Dean&Francis

ISSN 2959-6157

Advancements in 3D printing technology for electrochemical energy storage devices

Kuncheng Tang

Abstract:

Due to the escalating demand for energy transition, electrochemical energy storage devices such as batteries and supercapacitors are progressively emerging as pivotal power sources to shift reliance on inadequate fossil fuels towards sustainable and renewable resources. Nevertheless, conventional manufacturing systems still encounter significant performance barriers in meeting the requirements of Electrochemical Energy Storage (EES) devices, including high energy or power density, portability, and long cycle life. 3D printing, as a computer-aided design manufacturing process, can achieve enhanced precision in geometry, porosity, and morphology of products while improving specific energy and power density. This paper primarily examines the advancements in 3D printed energy storage devices and extensively discusses the merits and drawbacks of each 3D printing technology along with its future development.

Keywords: Electrochemical Energy Storage device, Additive manufacturing, Supercapacitor, Battery

1. Introduction

In recent years, global energy consumption has significantly increased due to the industrial revolution and globalization. Currently, fossil fuels [1] dominate the global energy production system. However, researchers are compelled to explore new methods of energy production and conversion due to the accelerated global warming and rapid depletion of non-renewable energy sources. Electrochemical Energy Storage (EES) [2] technology is one such method that facilitates easy conversion between chemical energy and electrical energy using electrodes along with electron and ion transfers. The electrochemical energy storage system plays a crucial role in the storage of energy generated by solar, wind, and water-based renewable energy sources. It is characterized by its cleanliness, efficiency, and high availability.

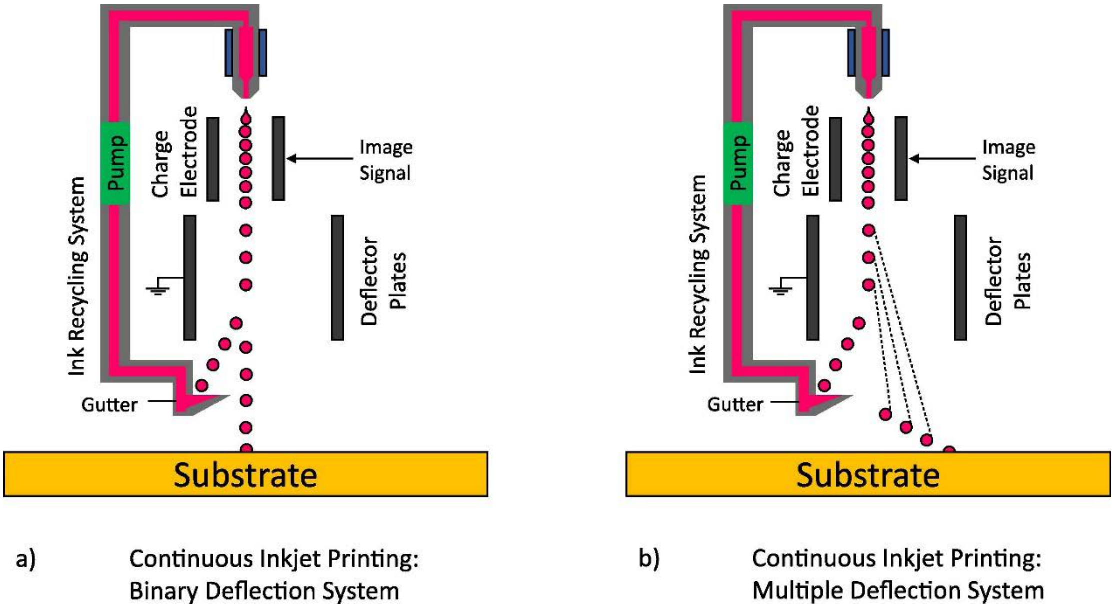
The traditional manufacturing of laboratory electrodes relies on various deposition techniques, [3]. However, these methods fail to meet the requirements of mass manufacturing and are limited in practical application due to complex material processing procedures, special chemical process requirements, and difficult to control the structure of the film [4]. Additionally, the yield is low. In industrial production, Electrochemical Energy Storage equipment is manufactured through fast roll processing followed by electrode machining [5]. The battery includes diaphragm insertion and electrolyte filling before final packaging through re-cutting [5]. This intricate technology requires a long production time and scale. Therefore, 3D printing technology has garnered significant attention as a more efficient, flexible, environmentally friendly and cost-effective alternative for manufacturing. Compared to the conventional manufacturing process of Electrochemical Energy Storage (EES), 3D printing demonstrates superior process flexibility and geometric controllability, enabling enhanced fulfillment of electrode pore and thickness requirements while elevating the energy density per unit area of the energy storage device. Simultaneously, 3D printing significantly minimizes material waste through precise material utilization control [5]. In this review, I will provide a comprehensive overview of the latest advancements in 3D printing for the manufacturing of electrochemical energy storage devices. By showcasing successful application cases of this technology, we will analyze the advantages it offers compared to traditional processes. Finally, we will explore its prospects and challenges.

