3D printing-enabled advanced electrode architecture design

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Abstract
A high-performance energy storage device plays an important role in controlling carbon emissions. The emerging additive manufacturing techniques bring a great revolution of electrode fabrication process and promote the performance of energy storage devices through the advanced electrode architecture design. In this paper, recent studies on the three-dimensional (3D)-printed electrode with advanced architecture have been mainly reviewed, including interdigitated structure, through-thickness aligned structure, hierarchical porous structure and fiber and fibric structure of electrodes, and expectations for the development of novel advanced electrode architecture generated and optimized by computational simulation and machine learning. The strategy of advanced electrode architecture design and fabrication enabled by the 3D printing technique represents a promising direction toward future energy storage devices with high electrochemical and mechanical performance.

KEYWORDS
3D printing, additive manufacturing, advanced structure, battery, supercapacitor

1 | INTRODUCTION

Energy storage devices such as batteries or supercapacitors play an important role in modern society and the main objective of energy storage device development is to reach the requirement of high energy density and high power density while maintaining a long cycling lifetime at practical serving conditions.1 Among those components of energy storage devices, electrodes play the most important role in deciding their electrochemical performance. Material optimization,2 developing new types of energy storage devices,3 adding chemical additives,4 and advanced architecture design of electrodes are efficient methods to improve the electrochemical performance of energy storage devices. However, traditional electrode manufacturing techniques, such as the two-dimensional (2D) slurry-coating method, limit electrode manufacture with advanced architecture.

Additive manufacturing technique makes the advanced electrode architecture design possible and focuses on improving the performance of energy storage devices.5,6 Additive manufacturing, which is also called three-dimensional (3D) printing, is the rapid-growing advanced manufacture technique with high freedom on the structural design. This advanced technique could realize almost any geometry of electrode with the aid of computer drawing. Besides, the 3D printing technology can extend to a range of materials such as polymer, metal, and metal oxides, carbon,
and ceramics, so high loading active materials such as graphite with various additives like organic binders are possible to be employed to fabricate electrodes. Moreover, the highly automatic manufacture process and facile synthesis routes reduce the cost for commercial electrode fabrication, compared with the traditional manufacturing process.

In this review, we highlighted the critical role of additive manufacturing techniques in advanced electrode architecture design and fabrication. First of all, a variety of 3D printing techniques promising for electrode fabrication had been introduced, and then, we talked about the pattern and its mechanism for the optimization of electrodes, which are shown in Figure 1. Next, the reported works about 3D-printed electrodes with advanced architecture design were classified according to the types of supercapacitors or batteries. Finally, the possible insights for the future development of 3D-printed electrodes with advanced architecture were provided.

2 | 3D PRINTING METHOD OF ELECTRODE

Architecture design of electrodes is an effective way to improve the energy density and power density of energy storage devices such as batteries and supercapacitors. Traditional fabrication techniques have limitations in controlling the geometry and architecture of electrode and electrolyte, whereas the emerging 3D printing method provides great opportunities to accurately control the architecture of materials (e.g., dimension, porosity, and morphology) and enhance the energy density and power density of energy storage devices. Therefore, different types of 3D printing techniques such as direct ink writing (DIW), fused deposition modeling, stereolithography, and binder jetting have been used to fabricate electrodes.

![Diagram of 3D printing for emerging advanced electrode architectures.](image-url)
2.1 | The generic 3D printing process

3D printing needs a series of procedures—from the model design by software to posttreatment, following basic principles of additive manufacturing (Figure 2). First, the materials are prepared by basement materials choice and additives adjustment to accommodate the printing condition and objects properties. Then, using slicer software, the computer-aided design 3D model is converted into sliced layer data, and printing parameters such as path planning and support constructing are set up. Finally, printing and posttreatment process are conducted to print the customized 3D objects with required properties, such as conductive electrodes with advanced architectures.

2.2 | Direct ink writing (DIW)

DIW, which is defined as those technologies designed to build freeform structures or electronics with feather resolution in one or more dimensions below 50 μm, is the most widely used 3D printing method for energy storage devices due to its ability to print 3D electrodes with high mass loading of active materials and easier operational processes. As shown in Figure 3A, the DIW techniques include continuous filament approaches and droplet-based approaches. As the DIW deposition is based on the shear-thinning mechanism, the preparation of inks with sufficiently high viscosity and shear-thinning behavior to allow for smooth extrusion and shape retention is essential. Besides, the high mass loading of active materials can be used in inks to improve the areal capacitance and energy density of energy storage devices. However, the DIW method shows difficulty to obtain high-resolution and large-volume objects, which is less suitable for commercial applications.

