Additive Manufacturing of Electrochemical Energy Storage Systems Electrodes

Davi Marcelo Soares,* Zhongkan Ren, Shakir Bin Mujib, Santanu Mukherjee, Carla Giselle Martins Real, Mabel Anstine, Hudson Zanin, and Gurpreet Singh*

Superior electrochemical performance, structural stability, facile integration, and versatility are desirable features of electrochemical energy storage devices. The increasing need for high-power, high-energy devices has prompted the investigation of manufacturing technologies that can produce structured battery and supercapacitor electrodes with optimized charge transport. While conventional electrode production techniques are becoming increasingly obsolete and incompatible with technological developments such as wearables and flexible electronics, additive manufacturing (AM) has emerged as one of several state-of-the-art tools to produce 3D-structured electrodes with morphology control, high yield, and scalability. Herein, a comprehensive review of the major AM technologies and most recent literature about designing and manufacturing electrode materials for batteries and supercapacitors is presented. A thorough discussion of research opportunities and challenges in this promising field is also presented to introduce the potential and importance of AM to current developments involving electrode materials.

1. Introduction and Motivation

The development of electrode materials that offer high redox potential, faster kinetics, and stable cycling of charge carriers (ion and electrons) over continuous usage is one of the stepping-stones toward realizing electrochemical energy storage (EES) devices such as supercapacitors and batteries for powering of electronic devices, electric cars, and grid storage applications.[1] However, a new multibillion dollar market based on stretchable microelectronic devices and 3D-printed electronics is expected to require novel EES electrode materials and innovative electrode manufacturing approaches for powering them because conventional batteries and supercapacitors may not be suitable for integration in such applications.[2] Although intrinsic properties of electrode materials play an important role in determining their electrochemical performance, electrode fabrication approaches that affect the architecture and design (i.e., features that present direct dependence on stability, rate capability, flexibility/load bearing capabilities) have become important in recent years.[3]

Developed in the 1940s, dr. blade is an conventional technique used for producing battery/supercapacitor electrodes in a lab or at the industry.[4] In this method, a desired gap between a blade and a current collector is maintained while a slurry material is injected onto the metal current collector—either the blade head or the electrode is stationary.[5] Consequently, the blade distributes the slurry material evenly on the current collector at the adjusted thickness—typically 5–200 μm.[6] This method, with its relatively simple working principle, allows relatively good thickness control and scalability. Yet, the produced thin films may present agglomeration of conducting or binding agents, thereby preventing the active material from being accessible for ion or electronic transport and decreasing the electrochemical performance.[7]

It is also important to highlight that although certain parameters in dr. blade method can be tweaked to produce high-performance electrodes, the obtained electrochemical response might not be as per expectation. For instance, one strategy can be to increase the electrode coating thickness by raising the gap between the blade and current collector. This approach is based on the assumption that gravimetric energy density is proportional to the mass of active material, so, in theory, by increasing the electrode active mass will increase net energy stored in the EES. However, a thicker coating by dr. blade yields an extended ion pathway and limits the transport of electrons; thus, leading to higher equivalent series resistance (ESR) and hence higher power losses.[8] Therefore, this approach has proven to be inefficient because it hinders the efficient ionic and electronic transport in the electrode.[9] Another strategy...
increases the packing density of the electrode materials based on the rationale that a high-volume fraction results in enhanced metal-ion and electronic transport in the electrode solid interface. This approach, however, hinders ion transport in the electrolyte.\[9\]

To overcome these drawbacks, tailored electrode materials based on 3D structures are one strategy that combines a number of important advantageous parameters: having a designed topology—with suitable degrees of freedom, ability to process different materials—e.g., liquid solution or powder form, conductive scaffold, high electronic conductivity, structural stability, for efficient insertion and extraction of ions in the material, and shorter diffusion pathways for ions. Therefore, controlling the periodic-printed planar structure and thickness of an electrode allows faster ion transport and a higher mass loading, showing the advantage that customizable electrode architecture of additive manufacturing (AM) possess.\[10\]

These factors together have driven researchers to adopt manufacturing techniques that allow fabrication of electrode features with higher resolution to achieve better EES.\[11\]

AM is a broad concept which consists of employing layer-by-layer advanced techniques using an optimized algorithm to produce functional materials with customized chemistries and architectures.\[12\] The process of using successive layers to build 3D objects is known as 3D printing, whose techniques are shown in Figure 1a.\[13\] Unlike materials subtraction techniques (cutting and milling) or forming procedures (such as stamping and molding), 3D printing allows the fabrication 3D structures via successive layer deposition of the desired material.\[14\] In addition, materials that are arduous when using conventional techniques can be processed into complex shapes with AM.\[15\] AM also simplifies process design and is less labor intensive than subtractive manufacturing.

For EES specifically, AM can provide precise control of a desired geometry to allow facile ion transport while withstanding mechanical stresses imposed by insertion or extraction of ions.\[16\] Zhang et al. found that, due to its computer-aided nature, prototypes may be rapidly available to the market, meaning that AM is not simply a fabrication technique, but it is also an enabling tool for industrialization.\[17]\ AM also has the potential to increase the yield by reducing waste and eliminating intermediate production steps, which is especially relevant when using high-cost materials.\[18]\ In addition, AM utilizes various electrode materials with porosity and electronic conductivity and allows the use of metal anodes with stable plating/stripping (dendrite-free). AM can also produce additive-free electrodes\[19]\ and permits the manufacturing of electrodes that do not require aluminum or copper current collectors, thereby reducing final product costs.\[20]\ As shown in Figure 1b, research on additive manufacturing techniques (AMTs) is gaining traction along with research on EES devices. As a consequence, nowadays the challenge is the manufacturing of EES electrodes with controllable micro- and nanomorphologies through a scalable technique toward higher energy and power densities, lightweight, low volume,\[6]\ and flexible of EES devices. Considering the advantages and potential of AM (Figure 1c), this work first presents a concise description of the main 3D printing techniques for researchers with general interest in AM. Because most reviews on AM for ESS are focused on lithium-ion batteries (LIBs), this Review also presents the latest relevant results of AM of electrodes for alternative technologies to LIBs, namely sodium-ion batteries (SIBs), lithium–sulfur (Li–S) batteries, supercapacitors (SCs), and microsupercapacitors (MSCs)—key technologies for the future of EES systems. Finally, research challenges and perspectives are comprehensively discussed to guide researchers for future studies in AM for EES electrodes.

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**Figure 1.** a) Schematic presenting the typical 3D printing techniques for fabricating electrode materials. b) Number of publications in the literature related to AM and EES. Search for “AM” and “electrochemical energy storage;” search from Web of Science; search time: December 15, 2020. c) Projection of market size for AM.\[213\]
2. Typical 3D Printing Methods

AMTs are resource-efficient, single-unit, production techniques that fabricate complex 3D structures from digital models or data files.\(^{21}\) Compared with the first report of 3D printing by Hideo Kodama in 1981,\(^{22-28}\) current AMTs can process polymers, metals, and ceramics. These state-of-the-art technologies are categorized based on differences in material states and deposition methods.\(^{29}\) AMTs currently can deposit or deliver liquids or solids (bulk or powdered) directly or indirectly to desired locations. AMTs typically used to fabricate solid structures are stereolithography (SLA), fused deposition modeling (FDM), 3D inkjet printing, binder jetting, and direct ink writing (DIW) (Figure 1a). This section concisely discusses AMTs and presents the main information of these technologies.

2.1. Lithography-Based Printing

Lithography-based AMTs fabricate layered structures from photosensitive resins via photocuring using ultraviolet (UV), visible, or infrared (IR) light or lasers.\(^{30}\) The resins are primarily monomers mixed with photoinitiators that initiate photopolymerization triggered by certain wavelengths.\(^{21}\) In most cases, cations or radicals are generated by photocatalysts via light excitation and locally induce polymerization of the monomers, which eventually phase transform into a solid phase.\(^{31}\) Lithography-based techniques are usually indirect AMTs with parts that are solidified in a resin pool and later removed from surrounding liquid environments after manufacturing is complete.\(^{28}\) In 1986, Hull produced SLA, one of the first lithography-based AMTs.\(^{32}\) Similar to other AMTs, SLA uses laser-scanning techniques to point-by-point, line-by-line, and layer-by-layer cure the entire cross-sectional layer, as shown in Figure 2a.\(^{25}\) The outstanding precision of high-quality lasers allows SLA techniques to deliver small feature sizes down to several micrometers (<5 \(\mu\)m).\(^{13}\) Therefore, precision designs, such as pore with controlled size, distribution, and interconnectivities can be fabricated at micrometer levels.