2. Additive manufacturing techniques

3D printing (3DP), also referred to as additive manufacturing (AM), typically employs computer-aided design (CAD) generated models for the direct fabrication of 3D objects. Additive manufacturing technology can be divided into the seven types according to the Astm standard [6]: (1) material extrusion; (2) powder bed melting; (3) reduction photopolymerization, exemplified by stereoscopic photocuring; (4) material injection; (5) adhesive injection; (6) sheet lamination, like laminated object fabrication; and finally, (7) directed energy deposition, represented by laser clean shape engineering. The currently prevalent 3D printing technologies for EESD encompass 3D Inkjet Printing (3DIJP), Direct Ink Writing, Stereolithography Apparatus (SLA).

2.1 Inkjet Printing

The inkjet printing technology is well established to produce 3D printed electrochemical energy storage devices by electrochemical materials [7]. Depending on how the droplet is produced, inkjet printing can be divided into continuous inkjet printing (CIJ) and on-demand inkjet printing [8]. Continuous inkjet printing involves emitting a continuous stream of ink droplets from a nozzle. These charged material will be deposited on the substrate under the influence of electric field, while the remaining ones are collected for subsequent reuse [8]. The continuous inkjet printing inkjet printing methods can be classified into two categorie (Figure 1). On-demand inkjet printing inkjet printing is more convenient as it ejects ink droplets only, when necessary, achieved by generating pressure pulses to force the droplets out of the nozzle [8]. Compared to continuous inkjet printing method, On-demand inkjet printing inkjet printing is generally more suitable for 3D printed electronics due to its simplicity and reduced wastage. Moreover, the On-demand inkjet printing printhead allows for closer proximity between the nozzle and substrate during the printing process, resulting in reducing the printing error. The inkjet printing methods employed in the on-demand inkjet printing can be categorized into thermal, piezoelectric, acoustic, and electrostatic based on their respective driving mechanisms. (Figure 2).



a) Continuous Inkjet Printing: Binary Deflection System

b) Continuous Inkjet Printing: Multiple Deflection System

Figure 1 a) binary deflection b) multiple deflection [9].