2.3 | Fused deposition modeling (FDM)

FDM is a 3D printing technique to create 3D objects by selectively depositing continuous filament from the nozzle under heating to form the designed 3D pattern on the platform layer-by-layer (Figure 3B). Most of the materials of filament are thermoplastics such as acrylonitrile–butadiene–styrene (ABS) or poly (lactic acid) (PLA), and they are heated to their melting state before extrusion from nozzles and solidified after deposition on the substrate. Similar to the DIW method, the FDM method can also be used in the electrode fabrication process. However, different from the DIW method, conductive active materials must be incorporated with thermoplastics such as ABS or PLA filaments for continuous extrusion from the nozzle. The printed 3D objects by fused deposition modeling showed excellent mechanical properties and durability over time. However, the leading component of nonconductive thermoplastics in the composite material greatly decreases the electrode conductivity. Increasing the percentage of conductive materials or removing the nonconductive thermoplastic materials through postprocess processes such as calcination and etching is an effective way to overcome this issue.

2.4 | Stereolithography (SLA)

SLA is a 3D printing process by solidifying photocurable resin using light scanning (Figure 3C). The photocurable resin is composed of photoinitiators, liquid monomers, and oligomers. During printing, the fine laser scans the photocurable resin and induces the photopolymerization process to solidify the liquid. Due to the focus of the small size of the laser spot, very fine structures with high resolution in the range of hundreds of micrometers can be produced by utilizing the SLA technique. However, similar to FDM method, photopolymers used in SLA can only be employed for prototyping use, some essential functional materials for photocurable resin such as graphene oxide and ceramics are
needed as additives, and the printed 3D objects require pyrolysis in an inert environment at high temperature to remove polymer materials for energy storage devices application.

2.5 Binder jetting (3DP)

Binder jetting (3DP) is an additive manufacturing process in which droplets of binder (such as photopolymer or thermoplastic materials) are selectively deposited on the powder bed to bind these loose particles together and form a 3D object with a specific structure (Figure 2D). Binder jetting can manufacture very large parts and complex metal geometries, and it is not limited by any thermal effects, which makes this method the most promising techniques for large-scale energy storage devices such as electric cars. Besides, binder jetting can print conductive metal or carbon parts with full-color prototypes due to the multiple nozzles printing together, which is suitable for electrode manufacture with multiple components. Figure 3D shows the binder jetting process with thermally reduced graphene oxide (rGO) as powder bed to fabricate 3D-printed electrode.18

2.6 Others advanced 3D printing methods

Besides carbon-based materials, metal materials can also be used in 3D printing techniques such as selective laser melting (SLM) or direct metal laser sintering (DMLS) for energy storage device application. SLM is a process that uses a high-power laser beam as an energy source to melt and fuse the fine metal particles together to form very dense 3D metal objects.8 However, DMLS only melts and binds the parts of particles at their contact points with saved energy to form the porous structure.19 Although it can save energy, it is not easy to change the formation, as the powders are not fully melted. As another 3D printing method, inkjet-based deposition methods can also print metal products using liquid materials mixed with metal nanoparticles. This 3D printing method has faster printing rates and better resolution than typical powder bed-based 3D printing methods such as SLM or DMLS.20 The 3D-printed metal objects can be employed as conductive 3D support for active materials and the well-designed structure creates and facilitates the path for ions penetration as well as electrons transportation.

3 Advanced Electrode Architecture Design

Electrodes are the main parts of a battery and a capacitor. With the increasing demand for high power density and energy density of battery and capacitor, electrode designs have been changed from 2D plane shape to 3D-architected structure, because there is a trade-off between power and energy density in the battery with 2D electrodes. The 3D-engineered electrodes enable to achieve the high performance of the battery and capacitor by the increased
surface area of electrodes for electrochemical reaction. In the past, researchers have used diverse techniques like etching and machining, but these are limitations to making optimized 3D structures. Recently, additive manufacturing, which is also called 3D printing, has got attention as the main manufacturing process, owing to its design flexibility and multiscale fabrication. The enhanced electrode structures achieve not only the high surface area but also high structural integrity, resulting in advanced electronic devices. In this section, several developed electrode designs including octet truss, lattice, and hierarchical structure are described.