Similar to SLA, digital light processing (DLP) (Figure 2b) is a new type of photocured lithography-based AMT that cures the entire cross-sectional layer simultaneously via digital mirror devices (DMDs).\(^{10}\) Resolution is controlled primarily by pixel dimensions (size of each digital mirror) that can provide a feature size of tens of micrometers. This new printing process advantageously cures the entire plane, thereby greatly reducing the printing time for each layer. Low-cost light sources, such as light-emitting diodes (LEDs), can replace the costly lasers used in SLA. In fact, in some systems, the entire curing of the cross-section is cured by liquid-crystal display (LCD) panels\(^{14}\) or LED arrays.\(^{15}\)

Although lithography-based AMTs usually process liquid materials, solid materials (e.g., ceramics, metals) can be indirectly manufactured via both SLA or DLP.\(^{28}\) The liquid mixtures for printing often contain photopolymers, initiators, and fine powders of target solid materials that are dispersed into the liquid polymers; during exposure, solid powder grains are bonded and shaped as the polymer hardens. However, postprocessing is essential to fully densify the printed components, including the removal of the bonding materials (or debonding) and sintering.\(^{16}\) Polymer binders can be removed via thermodecomposition, but some polymers (preceramic polymers) may also convert to ceramics, or polymer-derived ceramics (PDCs).\(^{36-38}\) Compared with direct AMTs for these solid materials, such as selective laser sintering (SLS) or selective laser melting (SLM), indirect techniques increase the quality (accuracy or smoothness) in bulk and surface of the parts.\(^{16}\)

![Figure 2. Schematic illustration of 3D printing methods. a) SLA. b) Lithography-based DLP. c) Two-photon lithography for template-assisted electrodeposition. d) Inkjet printing. e) Binder jetting. f) DIW. g) FDM. h) AJP.](image-url)
2.2. Template-Assisted Electrodeposition

Electrodeposition effectively controls and synthesizes magnetic alloys or intrinsically conductive polymers via tunable specs such as pH, additives, temperature, and current density. Therefore, template-assisted electrodeposition (TAE) has been widely used to produce micro- to nanofeatured wires, tubes, and films for electrochemical purposes via pre-grown or etched templates. Utilization of TAE as an AMT, however, often requires another 3D printing method to first process a 3D template for electrodeposition. Electrodeposition of solid materials into 3D templates is of interest due to the simplicity and feasibility of synthesizing dense nanocrystalline metallic structures. For example, Zeeshan et al. used photolithography-combined TAE to successfully manufacture microrobots from CoNi and polypyrrole. As shown in Figure 2c, in the initial stage of TAE, a piece of photoresist was exposed to a laser to form a 3D cavity for target materials to depose into the template. Then a 3D printing of nano- to microfeatured microrobots was manufactured via electrodeposition, followed by the removal of templates.

2.3. Inkjet Printing

The 3D inkjet printing method covers the cross-sectional area of targeted shapes with plastic or elastomeric polymer-based materials as liquid droplets to construct 3D structures, as shown in Figure 2d. Depending on the ink materials, a phase change (UV or IR curing), chemical reaction (polymerization), or solvent evaporation may be needed to fully harden ink materials. Droplet size directly affects the dimensions of the spots printed via inkjet printers, thereby controlling the resolution of the components. Inkjet printers allow the deposition of spot <100 μm via piezoelectric actuation. The precursor may contain particle fillers, mostly ceramic or conductive particles, in addition, bio-materials may also be used as precursors. Benefits such as tweakable properties (i.e., hardness, biocompatibility, electrical properties, and flexibility) and multicomponent printing are possible due to the droplet printing features. This AMT is capable of printing polymer matrix composites with nanomaterials as fillers with increased mechanical performances (e.g., tensile strength). The limitations of inkjet 3D printing include the requirement for ink morphologies, which should have viscosity between 8 and 25 mPa s and surface tension of 28–32 mN m⁻¹ at printing temperature.

2.4. Binder Jetting

Binder jetting, developed in 1992, was initially designed for 3D printing of solid powders, such as metals and ceramics, directly from computer-aided design (CAD) models. As with inkjet printing, binder jetting uses a jetting head to deposit liquid binder ink onto powder beds rather than substrates. As shown in Figure 2e, a second powder layer is spread on top of the existing powder beds following the completed layer. Binder jetting is an indirect process that requires multiple post-processes, including curing, debonding, sintering, hot isostatic pressing (HIP), infiltration, and finishing, after binders are deposited onto a powder bed. Secondary infiltration may be carried out with materials (e.g., elastomers, wax, or metals) that have lower melting temperatures to increase the density of the system. Binder jetting is unique among other powder-based AMTs, especially SLM or electron beam melting (EBM), because it does not melt the powders on site, which greatly reduces the costs associated with high-energy laser or electron beam printer capabilities.

Although binder jetting demonstrates less printing accuracy (coarser surface finish) and compromised mechanical properties, powder bed-based techniques advantageously provide a support-less printing process in which unbonded powders provide support to an entire structure, allowing the printing of multiple parts simultaneously with a slight gap between each component.

2.5. Direct Ink Writing

DIW, an AMT that utilizes direct material deposition (Figure 2f), is based on the direct extrusion of pastes/inks of specific rheology that are stored in a syringe cartridge. A computer-aided controller uses continuous extrusion of ink and layer-by-layer deposition to fabricate 3D architecture, and deposited patterns turn to solid due to cooling, solvent evaporation, or chemical change such as crosslinking of polymers. To achieve the desired yield stress and shear-thinning behavior of the extrusion inks, varying concentrations of powdered materials are systematically mixed into a liquid. Shear-thinning behavior demonstrates decreased ink viscosity and increased shear stress, which is favorable in the DIW technique, as high yield stress and mechanical strength of inks are necessary to maintain the shape of extruded 3D architecture. The mechanical properties and viscoelasticity of the ink greatly influence the rheological behavior and thus the printed electrode properties. Desired viscosity (0.1–10³ Pa s) ensures the smooth extrusion of the ink during printing, whereas the mechanical strength of the electrode structure is influenced by consistent deposition and fast drying process of the ink. The relationship between the shear stress and viscosity of the ink can be described by the following model (Equation (1)).

\[ \tau = n\dot{\gamma} + \gamma \dot{\gamma}^n \]  

This model is known as Herschel–Bulkley model, where \( \tau \) is the applied shear stress, \( n \) is the viscosity, \( \dot{\gamma} \) is the shear rate, \( \gamma \) is the yield point, \( k \) is the viscosity parameter, and \( n \) is the power law exponent of the ink. The ink flows smoothly when the shear stress surpasses the yield point. The rheological behavior for shear-thinning inks appears with higher \( \dot{\gamma} \) (shear rate) and lower \( n \) (viscosity), which allows uniform flow of the ink through the nozzle. Depending on the nozzle diameter and ink rheology, the 3D DIW process can obtain a printing speed of ~4 m min⁻¹ and printing resolution between 1 and 500 μm. Printing resolution influences the electronic conductivity and electrochemical performance of electrodes by controlling the thickness and porosity of the printed architecture. The favorable distance between the printed layers and thickness of the layers are pivotal in controlling the electron transfer and ion intercalation in the printed electrodes. Therefore, an appropriate ink rheology with surface tension and good electronic conductivity and energy
density of the raw materials are necessary in 3D printing of electrodes using DIW process.

DIW has been widely utilized as a 3D printing technique to fabricate batteries and supercapacitors because the low-cost technique offers a variety of printing materials, with a straightforward process.\textsuperscript{[65–69]} DIW can also be used for complex patterns with controlled thicknesses, resulting in least waste, and minimal risk of nozzle clogging. In addition, the DIW process allows the fabrication of 3D electrodes with high mass loading, which improves areal capacity and energy density.\textsuperscript{[10]}

Wei et al. used DIW to fabricate a fully 3D-printed LIB, for the first time including packaging seal, cathode, separator, and anode.\textsuperscript{[70]} Four printing inks were obtained with optimized rheological and shear-thinning behavior. They also investigated the cycling performances of LiFePO\textsubscript{4} (LFP) and Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} (LTO) electrodes with varying thicknesses ranging from 50 μm to 1 mm.