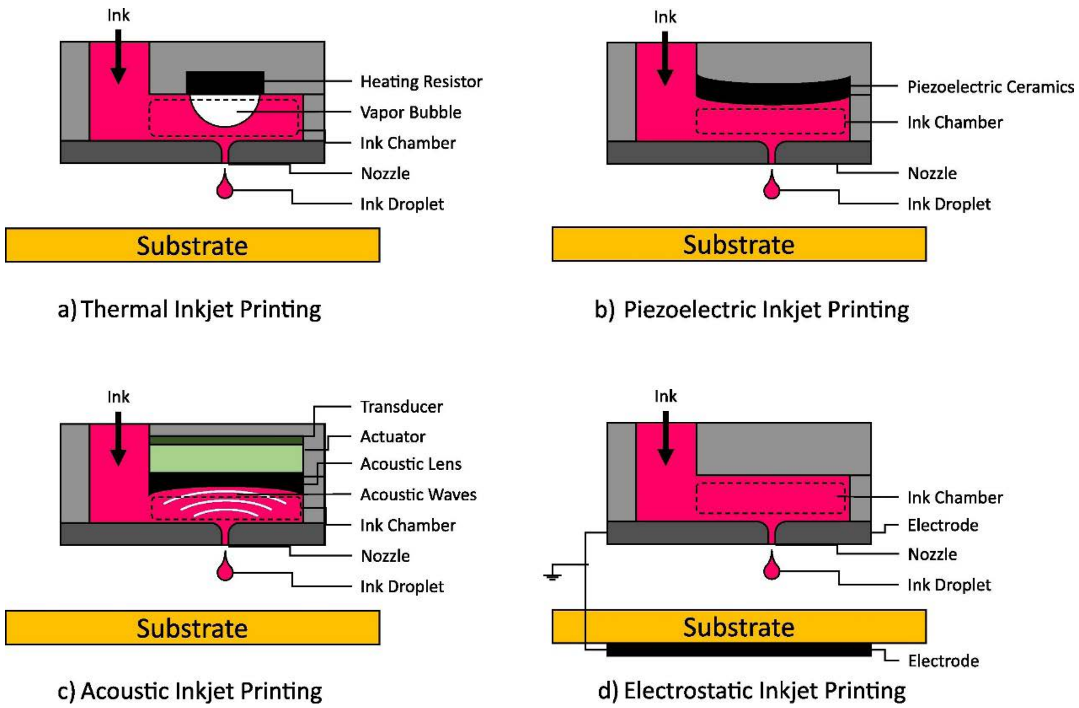


Figure 2 a) thermal inkjet printing; b) piezoelectric inkjet printing; c) acoustic inkjet printing; and d) electrostatic inkjet printing [9].

2.2 Direct Ink Writing

Direct ink writing technology utilizes a nozzle to extrude functional material in a continuous stream for product printing [10], [11]. This technique offers the advantage of accommodating a wide range of viscosities for material distribution [12] and experiencing minimal blockage issues. However, it is slower and has lower printing resolution compared to other methods. Extrusion-based printing can be further categorized into four types based on the extruder utilized (Figure 3) [11], [12].

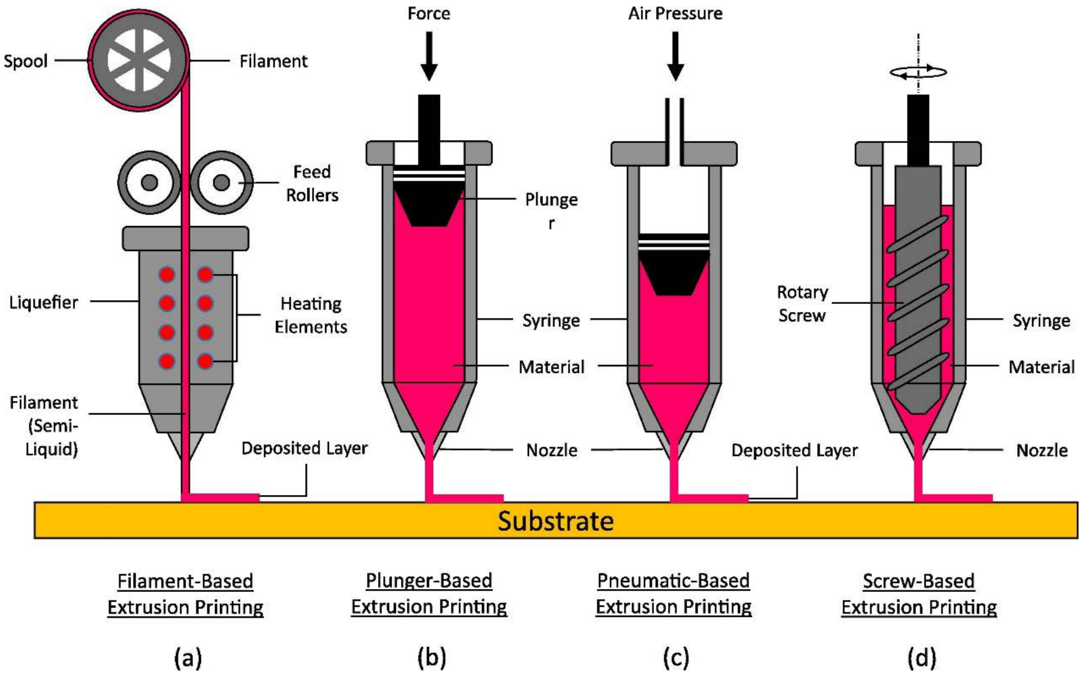


Figure 3. a) filament-based extrusion printing; b) plunger-based extrusion printing; c) pneumatic-based extrusion printing; and d) screw-based extrusion printing [9].

2.3 Stereolithography Apparatus

The stereolithography apparatus (SLA) utilizes computer-aided design (CAD) files to operate stereolithography equipment (Figure 4), which employs photopolymerization-induced liquid resin curing for product formation. By precisely targeting the laser at specific depths within the resin tank, localized polymerization occurs, resulting in resin solidification [13]. In comparison to other 3D printing technologies, stereolithography offers superior surface finish, intricate detailing, and higher resolution (20 m compared to 50-200 m in alternative manufacturing methods) [13], ensuring enhanced accuracy.