3.1 Traditional planar structure

The planar structure, which is shown in Figure 4A, is the most widely used architecture of electrodes in batteries and supercapacitors. Due to the limitation of the traditional slurry-coating method, the active materials of electrodes can only be coated on the current collector layer-by-layer to form the 2D geometries. The 2D planar structure electrodes perform well in the commercial and laboratory applications. But the requirement of high energy density and power density of next-generation energy storage devices needs the employment of thicker electrodes, which is one of the big issues of the 2D planar structure due to the sluggish ions and electrons transfer. Also, other practical applications of energy storage devices such as wearable batteries are difficult to realize on the 2D planar electrodes. In summary, the traditional planar electrode plays an important role in the energy storage application due to the easy access of manufacturing process through layer-by-layer coating, high surface area for ions/electrons transferring, and good flexibility properties, whereas such 2D structure shows apparent drawback when it is applied to the thick electrodes. As the electrodes become thicker to have high area capacity and high energy density, the actual power of batteries or supercapacitors using these electrodes is getting lower. This is mainly caused by the high tortuosity, which is defined as the ratio of effective actual path length to the straight-through path length of the electrode.21 The high tortuosity induced slower ions/electrons transport and lower actual power, the cracks and breakdown of layered thick electrodes, and the damage to the environment during the electrode manufacture process due to the organic solvent usage that limits the application of the traditional planar structure in thick electrodes.

3.2 Interdigitated structure

The interdigitated structure electrode is a kind of structure where the “fingers” of the cathode and anode of devices are closely interconnected with each other in an interleaved way (Figure 4B).14 Such interdigitated method increases the...
contact area of two sides of electrodes greatly, and the reduced ion transfer distances between cathode and anode decrease the conductive resistance of the whole device. Compared with planar structure electrodes, the relative complex interdigitated structure electrodes can only be fabricated by 3D printing methods and a variety of 3D printing techniques are possible to achieve the interdigitated structure electrode, such as DIW, FDM, SLA, and so forth. Among those 3D printing methods, the DIW methods are reported mostly due to their simple operational skills and adjustable active materials for ink printing.

3.3 | Through-thickness aligned structure

In the application of thick electrodes, the high tortuosity of traditional planar structure electrodes for ions/electrons transfer leads to the limited utilization of active materials and high resistance, which results in the confined energy storage and fast electrodes fading, whereas the through-thickness aligned structure reduces the tortuosity of ions/electrons transport and avoids such fatal issues. The high mobility of electrolyte ions and the reduced electron transportation pathways improve the power density, and at the same time, the increased thickness of electrodes enhances the energy density of the battery and supercapacitor, so the high energy density and high power density can be realized simultaneously by through-thickness aligned structure design. The low tortuous vertically aligned array helps the ion transport within the electrodes (Figure 4C), withstands volume change, and enhances the physical stability of electrodes by contributing to the cycling stability. Plenty of 3D printing methods can achieve such through-thickness aligned structure such as FDM and SLA. With precise controlled extrusion or curing of electrode materials on one axis, the thick electrode with an aligned structure can be fabricated.

3.4 | Hierarchical porous structure

The hierarchical porous structures own a high surface area for high-performance electrode applications (Figure 4D). The enhanced surface areas by macroscale and nanoscale porosity disperse the electrons distribution on the electrodes, which decreases the local current density during the charging/discharging process, and they can also strengthen mechanical properties (stiffness, strength, and toughness) of the structures by mitigating mechanical stresses in the electrodes. Moreover, hierarchical 3D electrodes facilitate electrolyte transport through the electrodes, which results in high power performance. For example, the hierarchical porous lattice grid structure is made up of a series of intersecting lines and widely used for 3D ordered porous electrodes with high surface area and short electrolyte ions diffusion pathways. The high surface-to-volume ratio increases the utilization of active materials and the engineered hierarchical microlattice structure helps electrolyte ions penetrate inside the electrodes, which provide the ideal performance of thick electrode at a high rate. Also, the hierarchical porous microlattice structure can be fabricated easily by 3D printing techniques such as DIW and FDM.

Among all kinds of hierarchical porous structures, the hierarchical octet truss structure is one of the special hierarchically porous structures with extraordinary mechanical properties (Figure 4E). The cellular octet truss structure has high stiffness and strength due to its stable triangular structure, and its stiffness and strength are linearly proportional to relative density (volume fraction of materials corresponding bulk state). The architected structures can obtain good mechanical properties at low density and they can be applied to the designs of electrodes requiring high mechanical properties.

3.5 | Fiber and fibric structure

Wearable energy storage devices with flexibility and breathability can be realized by fiber or fibric electrode design, which is impossible to meet the need for conventional electrodes. The scalable, low-cost, and high-efficiency 3D printing method can realize the flexible fibers that are woven into fibric structure electrodes (Figure 4F). The fibric electrodes own the sufficient porosity for air exchange and enough stretching ability like cotton textiles, and they demonstrate good flexibility and high electrochemical performance, and at the same time, the breathability of wearable energy storage devices textile is guaranteed. As a result, the 3D-printed fiber structure electrode can be potentially integrated into textile fabrics for future wearable electronic applications.