Zhang et al. used DIW to print SnO\textsubscript{2} quantum dot (QD)-based 3D electrodes for LIB.\textsuperscript{[71]} They utilized a sol–gel technique to prepare a monodispersed ink of SnO\textsubscript{2} QD/graphene oxide (GO), and 3D-printed various complex structures. Recently, Gao et al. used DIW followed by phase inversion and freeze drying to construct a self-standing electrode for a Li–S battery with high sulfur loading.\textsuperscript{[72]} They also proposed a DIW-printed carbon nanotube (CNT) interlayer with high Se-loading for Li–S batteries, and they integrated gel polymer electrolytes (GPEs) into the CNT/Se cathode during printing to improve the ionic conductivity of the electrode.\textsuperscript{[73]}

Lyu et al. adopted DIW to 3D print a hierarchically porous cobalt-based metal-organic framework (Co-MOF) for Li–O\textsubscript{2} batteries.\textsuperscript{[74]} The self-standing porous network, which was composed of micrometer-sized pores generated among Co-MOF-derived carbon flakes, improved the electrochemical performance of a Li–O\textsubscript{2} battery.

In summary, DIW has become one of the most favorable AMTs for energy storage devices because it offers controlled printing with increased material loading. However, preparing viscoelastic inks with high yield stress and then achieving high mechanical strength between the layers have been challenges for improving the DIW application process.

### 2.6. Fused Deposition Modeling

FDM is another 3D printing technology that has been used widely in academia and industry to manufacture complex objects with ease.\textsuperscript{[75]} Similar to DIW, FDM is an extrusion-based technique, but it uses solid filaments of thermoplastic materials for extrusion.\textsuperscript{[75,76]} Acrylonitrile–butadiene–stylene (ABS),\textsuperscript{[77]} polylactic acid (PLA),\textsuperscript{[78]} polypyrrolidone (NMP), and then GO was chemically reduced using hydrazine hydrate to yield G-ABS. The G-ABS was precipitated and dried, and then filaments with a diameter of 1.75 mm were extruded, which were then used to fabricate several conducting 3D samples. The results showed a highest concentration 7.4 wt% of graphene fillers in G-ABS composite and a 0.8 wt% G-PLA composite for FDM-printable models.

In 2017, Foster et al. utilized FDM to 3D print 1 mm-thick electrode discs from a commercially available graphene-based PLA filament, namely Black Magic.\textsuperscript{[79]} These graphene–PLA composite disks were explored as a potential anode for LIBs and solid-state graphene supercapacitors. However, the low amount of graphene materials (8 wt%) in the composite resulted in very poor capacities of the electrodes in LIBs. Maurel et al. adopted graphite into PLA to 3D-printed negative electrode for LIBs using FDM.\textsuperscript{[80]} In this study, 63 wt% of graphite was introduced into 26 wt% of PLA using a 11 wt% of PC plasticizer. The introduction of plasticizer influenced the thermal behavior and enhanced the ductility of the composite filaments. The graphite–PLA composite filaments were then extruded to obtain a 60 μm-thick circular conductive disk, and the graphite particles were homogenously distributed in the composite disk. As a result, the disk showed promising electrochemical performance for use as an anode in LIBs.

Bin Hamzah et al. studied the effect of printing orientation of layers and surface finishing on the electrochemical behavior of carbon black-ABS composite electrodes.\textsuperscript{[85]} They printed electrodes in horizontal and vertical directions and found that due to various redox couples, the vertical electrodes showed reduced charge transfer resistance and enhanced current response compared with the horizontal electrodes. They also found no capacitance difference between the smooth and rough surfaces of the electrodes.

Reyes et al. studied fully 3D-printed LIB coin cell and wearable electronics with integrated batteries.\textsuperscript{[86]} Using FDM, they developed the anode, cathode, separator, and the casings of the LIBS and integrated the batteries with 3D-printed LCD sunglasses. After evaluating several combinations of carbonate solvents and electrolytes, they increased the ionic conductivity of PLA to 0.085 mS cm\textsuperscript{-1}, which was four times higher than the previously reported values. The authors optimized the ratio of conductive to active materials to 80:20 in the electrodes, and as a result...
the 3D-printed coin cells showed a stability up to 100 cycles when tested at a current density of 20 mA g\(^{-1}\).

FDM is often used due to its high-speed prototype printing, large-size capability, low cost, minimal waste, and ease of material change. However, the electrochemically active materials must be mixed with thermoplastics, which results in poor electrical contact between the conductive and plastic materials and poor performance of the electrochemical devices. In addition, the low printing resolution of FDM negatively affects the printing accuracy and surface finishing on the printed objects.

2.7. Aerosol Jet Printing

Aerosol jet printing (AJP) is a novel, contactless AM method for 3D-printed batteries. Similar to inkjet printing, AJP utilizes functional inks for printing, but the differences in droplet formation and delivery techniques between the two printing methods result in various ranges and resolutions of printed patterns. AJP atomizes or aerosolizes a functional ink and then delivers that ink to the deposition head via an aerosol/carrier gas, and focused on the substrate by a sheath gas,\(^{[98]–[100]}\) The functional inks are usually aerosolized by an ultrasonic atomizer (particle size \(\leq 100\) nm) or a pneumatic atomizer (particle size \(\leq 500\) nm),\(^{[99]}\) and the atomized droplets have diameters in the range of 5–10 μm. Upon entering the deposition head, an annular sheath gas flow collimates the aerosol gas into a 10 μm–1 cm beam that is then projected onto the substrate with an approximate velocity of 80 m s\(^{-1}\).\(^{[89]}\) Depending on the properties, the ink is cured via UV light or oven sintering. A schematic of the AJP technique is shown in Figure 2h.

The AJP method has been used in a variety of electronics manufacturing, including transistors,\(^{[91],[92]}\) dielectrics,\(^{[93]}\) circuits,\(^{[94]}\) electrolytes,\(^{[95]}\) and electrodes.\(^{[96]}\) Contactless features and high resolution have also enabled AJP to be used for manufacturing 2D electronics and energy devices. In addition, AJP provides low contact resistance and improved adhesion, which improves the electrical performance of printed electronics. A versatile range of materials, such as metal nanoparticles,\(^{[97],[98]}\) carbon nanomaterials,\(^{[99],[100]}\) polymers,\(^{[101]}\) ceramics,\(^{[102],[103]}\) and piezoelectric materials,\(^{[104]}\) have been used to prepare the ink for the AJP technique.

The implementation of AJP in battery manufacturing is very recent, however, and only a limited amount of research has been published on AJP-printed batteries. In 2018, Saleh et al. used the AJP technique to 3D print batteries with a hierarchical porosity.\(^{[105]}\) A solvent-based Ag nanoparticle ink with particle size 30–50 nm was used to fabricate a 3D microlattice with an open octahedral structure. This highly porous structure of the electrode improved the surface-to-volume ratio and mechanical robustness; when compared with a solid Ag block electrode, the porous Ag electrode showed a 400% increase in specific capacity in LIBs. The proposed structure also improved the strain tolerance and mitigated volume expansion stress during lithiation/delithiation cycles.

Deiner et al. introduced AJP for manufacturing polymer–composite electrolytes for solid-state LIBs.\(^{[95]}\) The electrolytes, which consisted of polyethylene oxide (PEO), lithium difluoro (oxalato)borate (LiDFOB) salt, and alumina nanoparticles, were directly deposited onto LiFePO\(_4\) cathode substrates. The printed electrolytes were smooth and conformal with a conductivity >\(1 \times 10^{-3}\) S cm\(^{-1}\) at 45 °C. In another work, the authors reported the fabrication of a LiFePO\(_4\) cathode using AJP.\(^{[105]}\) LiFePO\(_4\) powder, carbon Super-P, and Kynar HSV 1800 were dissolved into 2-butanol NMP solvents to formulate LiFePO\(_4\) inks. The submicroporous-patterned surface resulting from AJP contributed to high capacity and stable performance of the LiFePO\(_4\) cathode in LIBs.

In summary, AJP is superior to many traditional printing techniques due to its noncontact, line-of-sight, versatility, scalability, and compatibility with a broad range of materials. However, challenges of AJP include determining optimal print parameters, drying aerosol droplets, clogging of the deposition head, consistency, and reproducibility. These drawbacks limit the printing outputs and lifetime. Extensive further research is needed to increase understanding of AJP for 3D-printed energy storage devices. The key features and the difference of 3D printing techniques are shown in Table 1.

