox reactions on the surface of active materials to store charges. Among them, functionalized nanocarbons, transition metal oxide/hydroxide/sulfide/nitride, conductive polymers, MXenes, and MOFs are commonly used as the active materials for pseudo-capacitors.111-114 Since the energy storage processes are largely confined at the surface of electrode materials, the energy density of SCs is much smaller than that of the rechargeable batteries.115 One viable solution to improve their energy density is to construct a thick electrode using high-performance nanostructured materials, which can be realized using 3D printing.40

The DIW process is also the most frequently used 3D printing technology to manufacture high-mass loading electrodes for SCs. Li et al. reported the print of ultra-thick electrodes with honeycomb structures using a printing ink consisting of MXenes, MnO NWs, and C60 (Figure 7(A)).116 The as-printed electrodes show a high specific surface area and hierarchical porosity (Figure 7(B)). The Ag NWs and MnO NWs are interpenetrated and uniformly distributed in the whole 3D matrix, allowing rapid charge transfer (Figure 7(C)). As a result, the assembled SCs still exhibit an excellent areal capacitance of 216.2 mF cm−2, a high energy density of 19.2 μWh cm−2, a large power density of 58.3 mW cm−2 with the electrodes as thick as 500 μm (Figure 7(D)).

Then, the DIW technology has been applied to manufacture porous networks for active species loading. A great breakthrough in fabricating super thick electrodes with ultrahigh mass loading via the DIW process was made by Yao et al.117 Specifically, GO and hydroxypropyl methylcellulose were dispersed in water to form a printing ink for the construction of the frameworks of interdigitated graphene aerogels. After subsequent heat treatment and electrodeposition, an ultra-high amount of nanostructured MnO2 was decorated on the frameworks for pseudocapacitive energy storage (Figure 7(E)). Compared with graphene aerogels synthesized by traditional methods, 3D-printed graphene aerogel shows superior conductivity with enhanced charge transfer (Figure 7(F)). Under the same MnO2 loading amount (~45 mg cm−2), 3D graphene aerogel/MnO2 electrodes exhibited a higher areal capacitance. Meanwhile, the recorded areal capacitance was realized on this electrode (44.13 F cm−2) with a thickness of 4 mm and the MnO2 loading mass of 182.2 mg cm−2 (Figure 7(G)). Moreover, the symmetric SC made of two thick 3D graphene aerogel/MnO2 electrodes still kept remarkable capacitive behaviors (Figure 7(H)).

Despite the popularity of the DIW technology, its applicability in the fabrication of freestanding 3D-printed energy storage devices is unsatisfactory because of the complicated layering and curing processes. To address this issue, the DIW process has been rationally combined with the FDM technology. For example, Tanwilaisiri et al. used the FDM process to print the frame of the SCs, after which the DIW was employed to prepare the current collector layer, electrode layer, and the separator (Figure 8(A)).118 They investigated the influence of electrode thickness on the capacitance, of which the value increases from 0.133 to 0.295 F when the electrode thickness increases from 0.5 to 2.0 mm. The promising results deny the adverse effects on capacitance with the increase of the electrode thickness.

The promising potential of the SLA technology in preparing electrodes of SCs has been highlighted by its low-cost, high efficiency, and high accuracy. By using the SLA, Chang et al. developed a 3D multicellular structure with negative Poisson’s ratio as the framework to load active materials for capacitive energy storage.119 Then, an electrophoretic deposition was jointly used to produce a 3D CoNi2S4/NiCo-LDHs electrode (Figure 8(B)). The as-obtained 3D-printed networks offer a step-shaped structure rendering a large specific surface area and abundant growth sites, which allow a high-mass loading (Figure 8(C)).