4 | 3D-PRINTED ELECTRODE FOR SUPERCAPACITOR

Supercapacitor, as one of the energy storage devices, is a high-capacity capacitor with a capacitance value much higher than other capacitors and it bridges the gap between electrolytic capacitors and rechargeable batteries. 3D printing techniques have been widely used to achieve high areal capacitance and long cycling lifetime of supercapacitors by rational control of high surface area
3D-conductive frameworks with precise interior hierarchical nanostructures and low-tortuosity structure-reversing traditional high-volume bulk-building electrodes of supercapacitors. Besides, the flexible customized electronics fabricated by highly stretchable polymer materials can be easily manufactured with the aid of 3D printing techniques. As a result, 3D printing techniques benefit a lot to electrode fabrication of supercapacitor. According to the energy storage mechanism, supercapacitors can be classified into a double-layer capacitance and pseudocapacitance supercapacitors.

4.1 Double-layer capacitance supercapacitor

Double-layer capacitance supercapacitor stores energy through electron absorption on the surface of two sides of electrodes (Figure 5A), such as graphene or carbon black electrode double-layer capacitor with high surface areas. DIW method has received more attention for double-layer capacitance supercapacitor due to the ability to print electrode with high mass loading of active materials. For example, Li et al. printed a double-layer capacitance microsupercapacitor with high-concentration graphene/DMF dispersion ink. The high viscosity (about 40 cP at 20°C) and environment-friendly terpineol was used to concentrate graphene and adjust ink rheology, and a small amount of polymer (ethylcellulose) was added into the harvested graphene/DMF dispersion to protect the graphene agglomeration. The combination of solvent exchange and polymer stabilization techniques enables the formulation of stable graphene inks with high-concentration and compatible fluidic characteristics for efficient and reliable inkjet printing, and the printed microsupercapacitors achieve a high specific capacitance of 0.59 mF cm\(^{-2}\) and a rapid frequency response time around 13 ms, which deliver a high areal power density of 8.8 mW cm\(^{-2}\).

4.2 Pseudocapacitance supercapacitor

Differing from double-layer capacitance supercapacitor, the pseudocapacitance supercapacitor stores energy by redox and intercalation reaction of metal oxide (Figure 5B,C), such as carbon/metal oxide supercapacitor and MXene supercapacitor. As a result, the pseudocapacitance supercapacitor owns a higher energy density, compared with the double-layer capacitance supercapacitor. For example, Yao et al. developed a 3D-printed graphene aerogel pseudocapacitive electrode with ultrahigh MnO\(_2\) loading (Figure 5D) by the DIW method. The pseudocapacitive materials such as manganese oxide (MnO\(_2\)) exhibit outstanding gravimetric capacitances, and the grid architecture realized by 3D printing avoids the sluggish ion diffusion in thick electrode, which achieves a record-high areal capacitance of 44.13 F cm\(^{-2}\) with high MnO\(_2\) loading of 182.2 mg cm\(^{-2}\) (Figure 5E). Besides, the FDM and SLA techniques have also been reported in double-layer capacitance supercapacitor fabrication. For example, opposed to the selection of typical thermoplastic materials such as ABS or PLA, Yang et al. used the highly electronically conductive active material MXene as the building material and printed electrode with high specific surface area architectures by FDM method, which addressed the challenge of electrical conductivity issue for traditional 3D-printed electrode by FDM method. The additive-free 2D Ti\(_3\)C\(_2\)Tx ink-printed current collector-free supercapacitor exhibited a high gravimetric capacitance of 242.5 F g\(^{-1}\) at 0.2 A g\(^{-1}\) with retention of above 90% capacitance for 10,000 cycles. Besides, Yang et al. reported a 3D-printed double-layer capacitance capacitor using high dielectric polymer/ceramic composite materials by SLA method, and the 3D-printed capacitor composed of photocurable polymer-based Pb(Zr,Ti)O\(_3\)/Ag composite electrode achieved the high specific capacitance of 63 F g\(^{-1}\) at the current density of 0.5 A g\(^{-1}\). The low resistance and ideal capacitive properties owe to the hexagonal patterns of the electrode fabricated by the SLA method.