3. Synthesized 3D Electrode Materials for Energy Storage

3.1. Introduction

The increasing need for portable and grid-scale energy storage has necessitated the development of robust, long-lasting,
economically viable electrode materials.\[20,106,107\] LIBs, SIBs, and supercapacitors are the most analyzed electrochemical EES devices.\[106,108\] As factors such as the transition from fossil fuels to renewable energy and exponential energy needs necessitate the deployment of more EES globally, novel electrode systems must be conceptualized and developed.

3.2. Lithium-Ion Batteries

Their high specific capacities and elevated power and energy densities have increased the dominance of LIBs in the EES sector, especially for portable electronics such as laptops and mobile phones.\[109,110\] However, improved electrode systems are required to keep up with increasing energy storage demands, particularly the exponentially burgeoning consumer electronics market.\[111\] The advantages of 3D electrodes include their charge structural stability and porosity as well as elevated charge transfer efficiency.\[112,113\] Electrode materials designed in a cellular/modular fashion are desirable as they are structurally stable as well as provide large surface area.\[114\] Cellular designs result in large surface-to-volume ($S/V$) ratios, and these ratios increase when the number of cells is increased, in a cellular design as against a block design, where the $S/V$ ratio remains constant with increasing size.\[114\]

Among 3D electrode materials, carbonaceous and noncarbonaceous materials are important classes that merit discussion as these have demonstrated the most promise as electrode systems.

3.2.1. Carbon Materials

The electrode system of 3D graphene foams in LIBs typically serve as one constituent of a multicomponent hybrid electrode. They act as the backbone of a composite system that is embedded with an electroactive species with subsequently enhanced electrochemical properties.

3D-printed composite graphene electrodes from precursor inks have shown promise when applied in LIBs. Vernardou et al. synthesized 3D-printed graphene-based electrodes from a precursor of PLA-based conductive graphene.\[115\] The 3D-printed structure had pyramid geometry ($\approx$5 mm height), a specific discharge capacity of 265 mAh g$^{-1}$, and a capacity retention of 93% after 1000 cycles of operation. The authors attributed the superior performance to the stability of the pyramidal structure as a result of 3D printing.\[115\]

Similarly, Sun et al. used 3D printing to synthesize a 3D graphene scaffold-based electrode.\[116\] Precursors included an ink of hierarchical silver nanowires (AgNWs), graphene, and Li$_4$Ti$_5$O$_12$ (LTO), resulting in a very conductive AgNW network with a porous 3D graphene scaffold with LTO interspersed along the structure.\[116\] The relatively thick electrodes provided a specific capacity of 121 mAh g$^{-1}$ at current densities as high as 10 C and a capacity retention of $\approx$95% after 100 cycles of operation, proving the practicability of this 3D system as an electrode in a LIB system.\[116\] A GO ink was used to 3D-printed composite electrodes, with GO/LiFePO$_4$ and GO/LTO acting as the cathode and the anode, respectively. A stable electrochemical performance was obtained with specific capacity of $\approx$170 mAh g$^{-1}$ at an electrode mass loading of $\approx$18 mg cm$^{-2}$.\[117\] The stability of the electrochemical system was correlated to the enhanced electronic conductivity due to the addition of the GO, vis-a-vis the stand-alone electrodes with added structural stability.\[117\]

Rocha et al. have used a water-based thermoresponsive ink as a precursor material to 3D-printed reduced chemically modified graphene (rCMG), which subsequently acted as the precursor for the active material of the anode.\[118\] The authors have been able to report specific energy and power densities of 26 Wh kg$^{-1}$ and 13 kW kg$^{-1}$, respectively.\[118\]

Other miscellaneous types of 3D electrode systems have also been studied using exotic synthesis techniques. For example, one study used an FDM system to synthesize a graphite/LiFePO$_4$ electrode for a Li-ion-based microbattery system, resulting in a specific capacity of 87 mAh g$^{-1}$ at C/20 rates, indicating feasibility as an electrode.\[119\] Redondo et al. conducted a significant work to determine the exact parameters to develop optimized 3D electrodes, demonstrating that carbonization temperature strongly influences the development of a carbon-based nanocomposite electrode from PLA/nanocarbon filament precursors.\[120\] Hu et al. 3D printed a LiMn$_{0.21}$Fe$_{0.79}$PO$_4$@C nanocrytal electrode, and they were able to obtain specific capacities as high as 108.45 mAh g$^{-1}$ at 100 C, the superior performance has been attributed to the high porosity and enhanced kinetics of the 3D crystal.\[121\]

3.2.2. Other Materials

Noncarbonaceous materials have also found importance for application as 3D electrode systems in LIBs. Liu et al. 3D-printed highly porous LiFePO$_4$ (LFP) electrodes using a low temperature direct writing (LTDW) for application in LIB systems, resulting in a maximum specific capacity of 82 mAh g$^{-1}$ at a current density of 10 C compared to 62 mAh g$^{-1}$ for a conventionally prepared electrode at the same current density.\[122\] Similarly, Hu et al. synthesized LiMn$_{0.21}$Fe$_{0.79}$PO$_4$@C (LMFP) electrodes for cathodes in LIBs.\[121\] The 3D-printed electrode delivered a specific capacity of 108.45 mAh g$^{-1}$ at 100 C. Theoretical studies have indicated that factors such as porosity and electrode thickness determine the rate capacity of the synthesized material.\[121\]

Wei et al. fabricated a completely 3D-printed LIB from semisolid inks of the cathode (LFP) and anode (LTO) precursors using a UV-based curing and packaging technique.\[123\] The entire 3D-printed cell, which was housed between a pair of glassy carbon current collectors, provided an aerial capacity of 4.45 mAh cm$^{-2}$ at a current density of 0.14 mA cm$^{-2}$. The authors also reported that the cells did not require drying, electrolyte-filling, or clamping, thereby decreasing the expense and time required for cell assembly.\[123\]

Izumi and coworkers synthesized LTO as a 3D-printed cathode for LIB applications.\[124\] The 3D-printed electrode with a Li metal anode demonstrated approximately a 60% capacitance retention rate at 10 C current density with low internal resistance. The authors also found that electrode height does not affect the net capacitance, whereas reduced spacing between successive electrode lines enhances net-specific capacity.\[124\] Similarly, Wang et al. used viscous polymer inks of LFP and LTO to 3D-printed LFP/LTO fiber-based electrodes.\[125\] When used with a polymer gel quasisolid gel electrolyte, the cell delivered a
specific capacity as high as 110 mAh g⁻¹ at a current density of 50 mA g⁻¹, thereby underscoring the potential for these cells to be used in wearable-electronics applications. In addition, Yu et al. analyzed aerosol-printed 3D electrodes on nonplanar substrates. When used as a full cell, the customized LFP cathode and LTO anode exhibited a maximum aerial capacity of 7.1 mAh cm⁻² with 78.4% capacity retention after 30 cycles of cell operation, all of which attributed to the nonplanar geometry and electrode thickness, as shown in Figure 3a–l.

Although carbon-based and noncarbon-based 3D electrodes (synthesized and 3D printed) have shown considerable promise due to their cycling stability and elevated specific capacities by synergistically combining various precursor materials, factors such as synthesis parameters, electrode geometry, and cost still must be optimized for these electrodes to gain greater prominence.

3.3. Sodium-Ion Batteries

As an evolving technology, SIBs are appealing due to low cost and the abundance of sodium in the Earth’s crust. Although SIB research was reported before the 1980s, SIBs have recently attracted new research interest as an alternative to LIBs due to concerns of lithium reserves and future demand. Intensive research before the year 2000 was limited due to SIBs’ large Shannon ionic radius, high redox potential, and low energy density. SIBs currently are used in large-scale electricity storage (e.g., stationary batteries) as evidenced by the ≈200 units of high-temperature Na-S batteries used by the NGK Company worldwide. SIBs are also considered complementary technology to LIBs for other applications.