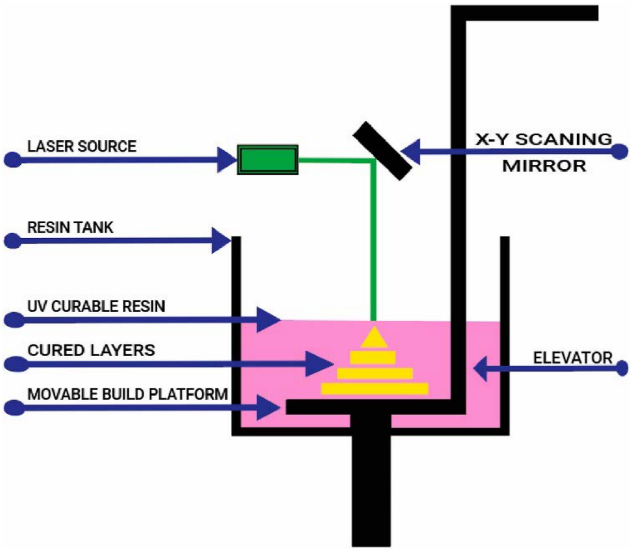


Figure 4. Stereolithography 3D printing. [13]

Table 1 The performance of different additive manufacturing technologies

3D Printing Techniques	Advantages	Disadvantages
Inkjet Printing	High printing accuracy Wide selection of materials High material utilization rate	The nozzle is susceptible to blockage. Functional materials typically require a flat surface for deposition, while the material itself usually has a low viscosity.
Direct Ink Writing	The production process is relatively straightforward. The production cost is low. The material viscosity range is extensive. Nozzles are less susceptible to clogging issues.	The printing speed is comparatively sluggish. The printing resolution is relatively lower.
Stereolithography Apparatus	The printing accuracy is high, enabling the manufacturing of complex three-dimensional structures.	High equipment cost The material is primarily limited to light-curable resins and may not be suitable for all types of electrochemical materials. Post-processing, such as cleaning and curing, is typically required after printing, thereby adding complexity to the process.

3. electrochemical energy storage devices

3.1 supercapacitor

The electrochemical energy storage equipment of supercapacitors enables the storage and utilization of energy by controlling the conversion between electric energy and electrochemical storable energy. As depicted in Figure 5(a), a supercapacitor comprises two electrodes (typically carbon-based materials), an electrolyte, and a separator. The two electrodes establish an electric double layer through the electrolyte, facilitating the storage of a significant amount of charge. Electrochemical energy storage devices can be categorized into electrochemical double layer capacitors (EDLCs), pseudo-capacitors (PCs), and hybrid capacitors (HCs) based on their electrode composition. EDLCs store energy by accumulating charge at the electrode-electrolyte interface while PCs rely on Faraday reactions for charge storage. Their performance primarily depends on factors such as the surface area providing ionic accessibility to the electrode and the conductivity of the

ISSN 2959-6157

electrode material [14,15].