4.3 Solid-state supercapacitor

Solid-state supercapacitor is a kind of supercapacitor where all the components of devices are in a solid-state. The solid-state supercapacitors (SCs) have attracted increasing interest because they can provide substantially higher specific/volumetric energy density, compared with conventional liquid supercapacitors, and they are promising as new energy storage devices for flexible and wearable electronics application. Similar to conventional supercapacitors, the electrodes are fabricated by active materials such as carbon or metal oxide and the electrolyte is cured gel, and the inks of cathode, anode, and electrolyte need to be adjusted with high viscosities and shear-thinning rheological behaviors, which is the prerequisite for ink writing printing. A large number of 3D-printed solid-state supercapacitors with areal energy density have been reported. For example, Shen et al. first developed the 3D-printed quasi-solid-state asymmetric microsupercapacitors with efficient interdigitated patterning electrodes by DIW method (Figure 6A). The V\(_2\)O\(_5\)/Graphene (GO) ink was used to construct cathode, and graphene–vanadium nitride quantum dots were printed as anode, combining with
quasi-solid-state LiCl–PVA gel electrolyte. The asymmetric capacitor design and integrated structure construction exhibit excellent structural integrity, a large areal mass loading of 3.1 mg cm\(^{-2}\), and a wide electrochemical potential window of 1.6 V (Figure 6B). Consequently, this 3D-printed asymmetric microsupercapacitor displays an ultrahigh areal capacitance of 207.9 mF cm\(^{-2}\) and areal energy density of 73.9 μWh cm\(^{-2}\) (Figure 6C,D), which is superior to the most reported interdigitated microsupercapacitors.

**5 | 3D-PRINTED ELECTRODE FOR BATTERY**

The manufacturing process of battery electrode plays an important role in the electrochemical performance of battery, such as capacity and capacity retention at high current density. For traditional battery electrodes, most of them are fabricated by the blade-casting method, which limits the transport of Li ions and electrons during charging/discharging due to the densely packed 2D
structure. However, 3D printing technique, owing to its freedom in geometry and structure design, can improve the Li ions and electron transport rate greatly by advanced electrode architecture design, and in this way, the power density of battery is improved. Also, the active materials’ loading can be controlled precisely by 3D printing techniques by adjusting the layers of printed active electrode materials to enhance the energy density of battery.

5.1 | Liquid electrolyte-based battery

5.1.1 | Li-ion battery

Li-ion batteries have been widely used as the portable power source for electronic devices in the past two decades. But the high capacity, large energy density and low cost of Li-ion batteries are still needed to achieve the aim of the department of energy. Conventionally, the Li-ion battery electrodes with 2D planar geometry are manufactured by blade-casting method. To improve the capacity of electrode and reach the ideal energy density of the Li-ion battery, a high thickness of the 2D planar geometry electrode is required. However, the thicker electrode means the long Li-ion transfer pathway, which subsequently leads to the poor rate performance and durability of Li-ion battery. Different from the traditional battery manufacturing method, 3D printing technique can be utilized to develop diverse architectures of electrode with high surface area, high electrical conductivity and ion transferability, and good structural stability, which is promising to reach the aim of next-generation Li-ion batteries.

There are various 3D architecture designs of Li-ion battery electrodes to achieve high energy density and high power density batteries. Among those 3D printing methods, DIW is one of the most commonly used 3D printing methods to print Li-ion batteries due to the simple printing mechanisms and low-cost fabrication processes. Besides, the DIW 3D printing method has a broad material selection including ceramics, metal alloys, polymers, and even living cells, which provides it with the ability to print active materials directly with high mass loading. For example, Sun et al. designed the Li-ion battery with LiFePO₄ (LFP) cathode and Li₄Ti₅O₁₂ (LTO) anode microelectrode arrays in an interdigitated architecture by DIW method (Figure 7A,B), which showed a high areal energy density of 9.7 J cm⁻² at a power density of 2.7 mW cm⁻² (Figure 7C). In addition, Fu et al. designed all-component 3D-printed lithium-ion batteries with GO-based electrode composite inks and solid-state electrolyte inks (Figure 7D),
and the entirely 3D-printed full cell with complex structure featured a high electrode mass loading of 18 mg cm$^{-2}$ and delivered initial charge and discharge capacities of 117 and 91 mAh g$^{-1}$ with good cycling stability (Figure 7E,F). Also, the fully 3D-printed LIBs in customized geometries were fabricated by Wei et al.,$^{32}$ which are composed of thick semisolid electrodes (Figure 7G,H). These fully 3D-printed and packaged LIBs delivered a high areal capacity of 4.45 mAh cm$^{-2}$ at a current density of 0.14 mA cm$^{-2}$ equivalent to 17.3 Ah L$^{-1}$, which outperform other reported integrating batteries (Figure 7I). Besides the DIW method, the (SLA) printing method is also used in Li-ion battery manufacturing. For example, Cohen et al.$^{33}$ designed 3D-printed microbatteries with various shapes and sizes by SLA method, which own a tri-layered structure comprising the LFP cathode, LiAlO$_2$–PEO membrane, and LTO-based anode by electrophoretic deposition. When the 3D LFP electrode was cycled from 0.1 to 10 C, a high areal capacity of 400–500 Ah cm$^{-2}$ was obtained on perforated graphene-filled polymer substrate, and the areal energy