As with LIBs, the sodium–metal anode in SIBs poses a risk due to unstable Na⁺ plating, which may lead to dendrite formation. In fact, the higher reactivity of sodium and its lower melting point (i.e., 97.8 °C compared with 179 °C of Li) may result in risky thermal-runaway reactions caused by dendrite. Although several dendrite-free materials have been studied, the theoretical specific capacity (1166 mAh g⁻¹), low anode potential, and low-cost of sodium metal (US $200 ton⁻¹) are difficult to surpass. Yu et al. introduced a graphene lattice made by DIW based on the concept that porous electrodes yield low current densities and homogeneous sodium plating distribution, as shown in Figure 4a–d. The printed periodical structure in Figure 4e shows that the current density distribution at the circumference rim regions was high, indicating preferential spots for sodium deposition (Figure 4e,f). At current density of 1 mA cm⁻², initially the wholes shown in Figure 4b were

![Figure 3](https://www.advancedsciencenews.com)

**Figure 3.** Aerosol printed of nonplanar electrodes, characterization, and their electrochemical cycling performance. a,b) Images of the aerosol-printed LFP cathode, c,d) similar images of the aerosol-printed LTO anodes, e,f) SEM micrograph demonstrating the characteristic bulk microstructure of the LFP cathode and LTO anode, respectively, h,i) SEM images of the 4-layered and 8-layered aerosol-printed LFP cathode, j) actual photograph of the nonplanar cell lighting a LED light, k) characteristic galvanostatic charge–discharge curves of the nonplanar and planar electrode cell, l) Specific capacity and Coulombic efficiency variation over 30 cycles, for the LFP cathode half-cell. Reproduced with permission. © 2021 The Authors. Advanced Energy and Sustainability Research published by Wiley-VCH GmbH.
Brown et al. used a 3D freeze-printing (3DFP) method to produce a novel hybrid, highly porous MoS$_2$-reduced graphene oxide (rGO) electrode. Using a nickel foam current collector, ink-jet printing deposited a water-based ink made from commercially available reagents, namely, ammonium thiomybdate (ATM) and GO. Preformed at $-30^\circ$C, the freeze cast caused the ATM–GO ink to freeze into ice crystals and form a porous and continuous matrix. Following the sublimation process—induced to completely remove the ice template—a single annealing process was conducted to preserve the porosity and convert the ATM into MoS$_2$ and the GO into rGO. Then the produced MoS$_2$–rGO aerogel was studied as a half-cell SIB. The charge and discharge curves showed unique behavior compared with a typical pristine MoS$_2$–SIB voltage profile, including surface pseudocapacitive behavior in accordance with cyclic voltammogram curves. Therefore, as surface pseudocapacitive behavior infers a charge storage mechanism based on fast surface reactions, the high porosity of MoS$_2$–rGO was shown to impact specific capacity. As processes rapidly occur at high current densities, the specific capacity at low current densities was low but stable. On the other hand, at lower rates, since a conversion-type mechanism has major contribution, a specific charge capacity closer to the theoretical value can be achieved. The authors also highlighted the advantages of rGO for a continuous and electronically conducting scaffold, which is essential at high rates. Overall, their research combined two promising EES materials, MoS$_2$ and rGO, and introduced a Na$^+$ host material with enhanced electrochemical properties during AM.

Down et al. reported a freestanding sodium-ion full-cell developed entirely using 3D-printed components. Microporous electrodes such as TiO$_2$ (anode) and NaMnO$_2$ (cathode) were printed with ABS and polyvinyl alcohol (PVA); the PVA was infused in ABS and later washed away to maximize the surface area of the electrodes, a relevant factor in electrochemical performance. In addition, no separator was required in this fully printed cell, meaning the electrolyte was inserted into the cell AA battery layout and the electrodes were kept apart due to the cell’s design. Also, the freestanding nature of the electrodes did not require a current collector. Full cells were tested in 0.5 M NaBF$_4$ in 1-ethyl-3-methylimidazolium-bis-tetrafluoroborate, and the AM/3D-printed full-cell presented 83.4 mAh g$^{-1}$ at 8.43 mA g$^{-1}$ (0.1 C). For comparison, an ink-based electrode—made by dr. blade—was also tested and presented a first-cycle specific capacity of 98.9 mAh g$^{-1}$ at 0.1 C. Overall, additive-manufactured electrode batteries may advantageously provide innovative production and cell design, porous microstructured films, and decreased component costs. However, challenges such as decreasing the viscosity of ionic liquids while increasing their ionic conductivity and enhancing the electronic conductivity of fully produced AM electrodes remain.

### 3.4. Li–S Batteries

Li–S batteries are promising EES due to their high theoretical specific capacity, power and energy density, and wide range of operational temperatures. Sulfur (S), which is the cathode electrode material for Li–S batteries, has a high theoretical gravimetric capacity of $\approx 1675$ mA h g$^{-1}$. In addition, S is naturally

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**Figure 4.** 3D printing of hierarchical graphene lattice (GL). a) Representation of a light-weight electrode sitting on a dandelion flower. b) Optical microscopy depicting the periodic structure of GL. c,d) SEM images showing Na deposition preferential spots covering the whole on the periodic structure. e,f) Current distribution plot at GL structure. Reproduced with permission$^{[137]}$. Copyright 2019, American Chemical Society.
abundant and inexpensive, which is favorable for commercial rechargeable batteries. However, the low electronic conductivity of S and lithium polysulfides (Li2Sx) shuttle result in poor sulfur utilization. Slow kinetics during cycling and dissolution of Li2Sx in electrolytes also limit the electrode rechargeability and cause poor cycling stability. A considerable amount of 3D printing research has been done to alleviate the effect of Li2Sx shuttle and improve the performance of S cathodes.

Using a conventional casting method to prepare the electrodes limits the loading of the active S material and affects the kinetics of the S chemistry and electron/ion transportation. As S has sluggish kinetics, it is imperative to find an efficient host for S with good conductivity. Well-designed conductive host structure with stable active sites improves the ion transportation of the electrodes. 3D printing techniques allows the meticulous control of the active material in the host matrix and thus enables improved ion transport and fast charge transfer. Therefore, 3D-printed cathode with enhanced S loading can improve the charge/discharge capacity of the Li–S batteries in comparison with the conventional blade-casting electrodes. Abundant active sites of the host will allow improved Li2Sx adsorption and catalytic activity. Controllable thickness of the 3D-printed electrodes will also allow the regulation of tap density to improve the volumetric capacity. In addition, minimal waste with high manufacturing efficiency gives 3D-printed Li–S batteries a broader application prospect such as wearable and cost-effective electronic devices. Milroy and Manthiram investigated micro-cathodes based on aligned multiwall carbon nanotubes (MWCNTs) for Li–S batteries. An MWCNT-S cathode was printed from an aqueous ink using a filtration-based manufacturing process such as ink jet printing. The homogeneous distribution of S within the MWCNT network facilitated the electronic conductivity of the cathode and mitigated the sudden change of volume during charge/discharge. The as-prepared cathode delivered a high areal capacity of 7 mAh cm−2 with 50 wt% S content in the electrode (7 mg cm−2 S loading). The microelectrode also showed a stable cyclability of 200 cycles with Coulombic efficiency >95%. Milroy et al. also introduced single-wall CNTs with electronically conductive straight-chain sulfur (S@SWNT) as a cathode for Li–S batteries. The S@SWNT cathode could be printed on a semiconductor substrate such as SiO2 or aluminum foil with <10 μm thickness. The confinement of straight-chain S within conductive SWNT reduced the formation of soluble Li2Sx. As a result, the inkjet-printed thin-film cathodes showed a high capacity of ≈800 mAh g−1 S at a current rate of C/2 and a capacity of ≈700 mAh g−1 after 100 cycles.

To reduce the dissolution of Li2Sx and improve the conductivity of the S cathode, Shen et al. introduced copolymer–graphene composites into S. They 3D printed the cathode (3DP-pSG) using an ink of S particles mixed with dispersed GO and 1,3-disopropylbenzene (DIB) polymer and dried it at 200 °C. The SEM image revealed the structural integrity of the 3D-pSG electrode with macroporous architecture, and the elemental mappings of the electrode revealed uniform distribution of the S and C in the architecture. The S–C strong covalent bonding was further confirmed by the X-ray photoelectron spectroscopy (XPS). According to the authors, the S–C covalent bonds of the S copolymer contributed to the low dissolution of Li2Sx during the charge/discharge of the cells. The 3DP-pSG cathode, which became stable after 50 cycles, delivered a high reversible capacity of 812.8 mAh g−1 compared with 680.7 mAh g−1 of 3DP-SG cathode (without DIB polymer) at a current density of 50 mAg−2.