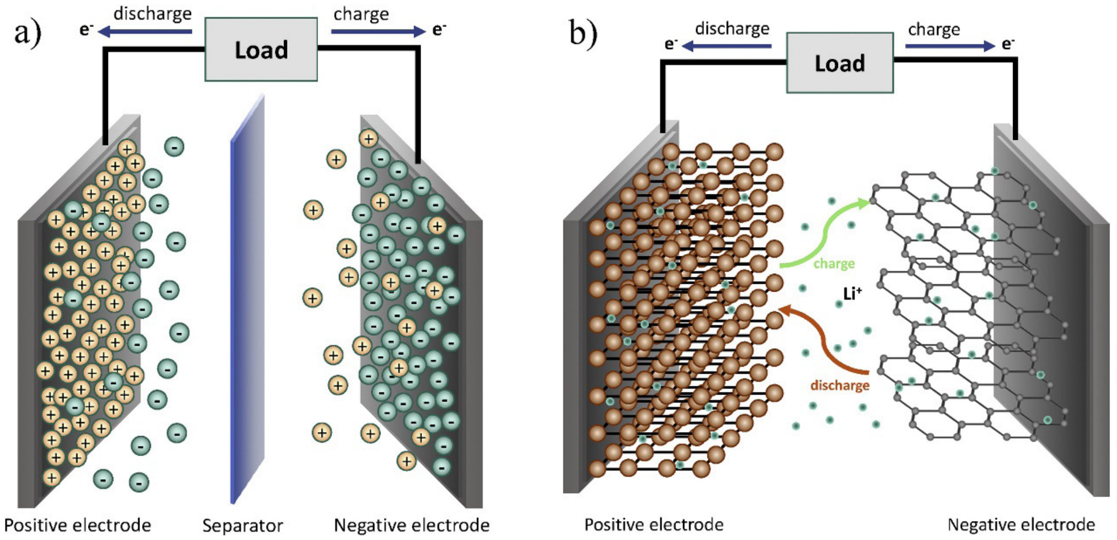


Figure 5. Schematic drawings of (a) supercapacitor and (b) lithium-ion battery. [3]

3.2 battery

The types of batteries include sodium-ion, sodium-sulfur, nickel-metal hydride, nickel-zin, vanadium-redox, zinc-bromine, molten salt, and metal-air batteries et al [3]. Lithium-ion batteries are the dominant technology powering most devices [16]. In lithium batteries, lithium compounds serve as the positive electrode material in LIBs while carbon-based materials are commonly used as negative electrode materials. These materials offer advantages like high conductivity, easy lithium-ion insertion, low charge fluctuation, and affordability. Common electrolytes in lithium-ion batteries consist of lithium salts such as $LiPF_6$, $LiBF_4$ or $LiClO_4$ dissolved in organic solvents [17]. However, the utilization of organic solvents poses hazards due to their inherent flammability and toxicity. [18]. In LIBs, energy is stored during discharge/charge through reversible Li-ion delamination/intercalation on both electrodes as depicted in Figure 5(b).

4. Additive manufacturing method for electrochemical energy storage

4.1 Additive manufacturing applications for supercapacitors

The utilization of 3DP technology allows to produce intricate and sophisticated structures using electrochemistry materials, including graphene and its derivatives. The capacity and efficiency characteristics are predominantly determined by the electrodes. Therefore, it is anticipated that the utilization of 3D printed conductive carbon materials with unique structures will significantly enhance electrode performance.

The Mevada C team drew inspiration from biology to develop a method for 3D printing flexible, long-lasting, harmless supercapacitors specifically designed for low-energy consumption in wireless sensors. [19]. By utilizing substrates, graphite, catechins grafted with activated carbon, electrolytes, cellulose, and corresponding components (e.g., substrates, fluid collectors, electrodes, electrolytes, and membranes), The team successfully developed capacitors that exhibited exceptional capacity, high specific energy, and excellent cyclic stability in experimental trials. The production of electrolytes is achieved through state-of-the-art 3D printing technology, playing a crucial role in facilitating environmentally sustainable manufacturing processes. Figure 6 illustrates the electrode manufacturing and device assembly process. The 3D printing tools utilized can handle a wide range of ink viscosities without the need for electrode masking and eliminating the requirement for overnight soaking. Additionally, they possess an extremely slender nozzle size to facilitate high-precision printing while decreasing electrolyte waste. As depicted in Figure 7(a-b) using the assistance of this technology both bare activated carbon and catechin-grafted activated carbon exhibit galvanostatic charge-discharge curves resembling quasi-rectangular shape or quasi-triangular shape which aligns with the iconic characteristics displayed by electrochemical double-layer capacitors.

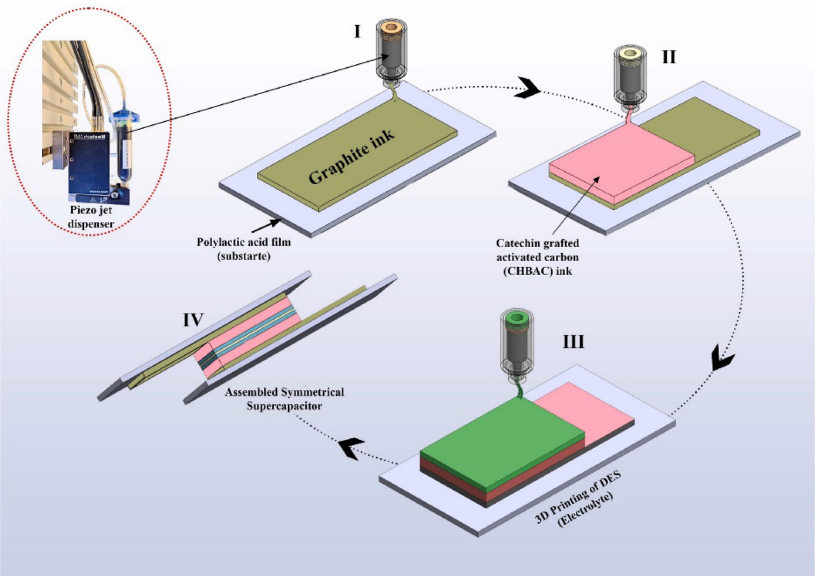


Figure 6. The process of making supercapacitors [19].