![Figure 7](https://example.com/figure7.png)

**Figure 7** Three-dimensional (3D) printable Li-ion batteries. (A) Schematic illustration of 3D interdigitated microbattery architectures. (B) Optical image of LiFePO$_4$ (LFP) ink (60 wt% solids) deposition through a 30-μm nozzle to yield multilayer structure. (C) Comparison of the energy and power densities of printed, unpackaged 3D interdigitated microbattery architectures (3D-IMA) to reported literature values. Reproduced with permission: Copyright 2013, Wiley.$^{13}$ (D) Schematic of the 3D-printed interdigitated electrodes. (E) Cycling stability of the 3D-printed full cell. The inset is a digital image of the 3D-printed full cell consisting of LFP/rGO, Li$_4$Ti$_5$O$_{12}$ (LTO)/rGO, and polymer electrolyte. (F) Charge and discharge profiles of the 3D-printed full cell. Reproduced with permission: Copyright 2016, Wiley.$^{14}$ (G) Schematic representation (expanded view) of fully 3D-printed Li-ion square cell battery. (H) Images (left) and schematics (right) of direct writing of four functional (cathode, separator, anode, and packaging) inks. (I) Ragone plot comparing areal capacity versus current density for the LFP/LTO Swagelok cell with 1-mm-thick electrodes and other reported fully printed and packaged 3DP LIBs. Reproduced with permission: Copyright 2018, Wiley.$^{32}$
density of these full cells was three times more than that of the commercial planar thin-film battery. With these 3D electrode architecture designs, the ideal rate performance of high energy density Li-ion batteries can be realized.

5.1.2 | Li–S battery

Li–S electrode, which has a high theoretical capacity of 1675 mAh g\(^{-1}\) and theoretical energy of 2600 Wh kg\(^{-1}\) when combined with metallic lithium anodes, enables the Li–S battery to be considered as a highly promising candidate for next-generation battery application ranging from electric vehicles to large-scale grid energy storage.\(^{34}\) As for Li–S battery, areal capacity determines the total capacity of the electrode and, consequently, the energy density of full battery. As a result, thicker sulfur electrode with high active material loading is required for high energy density Li–S battery. Thicker sulfur electrode can be realized by the 3D printing method through stacking multilayer active materials during printing. For instance, Shen et al.\(^{35}\) had demonstrated that a thickness of 600-μm sulfur electrode can be printed by stacking six layers, which results in a high reversible capacity of 812.8 mAh g\(^{-1}\).

The limited electronic conductivity of the sulfur leads to low capacity and low capacity retention, especially at high rate performance. Higher electronic and ionic conductivity of sulfur electrode can be optimized by architecture design. For example, Gao et al.\(^{36}\) developed a 3D-printed grid architecture sulfur/carbon (S/C) cathode with commercial carbon black (BP-2000) as host material for sulfur (Figure 8B,C), which contains abundant micropores. Such hierarchical porous structure owns the macro sized pores (several hundred micrometers) produced by 3D printing and nanosized pores (Figure 8A) produced by phase inversion of the polymeric binder polyvinylidene fluoride-hexafluoro propylene, which increased the surface areas of electrode for Li\(^+\) transport channels. At high active sulfur loading of 5.5 mg cm\(^{-2}\), high initial discharge specific capacity of 912 mAh g\(^{-1}\) and capacity retention of 85% within 200 cycles at high C-rates of 2 C are realized (Figure 8D), much better than sulfur electrode without such microarchitecture design, which showed a low capacity of 186 mAh g\(^{-1}\) and low capacity retention of 43.4% at C-rate of 0.5 C.