Similarly, Gao et al. reported an integrated structure of S and carbon black as a 3D-printed freestanding cathode for Li–S batteries. They used a customized DIW 3D printer, and the functional ink was prepared from a mixture of S with conductive C (wt. ratio 6:4). This mixture was then added to polyvinylidene fluoride-hexafluoro propylene, CNTs, and acetylene black with a weight ratio of 7:2:0.5:0.5 to make a homogenous dispersion in the NMP, as shown in Figure 5a. The 3D-printed electrode was then freeze-dried (3DP-FDE), demonstrating minimum shrinkage and a well-defined grid structure. The SEM images shown in Figure 5b–d reveal the nano- and micropores in the grid structures, which contributed to the decreased shuttling effect and improved capacity and cycling stability. The 3DP-FDE cathode showed an initial capacity of 1172 mAh g−1 at a current rate of 0.2 C and a stable capacity of 917 mAh g−1 after 200 cycles. Furthermore, when the S loading was enhanced to 5.5 mg cm−2, the electrode delivered a capacity of 1188 mAh g−1 at 0.1 C. The performances of the 3DP-FDE electrodes in Li–S batteries are shown in Figure 5e–g.

Gao et al. recently improved their earlier work by implementing the ice-template method with 3D printing. They converted 3D-printed electrodes to 2D thin electrodes, whose performances as cathodes in Li–S batteries were completely independent of the printed thickness and S loading. Results showed that the constant local thickness of the thin electrodes significantly improved Li+ and electron transport between the layers, thus enhancing the electrochemical kinetics of the electrodes. Therefore, whether their thickness was 250 μm (2 mg cm−2 S loading) or 750 μm (6 mg cm−2 S loading), the printed electrodes delivered high capacities of 854 and 885 mAh g−1, respectively, at a current density of 1 mA cm−2. Surprisingly, at a high current density of 10 mA cm−2, the two electrodes delivered capacities of 531 and 532 mAh g−1, respectively.

Cai et al. conducted a novel study of the use of an electrocatalyst into functional ink to 3D print a Li–S battery cathode. They introduced metallic LaB6 into S/C composite inks and printed 3DP-LaB6/SP@S cathodes. The hierarchical porosity and open grid structures of the cathodes ensured the improved kinetics of the cathode in the presence of V8C7−VO2 scaffolds, the as-prepared 3DP-V8C7−VO2/S cathode not only successfully suppressed the Li2Sx shuttling, but they also reduced the dendritic growth of Li. SEM images revealed the hierarchical macro- and microporosity of the structure, and elemental mappings confirmed the uniform distribution of the V, C, O, and S throughout the printed electrode. With the improved kinetics of the cathode in the presence of V8C7−VO2 scaffolds, the as-prepared 3DP-V8C7−VO2/S electrode delivered a high initial capacity of 1294 mAh g−1 at a current rate of 0.2 C. The 3DP-V8C7−VO2/S electrode also showed a stable performance of 1139.6 mAh g−1 at 0.5 C after 100 cycles with a capacity retention of 89.5%.
Recently, Wei et al. introduced a metal oxide/MXene heterostructure for 3D-printed Li–S batteries. Using a hydrothermal approach, they synthesized in situ MOₓ/MXene (M: Ti, V, Nb) heterostructures as S host. The heterostructure acted as a multifunctional host providing abundant active sites for Li₂S adsorption and catalytic activity. As a result, the as-synthesized 3D-printed MOₓ/MXene electrodes provided high gravimetric capacities up to 1083 mAh g⁻¹ at 0.2 C. Among the 3D-printed electrodes, VO₂–V₂C/S cathode also showed a stable cycling ability over 1500 cycles delivering 438 mAh g⁻¹ at a current rate of 2 C. Kim et al. also studied all-solid-state bipolar Li–S batteries (ASSLSB). They introduced tetra ethylene glycol dimethyl ether (TEGDME) into S and used UV curing to fabricate bipolar ASSLSB. The printed bipolar ASSLSB powered a toy aircraft and an LED lamp and showed exceptional flexibility without any capacity decay during a continuous folding test. Chen et al. recently conducted a study of a wearable Li–S battery and 3D-printing technology. They printed cathode materials using DIW and the battery case using the FDM printing method. Using the AM enabled them to control the thickness of the printed cell and fabricate a bracelet battery. A 3D-printed graphene cathode skeleton was manufactured using a SiO₂.

Figure 5. 3D-printed Li–S battery cathode. a) Schematic illustration of the printing process of 3DP-FDE electrode. b) SEM image of the 3DP-FDE electrode (top view). c,d) Cross-sectional SEM image reveals the micro- and nanoporosity of the electrode. e) Specific capacities of the electrode with 3 mg cm⁻² S loading at various C rates. f) Charge/discharge profiles of the electrode at various C-rates shows good rate capability. g) Cycling performance shows excellent stability of the electrode at current rates of 0.2 and 3 C with S loading of 3 mg cm⁻². Reproduced with permission. Copyright 2018, Elsevier Ltd.
template. The as-printed cathode framework with high S loading (10 mg cm\(^{-2}\)) provided a conductive network and enhanced charge transfer at the electrode/electrolyte interface. With the improved transmission path for ions and electrons, this 3D-printed cathode delivered a specific capacity of 505 mAh g\(^{-1}\) over 500 cycles at a current rate of 0.2 C. This Report for the first time provided a significant guidance toward the manufacturing techniques of Li–S battery for wearable devices. Overall, 3D-printed Li–S battery technologies hold a promise of low costs, flexibility, wearability, and application in practical electronic devices.

### 3.5. Supercapacitors and MSCs

Electrochemical supercapacitors (ESs) are EES usually with higher power density than batteries as exhibited by the Ragone plot in Figure 6a. Having a broad range of applications—from small electronic devices to electric cars—ESs are EES that can complement batteries, reason why its research has gained traction in the past years.[156]

ESs may store charge through rapid ion adsorption on the electrodes’ surface, forming an electric double layer (EDL), which is an interfacial electrostatic structure of electronic and ionic charges forming a dielectric-oriented dipole layer.[157] Capacitors governed by EDL are known as electric double layer capacitors (EDLCs), and they are composed of porous solid electrodes that commonly exhibit a “distributed capacitance” due to the existence of hierarchically interconnected pores of different sizes—from macropores to micropores.[157]

Ultrafast redox reactions, known as solid-state redox reactions (Faradaic processes), simultaneously occur with the electrostatic physical process in pseudocapacitor.[157] To give the readers a perspective of the difference between EDLCs and pseudocapacitors, EDLCs have a specific capacitance of 100 F g\(^{-1}\) and a long life span of up to a million cycles with more than 90% capacitance retention. In contrast, pseudocapacitors have much higher specific capacitance—from 100 to 1000 F g\(^{-1}\)—but a much lower life span, i.e., \(\approx\)100 thousand cycles.[158,159] For example, Zheng and Jow found that hydrous RuO\(_2\) had a specific capacitance of 720 F g\(^{-1}\) and a distinctive cyclic voltammetry (CV) curve due to rapid surface redox reactions;[160] however, the high cost of RuO\(_2\), low conductivity, and reduced life cycle are drawbacks of transition metal oxides (TMOs) for pseudocapacitors. As alternatives to RuO\(_2\); MnO\(_x\),[161] NiO,[162] and FeOOH[163] among others have been studied and reported by literature as outstanding materials. In that sense, EDLC and pseudocapacitors are suitable for AM, which offers is the ability to produce controlled distributed pores with customized inspired structures, as reported by Jiang et al.[164] Considering several application of ESs, MSCs may have some advantages considering AM. MSCs were developed around 2010 to contribute to future developments involving the internet of things (IoTs).[165] Despite their small size, MSCs have high-power density and they can be printed on textiles or flexible substrates and use novel materials, as shown in Figure 6b. They also can be integrated into health monitoring or energy harvesting. Because MSC research is commonly associated with AM, the following sections detail the latest developments in materials and AM.

#### 3.5.1. Carbon-Based Materials

3D printing is emerging as a promising method for fabricating supercapacitors and MSCs. 3D-printed supercapacitors have been studied extensively over the past decade due to their enhanced capacitance, high-power density, high flexibility, and cost effectiveness.[166–168] The interdigitated of 3D-printed supercapacitors decreases the ESR, which results in increased power and energy densities. Carbon-based materials such as graphene, CNTs, carbon black, and activated carbon (AC) have been widely utilized in the 3D-printed electrodes. High conductivity, large surface area, and superior mechanical properties make carbon suitable electrode material for supercapacitor applications.[169]

Graphene, an elemental carbon material, is atomically thin but has an exceptionally large surface area and superior electrical...