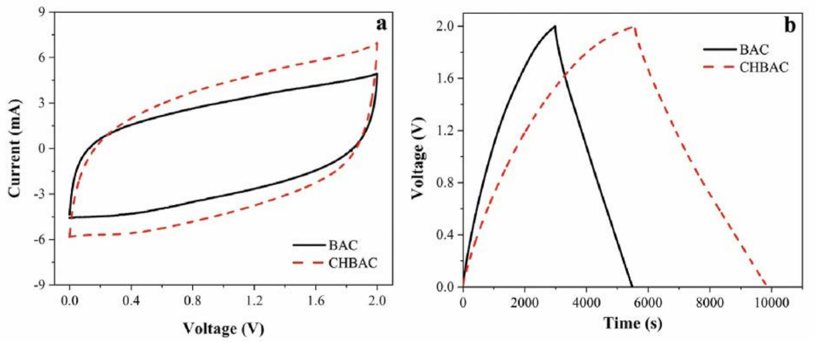


Figure 7. (a) Current and voltage curves of the activated carbon and synthesis of catechin modified bare activated carbon devices compared at a scan rate of 5 mVs^{-1}, (b) Galvanostatic charge-discharge curves of the activated carbon and synthesis of catechin modified bare activated carbon devices recorded at a constant current of 1 mA [19].

The team led by Huang Q, Liu X, and Wang J successfully developed a 3D carbon electrode for the active carbon//$ZnSO_4$(aq)//Zn supercapacitors using 3D printing technology [20]. They conducted comparative experiments on various formulations of electrode slurry to analyze their impact on the mechanical structure, surface area, graphitization concentration, and crystallization properties of the electrodes. The study revealed the effect of assembled zinc-ion hybrid supercapacitors on electrochemical performance. The findings demonstrated that 3D electrodes containing carbon grades ranging from 35% to 40% exhibited superior performance during the process of 3D printing. The elevated concentration of activated carbon significantly enhanced electrochemical performance, primarily attributed to the reduced resistance encountered during charge movement in electrolyte ion reactions. By employing F127 as a binder for printable pastes, this study enables the production of independently layered porous electrode materials suitable for supercapacitors.

Liu Y's team developed a comprehensive 3D printing strategy for fabricating an interdigital MSC_2(micro-supercapacitor) WIS (water-in-salt) gel electrolyte ink with exceptional rheology properties, utilizing a water-based electrode ink and LiCl/SiO [21]. The interconnected exfoliated graphene sheets serve as three-dimensional structures that facilitate the accommodation of active carbon active materials for efficient electron transport, while the self-supporting active carbon/EG electrodes with a porous architecture provide high speed ion transport pathways to increase capacity and capacitance. Consequently, the water-based fully printed planar active carbon- micro-supercapacitor exhibits a steady operating voltage and an ultra-high surface capacitance-energy density, exceeding previous water-based planar micro-supercapacitors. This study thus demonstrates the feasibility and applicability of extrusion-based 3D printing in high-performance electrochemical energy storage devices.

The Gu S's team utilized additive manufacturing techniques to optimize the internal structure of the electrode, thereby enhancing the performance of the miniature supercapacitor. [22]. The layered electrode structure improves the efficient ion transfer in the electrolyte and enhances its permeability. In addition, when comparing the different types of electrodes, his team confirmed that the internal structure of the electrodes is affected by the material. Among them, VCG/MXene micro-supercapacitor exhibited superior electrical property, achieving the best energy density, providing a novel research direction for advancing high-performance 3D printing micro-supercapacitor devices.

4.2 Additive manufacturing applications for batteries

Qiang Li's team conducted experimental analysis on the ion concentration distribution and electrochemical performance of 3D printed graphene aerogel assembled batteries [23]. The findings demonstrate that the pore structure, designed through additive manufacturing, effectively enhances the battery's electrochemical performance. Furthermore, electrodes based on the gradient pore structure proposed by additive manufacturing exhibit significant potential in designing electrodes for various electrochemical energy storage devices.