Also, the “shuttle effect” of sulfur electrode is another important challenge of Li–S battery for practical application, which leads to the dramatic losses of active sulfur and capacity decay during cycling process. Shuttle effect refers to the formation of soluble intermediate lithium polysulfides (Li\(_{3}\)S\(_n\), 3 < n < 8) as ions transport media during cycling, which come from the reversible dissolving of sulfur electrode into the liquid electrolyte and are deposited on the anode.\(^{37}\) To hamper the shuttle effect, numerous studies concentrated on developing electrolyte additives to suppress the polysulfide shuttle and passivate the lithium metal surface.\(^{38}\) Besides chemical strategies, there are amounts of the structural design of electrodes to encapsulate sulfur into a conductive matrix such as porous/hollow carbon.\(^{39}\) However, for traditional hydrothermal method, low-level sulfur loading and complex preparation steps are inevitable and the structure of the conductive

![Figure 8](https://example.com/figure8.png)

**FIGURE 8** Three-dimensional (3D) printable Li–S batteries. (A) Schematic illustration of 3DP-FDE (freeze-dried electrode) applied in Li–S batteries with excellent Li\(^+\)/e\(^-\) transport in both micro- and nanoscale. (B) Schematic illustration of the 3D printing process for S/BP 2000 thick cathodes. (C) Optical images S/BP 2000 cathodes. (D) Cycling performance of Li–S cells assembled with 3DP-FDE with a sulfur loading of 5.5 mg cm\(^{-2}\) at 0.1, 0.5, 1, and 2 C. Reproduced with permission: Copyright 2019, Elsevier\(^{36}\)
matrix is dominated by thermodynamics and impossible to adjust. But the rational architecture design of conductive matrix with the aid of the 3D printing method to restrict sulfur from dissolving is promising in the future and it is the area where researchers would concentrate.

5.1.3 | Lithium–air (Li–air) battery

The Li–air battery is a metal–air electrochemical cell that uses oxidation of lithium at the anode and reduction of oxygen or carbon dioxide at the cathode to induce a current flow. The Li–air batteries have attracted considerable attention over the past few years, owing to their extremely high theoretical specific energy (energy per unit weight) (3840 mAh g⁻¹) and energy density (energy per unit volume), which are much higher than that of conventional ion-based batteries, so they are promising as the next-generation high energy density batteries. But there is far less practical performance than the ideal theoretical specific energy, which can be optimized by the 3D printing method.

The most significant reason for the limited practical specific energy density of Li–O₂ battery is the insulating effect caused by the deposition of nonconductive Li₂O₂ solid product on the surface of the O₂ cathode upon discharging. An effective strategy to solve the insulating effect of Li₂O₂...
solid product is to modify the thermodynamics of Li$_2$O$_2$ growth inside the solution, in which the Li$_2$O$_2$ can grow as large particles (>100 nm) rather than in the form of thin films on the cathode surface. In this way, the porous conducting matrices are desired to accumulate the large-sized Li$_2$O$_2$ particles, and the increased large contact surface between Li$_2$O$_2$ particles and cathode could facilitate the decomposition of Li$_2$O$_2$ particles during the charging process. For example, Lacey et al. designed the stacked mesh structures with hierarchical porosity and printed them with aqueous 3D-printable holey graphene oxide (hGO) as ink (Figure 9A). Among such 3D-printed hGO porous conducting matrices, accessible large surface area comes from hierarchical (macroscale, microscale, and nanoscale) porosity structure. Compared with a 2D vacuum-filtrated film (VF r-hGO mesh) in which the porosity was induced by the freeze-drying procedure, the 3D-printed mesh's macroscale and microscale porosity enhanced large Li$_2$O$_2$ particles' accumulation and Li$^+$/O$_2$ diffusion, respectively, and dramatically enhanced overall Li–O$_2$ battery performance (42- and 63-fold improvement in full discharge capacity by mass and area) (Figure 9B).

Another important factor that reduces the practical specific energy is the limited mass loading of cathode catalysts on the conducting supporting materials, especially for the porous matrices. The self-standing catalytic monolith is an effective approach to improve the mass loading of the catalysts material and enhance the practical specific energy density of the Li–O$_2$ battery. For example, Lyu et al. designed a self-standing catalyst framework with a hierarchically porous network geometry by 3D printing of cobalt-based metal–organic framework (Co-MOF) (Figure 9C). Rather than just coating or growing the catalysts on the surface of extra porous conducting matrix, they embedded the nanocatalysts into densely packed MOF-derived carbon nanoflakes to form an self-standing framework, which increases the mass loading of catalysts greatly on the porous conducting matrix and electrode performance (Figure 9D,E). Such self-standing cathode architecture with good conductive and necessary mechanical stability carbon materials achieves a high value of 1596 Wh kg$^{-1}$ when discharged at 5.5 W kg$^{-1}$, which is much closer to the theoretical specific energy of Li–O$_2$ battery cathode (Figure 9F).