![Figure 6](image-url)\[a) Ragone plot illustrating characteristic values of specific power and specific energy of different ESSs. Adapted with permission.[214] Copyright 2019 Wiley-VCH GmbH. b) Illustration of relevant aspects of printed supercapacitors. Adapted with permission.[215] Copyright 2011, American Chemical Society.

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conductivity. Recent publications have demonstrated several applications of graphene in 3D-printed supercapacitors, including graphene aerogels\textsuperscript{170–173} with engineered porous architecture. For example, Zhu et al. fabricated 3D-printed graphene composite aerogel for supercapacitor applications.\textsuperscript{171} They used the DIW technique and a functional ink with GO and graphene nanoplatelets (GNPs). The GNPs were added to the GO to increase the electrical conductivity and achieve ideal rheology for 3D-printable inks. The as-prepared composite aerogel had macroarchitecture that enabled rapid ion diffusion throughout the electrode. As a result, even a 1 mm-thick aerogel electrode delivered a high capacitance of 63.6 F g\textsuperscript{-1} at a high current density of 10 A g\textsuperscript{-1}. The graphene composite aerogel also showed a remarkable power density >4 kW kg\textsuperscript{-1} and cycling stability up to 10 000 cycles.

Wang et al. used DIW to 3D print with rGO and polyaniline (PANI).\textsuperscript{174} The functional ink of GO-PANI was synthesized via self-assembly of PANI and GO in NMP and water. The composite of PANI with rGO improved the shear-thinning ability of the ink and increased shape retention and structural strength of the electrode. The printed composite electrode, which was used in a planar supercapacitor, exhibited a high areal capacitance of 1329 mF cm\textsuperscript{-2} at a current density of 5 mA cm\textsuperscript{-2}. The supercapacitor also retained 75% capacitance after 1000 cycles at a current density of 50 mA cm\textsuperscript{-2}. This research provided a low cost, practical method for utilizing DIW for micro- and nanoscale devices. Additional studies have used DIW printing technologies for all-solid-state graphene-based in-plane MSCs,\textsuperscript{175} highly transparent and flexible graphene MSCs,\textsuperscript{176} rGO-coated textile fabrics as electrodes in supercapacitors,\textsuperscript{177} and MSCs with inter-digitated graphene patterns.\textsuperscript{178}

Ujjain et al. used DIW to print a CNT electrode for supercapacitors.\textsuperscript{179} They utilized an MWCNT ink with enhanced solubility, which was a result of the functionalization of MWCNT by 1,3-dipolar [3+2] cycloaddition of azides. The functionalized MWCNT (fMWCNT) inks were printed into films and used as electrodes in supercapacitors in aqueous electrolytes such as 1 M Na\textsubscript{2}SO\textsubscript{4}, 1 M H\textsubscript{2}SO\textsubscript{4}, and 1 M KOH. The fMWCNT electrode showed capacitance of 240 F g\textsuperscript{-1} at a scan rate of 5 mV s\textsuperscript{-1} in a cyclic voltammetry test in 1 M H\textsubscript{2}SO\textsubscript{4} electrolyte with an energy density of 86.8 Wh kg\textsuperscript{-1} at 0.3 A g\textsuperscript{-1}. Gao et al. distributed AC microparticles into a homogenous ink of CNT/rGO to 3D print an ultrathick AC/CNT/rGO electrode for supercapacitors using DIW.\textsuperscript{180} The binder-free composite electrode provided a conductive network with hierarchical porosity. This open architecture of the electrode with multidimensional carbon materials allowed abundant active sites for ion diffusion. The self-supported ten-layer-thick electrode offered high volumetric mass loading of 256.3 mg cm\textsuperscript{-3}, which delivered a volumetric capacity of 41.3 F cm\textsuperscript{-3} at a scan rate of 10 mV s\textsuperscript{-1}. This ultrathick cell also showed a stable performance over 5000 cycles retaining 93.3% of the capacitance when tested in a symmetric cell.

Chen and coworkers developed a fully packaged flexible CNT supercapacitor with integrated electrodes, electrolyte, separator, and casings.\textsuperscript{181} The authors used DIW to 3D print single-wall CNT (SWCNT) electrodes, in which the electrolyte was PVA-based gel and the packaging material was silicone rubber. This process enabled a precise and repeatable printing pattern with a mask and alignment-free DIW setup. The printed electrode showed a thin gap with wide patterns, resulting in higher specific capacitance. The as-printed fully packaged CNT supercapacitors delivered a high volumetric capacitance of 15.34 F cm\textsuperscript{-3}, energy density of 1.2 mWh cm\textsuperscript{-3}, and power density of 11.8 W cm\textsuperscript{-3} at a current density of 1.32 A cm\textsuperscript{-3}.

Azhari et al. introduced a powder-bed AMT for graphene-based electrode fabrication with mm thickness and crack-free 3D structures for high-performance supercapacitors.\textsuperscript{182} POWders were first thermally reduced rapidly to create a high specific surface area, bound using inject-customized binders, and then printed layer-by-layer in a powder-bed printer. The folds and wrinkles generated in the powders during thermal decomposition impeded the layers restacking, conserving the high surface area of the printed electrode. The electrodes in this technique delivered a high specific capacitance of 260 F g\textsuperscript{-1} and an areal capacitance of 700 mF cm\textsuperscript{-2} at a scan rate of 5 mV s\textsuperscript{-1}. The authors also infiltrated <9 wt% of Pd nanoparticles into the printed disks, which helped to reduce electrical contact resistance between the layers.

Tawilaisiri et al. combined FDM and a paste extruder to manufacture modular ESs.\textsuperscript{183} The FDM was used to fabricate the ES casings, and the paste extruder was used to print the electrodes, current collectors, and separators. AC with sodium carboxymethyl cellulose (CMC) slurry was used to print electrodes for the supercapacitors; the gel electrolyte was made from H\textsubscript{3}PO\textsubscript{4} and PVA in deionized water, and the frame was printed from PLA filament. The as-printed EDLC supercapacitor showed a specific capacitance of 238.42 mF g\textsuperscript{-1} and a power density of 95.36 mW g\textsuperscript{-1} at a current of 15 mA.

Fieber et al. utilized FDM and DIW to print a fully packaged supercapacitor.\textsuperscript{184} AC was used to prepare the functional ink, the PP was used to fabricate the casings, and 1 M KOH hydrogel was used as the electrolyte. The whole device required less than 30 min for printing. The areal and volumetric electrode capacitance was 599.2 ± 3.0 mF cm\textsuperscript{-2} and 61.7 ± 0.6 mF mm\textsuperscript{-3} at a scan rate of 10 mV s\textsuperscript{-1}, normalized by the electrode foot-print area and electrode volume, respectively. The as-prepared supercapacitor delivered an areal capacitance of 599.2 mF cm\textsuperscript{-2} and a volumetric capacitance of 61.7 mF mm\textsuperscript{-3} at a scan rate of 10 mV s\textsuperscript{-1}. The ring-shaped EDLC also showed a capacitance retention of 97.1% at 25 mV s\textsuperscript{-1} over 250 cycles.

Wei et al. recently used DIW to produce quasi-solid-state flexible supercapacitors with high power and energy density.\textsuperscript{172} A nitrogen-doped GO ink was prepared with suitable viscosity to print the electrodes on a polyethylene terephthalate (PET) substrate. In the doped graphene ink, the storage modulus was higher than the loss modulus, which enabled a stable flow of ink during printing. Vanadium nitride was infiltrated to increase the intrinsic conductivity of the electrode. The printed electrode achieved a capacitance of 15.2 F g\textsuperscript{-1} at a high scan rate of 500 mV s\textsuperscript{-1} and a long-term cycling stability of 5000 cycles with 90% capacitance retention at a current rate of 12 mA cm\textsuperscript{-2}.

Idrees et al. recently developed a solid-state supercapacitor using extrusion-based printing of carbon synthesized from packaging waste.\textsuperscript{185} The packaging waste was dried, ground, and heated at 750 °C to prepare the AC, and then 35 wt% of AC was mixed with a PVA/H\textsubscript{3}PO\textsubscript{4} solution as an ink to print the electrodes, as shown in Figure 7a. The printed electrodes were...
0.5 mm thick. PVA/H₃PO₄ was used as the electrolyte and conductive metal tapes were used as the current collectors. The structure and porosity of the AC improved the surface area and electrical conductivity of the printed electrodes. The SEM images shown in Figure 7b–d confirm the microporosity of the AC and the electrodes. Galvanostatic charge–discharge (GCD) of the printed supercapacitors at various currents showed the rate capability of the electrodes, with the highest capacitance of 328.95 mF cm⁻² at 2.5 mA (Figure 7e). CV plots at various scan rates showed lower capacitance at higher scan rates due to the decreased amount of ion diffusion into electrodes. The 3D-printed supercapacitor achieved 90% capacitance retention after 500 cycles (Figure 7f).