The discharge capacity of the 2-3mm graded pore electrode is optimized through 3D control, as illustrated in Figure 8 (a). This can be attributed to the presence of larger pores adjacent to the flow field plate, which is conducive to the rapid transport of the electrolyte to the membrane, thus achieving efficient conduction. The presence of small pores adjacent to the membrane side not only increases the surface area and reaction sites, but also contributes to a more efficient cell performance. Additionally, the layered pore structure depicted in Figure 9 (b) enhances energy efficiency by facilitating the redistribution of electrolyte concentrations during flow. Notably, when utilizing a pore size of 2-3 mm, an impressive energy efficiency of 71.18% is achieved. Figure 8 (c) illustrates charge and discharge for batteries with different electrode. It is evident that electrodes featuring a graded hole structure with dimensions of 2-3 mm exhibit prolonged charge and discharge times.

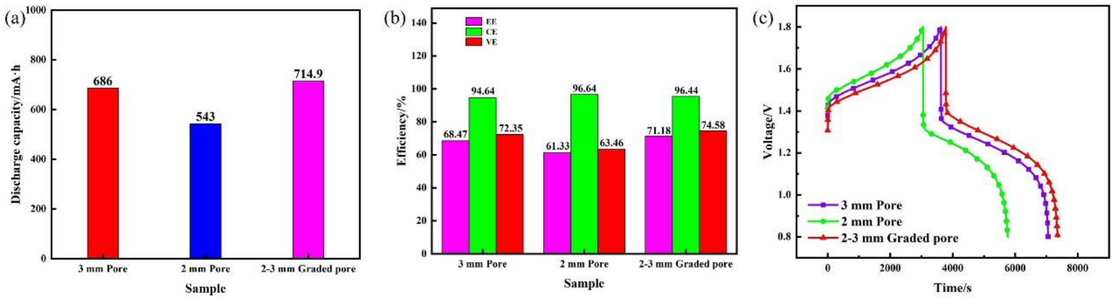


Figure 8. (a) discharge capacity of different samples, (b) coulomb efficiency, voltage efficiency and energy efficiency of different samples, and (c) charge and discharge of batteries with different electrodes [23].

By utilizing additive manufacturing technology, Li Mengrui's team successfully achieved electrodes with high energy density through the construction of conductive nanofiber networks and the incorporation of specialized pore structures [24]. Additive manufacturing technology enables the fabrication of intricate 3D structures due to its inherent advantages in terms of simplicity, versatility, and adjustability in object geometry. Through the utilization of a one-way ice template process during 3D printing, his team successfully created layered porous structures that facilitated efficient ion transfer, mass loading, and enhanced mechanical properties without compromising the integrity of the electrode structure. Ultimately, the researchers developed whole cells consisting of 8 layers, boasting high-performance loads, exceptional surface capacity, impressive energy density, and commendable maximum power density.

5.Conclusion and perspectives

This paper provides a review of the recent advancements in printing technology for electrochemical energy storage devices. Firstly, we introduce the various types of additive manufacturing and their respective performance in electrochemical energy storage devices. Subsequently, we discuss the potential applications, principles of energy storage, and the structure of the supercapacitors and the battery. Finally, we present the latest research on additive manufacturing electrochemical energy storage equipment to demonstrate their immense potential in manufacturing processes. This technology not only enables efficient, cost-effective, and environmentally friendly production but also allows precise control over internal structures and material selection to enhance device performance. Furthermore, there are several areas that can be further improved through enhancements in printing instruments, innovative printing methods, and development of new materials. These improvements hold great promise for optimizing and enhancing additive manufacturing electrochemical energy storage equipment. In conclusion, it is evident that additive manufacturing technology based on electrochemical energy storage equipment holds significant promise and will have a profound impact on future applications within the field of energy storage.

References

[1] Abas N, Kalair A, Khan N. Review of fossil fuels and future energy technologies[J]. Futures, 2015, 69: 31-49.

[2] Ulissi U, Raccichini R. Past, present, and future of electrochemical energy storage: a brief perspective[M]//Frontiers of Nanoscience. Elsevier, 2021, 19: 1-28.

[3] Mensing J P, Lomas T, Tuantranont A. 2D and 3D printing for graphene based supercapacitors and batteries: A review[J]. Sustainable materials and technologies, 2020, 25: e00190.