Besides Li–O$_2$ battery, Li–CO$_2$ battery is also popular in special missions such as space exploration. The consumption of carbon dioxide relieves the accumulation of harmful exhaust gases in the space station, and at the same time, sufficient energy is supplied for equipment operation. But due to the limited catalytic activity toward reversible reaction between lithium and CO$_2$, a high charge overpotential, low recyclability, poor rate capability, and relatively low energy density on the device level become the bottlenecks of Li–CO$_2$ battery application. Qiao et al. explored an ultrathick electrode (≈0.4 mm) with high catalytic activity by anchoring ultrafine Ni nanoparticles (≈5 nm) on a 3D-printed reduced graphene oxide framework via thermal shock (1900 K for 54 ms), which displayed a low overpotential of 1.05 V at 100 mA g$^{-1}$, high cycling stability of over 100 cycles, and good rate capability (up to 1000 mA g$^{-1}$). Also, a high areal capacity of 14.6 mAh cm$^{-2}$ was achieved due to the thick electrode design and uniform distribution of ultrafine catalyst nanoparticles.

### 5.2 Solid electrolyte-based battery

Solid electrolyte-based battery owns extraordinary advantages in terms of safety and stability, which is the most promising high energy density next-generation battery. The solid-state electrolyte generally uses safer nonflammable materials rather than organic carbonate solvents and reactive lithium salts used in conventional Li-ion battery electrolytes, and the strong mechanical properties and high electrochemical stability provide the solid electrolyte-based lithium metal battery with ability to inhibit the growth of lithium dendrite and chemical deposition at high voltage.

However, the solid-state electrolytes lead to extreme high resistance as compared with traditional liquid electrolytes. Poor interfacial contact between the electrolyte and the electrode and the limited ionic conductivity of the thick solid electrolyte are the major cause of high resistance. As for traditional manufacturing method of solid-state electrolytes, flat pellets are the most common architecture and the planar interface minimizes interfacial contact area and increases the battery resistance. However, 3D printing method provides the solution to reduce the battery resistance by constructing complex architecture. There are multiple ink formulations developed for 3D printing and the unique solid electrolyte structures with a variety of patterns can be formed after further sintering. For example, McOwen et al. printed solid electrolyte microstructures by 3D printing method with ceramic material garnet-type Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZ) as a model solid electrolyte material (Figure 10A). The stacked-array pattern provides the electrolyte with higher surface area than traditional planer structure to combine with lithium metal electrode (Figure 10B), and as a result, the interfacial resistance of full cell is reduced (Figure 10C). The dramatically decreased full cell resistance induced by improved interfacial contact areas leads to the higher energy and power density of solid electrolyte-based battery.
6 | CONCLUSION AND PERSPECTIVES

In summary, additive manufacturing techniques performed well in electrode fabrication with advanced architecture and property improvement. Among the various 3D printing techniques, direct writing or ink-jet printing method has been reported surprisingly frequently due to its advantage in high mass loading of electrochemically active material and relative facial manufacturing process. With the development of 3D printing techniques, more and more other advanced printing methods will be employed, which will give their advantage a full play. And additive manufacturing techniques are huge revolution for electrode fabrication. Compared with traditional 2D planar structure fabrication techniques, 3D printing provides a new method to solve the issues of energy storage devices by electrode 3D architecture design. The performance of electrode and assembled energy storage devices such as specific power density, energy density, cycling lifetime, mechanical properties, and so forth, was promoted greatly by advanced and rational architecture design.

Although the 3D printing technique has shown its benefit in the electrochemical performance enhancement such as high power and energy density and mechanical properties improvement by architecture optimization of electrode, there are still several challenges needed to be overcome. One of the greatest challenges of 3D-printed electrodes is material development. Due to the limitation of 3D printing techniques such as FDM and SLA, a large number of nonconducting polymers, such as PLA, are added, so as to form stable 3D-printed objects. And addition of the exceeded liquid electrolyte is another big issue. Although the liquid electrolytes can be replaced by ions-conductive solid-state electrolytes, the development of ultrathin solid-state electrolytes by 3D printing techniques has reached a deadlock. Besides, the posttreatment such as thermal annealing or carbonization is needed to increase the electrode performance further, and the manufacturing techniques to direct fabrication of energy storage devices are scarce. Also, the novel and efficient advanced architectures of electrodes need to be designed with the aid of software design and simulation. Recently, more of the geometries of 3D-printed electrodes are simple and designed by human image rather than scientific theoretical calculation. With the rapid development of machine learning algorithm, more and more advanced architectures of electrodes will
be designed and optimized automatically by artificial intelligence, which not only saves a large amount of time but also develops the full potential of electrode architecture design. Overall, as a revolutionary tool, 3D printing should be used to address fundamental issues of energy storage devices, and it provides more opportunities for the design and manufacturing of high-performance electrodes.

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