The SLS has also been used to produce high-mass loading electrodes for SCs. Zhao and co-workers created an interdigitated SC using the SLS (Figure 8(D)).120 Interestingly, the thickness of interdigitated electrodes could be adjusted in a wide range (from hundreds of nanometers to millimeters) without deteriorating the specific capacitance and rate performance. Compared with its planar counterpart, the areal capacitance is obviously enhanced at least by one order of magnitude.120-122 In addition, the binders and separators could be eliminated, which would further increase the capacitive performance.123

4 SUMMARY AND OUTLOOK

The rapid development of nanotechnology enables the full utilization of the electrochemical properties of nanostructured materials at low-mass loading but fails to scale their extraordinary performance to commercial-level electrodes. One key reason is that the traditional blade-casting process for constructing electrodes exerts insufficient control over their microstructures where the ion diffusion and electrical conductivity deteriorate at thick electrodes. As an emerged additive-manufacturing technology, 3D printing has aroused increasing attention because of its capability to address this daunting issue. By employing this technology, the hierarchical porosity and electrical conductivity network could be rationally organized even within in thick electrodes. Currently, 3D printing can be divided into seven categories where four
types of them, namely DIW, FDM, SLA, and SLS, have been widely used in the field of energy storage. These different printing processes are compared in Table S1. Among them, the DIW offers the highest applicability where a wide range of materials could be printed into high-mass loading electrodes but the restrict requirements on the rheological behaviors makes the formulation of suitable printing inks challenges. The FDM is capable of rapid printing at a relatively low cost. However, the resolution of this process is low that limits its wide applications. The SLA partially combines the advantages of the DIW and FDM processes, which makes it quite promising. The further utilization of this technology requires the extension of the range of raw materials. As for the SLS, the low resolution and high operation cost remain the formidable challenges for its wide applications. The typical thick electrodes with high-mass loading are summarized in Table S2. Due to the rationally modulated electrode architectures, the decent electrochemical performances could still be harvested even at mass loading as high as 100 mg cm$^{-2}$ which really represents a breakthrough in exploring the electrochemical properties at commercial-level mass-loading. As a result, the tremendous efforts devoted to these emerging fields may help the further commercialization of energy storage devices employing the nanostructured electrode materials.

Despite the remarkable progress made in the past few years, the real application of 3D printing technology in constructing high-mass loading electrodes remains challenging and the main unsolved issues at present are as follows: (1) At the current stage, only a small number of electrode materials could be 3D printed. The 3D printing
processes generally obey very strict operation principles that impose strict requirements on the fundamental properties of the raw materials. As a result, the electrode materials that can be printed have been restricted to a very limited range. In some printing processes, additives need to be involved in the printing inks to regulate the rheological behaviors which may need to be removed after the architectures are constructed. This may result in undesired pores and even cracks within the thick electrodes that deteriorate their mechanical stress. (2) Most studies about 3D printing techniques paid little attentions to packaging materials, separators and current collectors for rechargeable batteries and SCs. Therefore, the manufacture of all-3D printed integrated energy storage systems by one printing procedure is still challenging. (3) Since each type of 3D printing processes has its own unavoidable limitations so that when diverse types of 3D printing techniques need to be integrated. However, the drawback of one process may hide the merits of others, rendering troubles for the rational combination of different printing processes. (4) The resolution of the most type of 3D printing is by far restricted to micrometer scale, making the precise regulation of the nanoscale pores difficult. To essentially address the aforementioned challenges, knowledge from different disciplines such as physical chemistry, physics, mechanical engineering, optical engineering, and so forth, are urgently needed. As a result, the collaborations of researchers with different backgrounds are highly demanded.

The potential of 3D printing in manufacturing thick electrodes for robust energy storage has been unraveled recently. Within a few years, the mass loading of 100 mg cm\(^{-2}\) has been realized without deteriorating the outstanding electrochemical performance of nanostructured materials, of which the loading mass has increased by two order of magnitude. The devices based on such electrodes will undoubtedly offer a several-fold increase in the practical performance. It is well known that the progress of energy storage devices largely lags behind the development of other modern technologies, such as information technology and consumer electronics. With the arrival of the 5G era, higher requirements on energy storage devices will undoubtedly be imposed while 3D printing technology may provide a viable solution to address this formidable challenge. Based on this consideration, we highly believe the 3D printing-mediated construction of high-mass loading electrodes will be one of the research frontiers in energy storage devices and deserve worldwide attention.

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**CONFLICT OF INTEREST**

The authors declare no conflict of interest.

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SUPPORTING INFORMATION
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