[4] S. Vozar, Y.-C. Poh, T. Serbowicz, M. Bachner, P. Podsiadlo, M. Qin, E. Verploegen, N. Kotov, A. J. Hart, Review of Scientific Instruments 80 (2009) p. 023903.

[5] Zhang F, Wei M, Viswanathan V V, et al. 3D printing technologies for electrochemical energy storage[J]. Nano Energy, 2017, 40: 418-431.

[6] Astm standard f2792, standard terminology for additive manufacturing technologies. 2013. URL: http://www.astm.org/Standards/F2792.htm.

[7] Espera A H, Dizon J R C, Chen Q, et al. 3D-printing and advanced manufacturing for electronics[J]. Progress in Additive Manufacturing, 2019, 4: 245-267.

[8] Fuh J Y H, Sun J, Li E Q, et al. Micro and bio-rapid prototyping using drop-on-demand 3d printing[M]/Handbook of Manufacturing Engineering and Technology. Springer-Verlag London Ltd, 2015: 2567-2583.

[9] Tan H W, Choong Y Y C, Kuo C N, et al. 3D printed electronics: Processes, materials and future trends[J]. Progress in Materials Science, 2022, 127: 100945.

[10] Ng W L, Chua C K, Shen Y F. Print me an organ! Why we are not there yet[J]. Progress in Polymer Science, 2019, 97: 101145.

[11] Gonzalez-Gutierrez J, Cano S, Schuschnigg S, et al. Additive manufacturing of metallic and ceramic components by the material extrusion of highly-filled polymers: A review and future perspectives[J]. Materials, 2018, 11(5): 840.

[12] Derakhshanfar S, Mbeleck R, Xu K, et al. 3D bioprinting for biomedical devices and tissue engineering: A review of recent trends and advances[J]. Bioactive materials, 2018, 3(2): 144-156.

[13] Husna A, Ashrafi S, Tomal A N M A, et al. Recent Advancements in Stereolithography (SLA) and their Optimization of Process Parameters for Sustainable Manufacturing[J]. Hybrid Advances, 2024: 100307.

[14] Ke Q, Wang J. Graphene-based materials for supercapacitor electrodes–A review[J]. Journal of Materiomics, 2016, 2(1): 37-54.

[15] González A, Goikolea E, Barrena J A, et al. Review on supercapacitors: Technologies and materials[J]. Renewable and sustainable energy reviews, 2016, 58: 1189-1206.

[16] Gallo A B, Simões-Moreira J R, Costa H K M, et al. Energy storage in the energy transition context: A technology review[J]. Renewable and sustainable energy reviews, 2016, 65: 800-822.

[17] Hwang S, Kim D H, Shin J H, et al. Ionic conduction and solution structure in LiPF6 and LiBF4 propylene carbonate electrolytes[J]. The Journal of Physical Chemistry C, 2018, 122(34): 19438-19446.

[18] Zhao W, Yi J, He P, et al. Solid-state electrolytes for lithium-ion batteries: fundamentals, challenges and perspectives[J]. Electrochemical Energy Reviews, 2019, 2: 574-605.

[19] Mevada C, Tissari J, Parihar V S, et al. Bio-inspired 3D-Printed supercapacitors for sustainable energy storage[J]. Journal of Power Sources, 2024, 624: 235529.

[20] Huang Q, Liu X, Wang J. 3D printed pure carbon-based electrodes for zinc-ion hybrid supercapacitor[J]. Carbon Trends, 2022, 9: 100222.

[21] Liu Y, Zheng S, Ma J, et al. Aqueous high-voltage all 3D-printed micro-supercapacitors with ultrahigh areal capacitance and energy density[J]. Journal of Energy Chemistry, 2021, 63: 514-520.

[22] Gu S, Du G, Su Y, et al. Architectural design and optimization of internal structures in 3D printed electrodes for superior supercapacitor performance[J]. Journal of Colloid and Interface Science, 2025, 677: 21-29.

[23] Li Q, Xu J, Wu X, et al. 3D-printed graded graphene aerogel electrode for vanadium redox flow battery[J]. Journal of Energy Storage, 2024, 101: 113951.

[24] Li M, Zhou S, Cheng L, et al. Vertical-channel hierarchically porous 3D printed electrodes with ultrahigh mass loading and areal energy density for Li-ion batteries[J]. Energy Storage Materials, 2024, 72: 103754.