3.5.2. MXenes

In 2011, Naguib et al. reported the first transition metal carbide and nitride (MXene). Nowadays, transition metal carbides and nitrides (MXenes) are a fast-growing family of layered materials with generalized formulation of Mₙ₋₁XₙTₓ, where M is a transition metal, X is a carbon or nitrogen atom (n = 1–3), T is a termination group (i.e., —O, —OH, —H, —F, and/or —Cl), and x is the number of functionalities. The physical and electrochemical properties of MXenes make them attractive layered materials due to oxygen (OH terminations, leading to water solubility and subsequent ease of manufacturing), hydrophilicity, the production of several grams of material in a single batch.
using a top-down approach (enabling large-scale applications\textsuperscript{[188]}), metallic conductivity (>6000 S cm\textsuperscript{-1})\textsuperscript{[189,190]} and mechanical flexibility. Concerning EES systems, MXenes exhibit high surface area, faster ion transport—due to high electronic conductivity—and pseudocapacitive contribution that outperforms the traditionally known carbon materials at rates of 10 V s\textsuperscript{-1}, as shown by Lukatskaya and coworkers.\textsuperscript{[191,192]}

Although 30 species of MXenes have been determined, less than 10 species have been identified as supercapacitor electrodes.\textsuperscript{[193]} Moreover, only the Ti\textsubscript{3}C\textsubscript{2} species has been reported for AM. Therefore, this field offers substantial research opportunities due to the advantageous layered material properties and production techniques of MXenes and AM, respectively.

Yu et al. formulated a water-based ink with nitrogen-doped Ti\textsubscript{3}C\textsubscript{2} and carbon-based materials, such as GO, AC, and CNTs, for ink viscosity control.\textsuperscript{[194]} The authors found that surface modification in the N-doping of Ti\textsubscript{3}C\textsubscript{2} prevented the MXene sheets from restacking and increased the electronic conductivity. Produced by 3D extrusion printing, the N-doped Ti\textsubscript{3}C\textsubscript{2} (MXene-N) SC electrode was studied in 3 M H\textsubscript{2}SO\textsubscript{4}. In a symmetric configuration, the material presented specific capacitance of 66.7 F g\textsuperscript{-1} at 12 mA cm\textsuperscript{-2}. Moreover, at 10 mV s\textsuperscript{-1}, the material presented an areal capacitance of 8.2 F cm\textsuperscript{-2} with high areal energy density of 0.42 mWh cm\textsuperscript{-2}.\textsuperscript{[194]}

As a MSC, in a study that also produced water-based MXene ink, Orangi et al. reported ultraconcentrated (\textgreek{\textalpha}\textsuperscript{25} 28.9 wt\%) Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} dispersion to produce all-solid-state MSCs through DIW at room temperature, as shown in Figure 8a,b.\textsuperscript{[195]} Because MXene dispersions of 10 mg mL\textsuperscript{-1} do not provide the rheological properties required for extrusion printing, the authors used superabsorbent polymer (SAP) beads to achieve a Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} dispersion as high as 290 mg mL\textsuperscript{-1}, whose viscoelastic properties allowed a deposition of several layers of active material (Figure 8c). The electrolyte-based PVA/H\textsubscript{2}SO\textsubscript{4} gel was used as electrolyte in the electrochemical studies, and the MSC with 10 printed MXene-ink layers (MSC-10), at 2 mV s\textsuperscript{-1}, presented 1035 mF cm\textsuperscript{-2} with maximum energy 51.7 \textmu Wh cm\textsuperscript{-2}. Figure 8d,e shows that the CV response was dependent on the number of printed MXene layers and the capacitive behavior, respectively. In terms of energy density, electrochemical results of MSC-10 outperformed previously reported Ti\textsubscript{3}C\textsubscript{2} MSc\textsuperscript{[196]} produced by 3D-printing techniques.\textsuperscript{[12,65]} Orangi et al. found that MXene inks can be printed at room temperature and on polymer film substrates, thus opening new avenues for use in sensors, electromagnetic shielding, and flexible electronics.

Zhang and coworkers used stamping to manufacture MXene electrodes using a Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} viscous ink.\textsuperscript{[197]} In this method, cylindrical and pad stamps were 3D printed, coated with MXene ink, and transferred onto substrates. Results showed that stamping of MXenes led to increased production and decreased production costs because stamps can be used repeatedly, aspects that may contribute to large-scale production. The Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} micro-SC demonstrated areal specific capacities of 61 and 50 mF cm\textsuperscript{-2} at 25 and 800 \textmu Ac m\textsuperscript{-2}, respectively.\textsuperscript{[197]}

3.5.3. Transition Metal Dichalcogenides

In the 1920s, Linus Pauling first reported a class of layered materials called transition metal dichalcogenides (TMDs or TMDCs), with generalized formula MX\textsubscript{2}, where M is a transition metal and X is a chalcogen atom.\textsuperscript{[198]} More than 60 TMDs are known to

![Figure 8. Electrochemical characterization of 3D-printed MXene Ti3C2Tx. a) Schematic of 3D printing of micro-SC, which shows alignment of Ti3C2Tx flakes due to shear stress in the nozzle. b) MSC-10 (ten layers of Ti3C2Tx printed) on a substrate. c) SEM image of MSC-10 sample demonstrating the aligned flakes of MXene. Electrochemical results of 3D-printed MXene electrodes. d) CV curves of different samples at scan rate of 5 mV s\textsuperscript{-1}. e) Voltage profile curves for different samples at current density of 0.5 mA cm\textsuperscript{-2}. f) Areal capacitance as a function of scan rate for different samples. Reprinted with permission.\textsuperscript{[195]} Copyright 2020, American Chemical Society.](image-url)
exist, among which at least two-thirds present a layered structure, thereby presenting diverse chemistry, mechanical, and electronic properties, as well as polymorphism.\textsuperscript{[199]} These aspects make TMDs attractive materials for applications in catalysis, hydrogen evolution, sensors, and EES. A detailed review of TMDs for EES is available in previous studies.\textsuperscript{[200]}

Relevant literature has identified phase engineering strategies due to polymorphism to achieve desired properties in TMDs. For example, although the most stable thermodynamic phase, reported as 2H, of molybdenum disulfide (MoS\textsubscript{2}) is semiconducting, MoS\textsubscript{2} may also present a metallic 1T phase with electronic conductivity that can be up to 10\textsuperscript{7} times more conductive than 2H-MoS\textsubscript{2}, meaning attractive for catalytic hydrogen evolution and EES because this metallic phase may effectively decrease charge transfer resistance.\textsuperscript{[201]} Finally, the literature has proven that, depending on the TMD species, other phases, such as T\textsubscript{d}-WTe\textsubscript{2} and 1T\textsuperscript{−}WTe\textsubscript{2}, can be evident.\textsuperscript{[202]}

Shao et al. used the high electronic conductivity and hydrophilicity of 1T-MoS\textsubscript{2} to prepare 3D-crumpled ultrathin 1T-MoS\textsubscript{2} (3D 1T c-MoS\textsubscript{2}) using the electrohydrodynamic-assisted method, or electrospray.\textsuperscript{[203]} The crumpled morphology of 1T-MoS\textsubscript{2} nanosheets presented higher volume than bulk 1T-MoS\textsubscript{2}, during electrospray, potentially leading to increased surface area for facilitated ion adsorption and electrolyte diffusion among the MoS\textsubscript{2} nanosheets. The most stable dispersion of 3D 1T c-MoS\textsubscript{2} was obtained using isopropyl alcohol (IPA) mixed with a 2-butanol solvent to achieve uniform material deposition in the inkjet process. The printed asymmetric MSCs comprised a negative electrode of 3D 1T c-MoS\textsubscript{2} and a positive electrode of rGO. Electrochemical results showed a triangular voltage profile with an output voltage of 1.75 V at 20 mA cm\textsuperscript{−2} in 1 M MgSO\textsubscript{4}. The stable output voltage of 1.75 V exhibited 96\% capacitance retention after 20 000 GCD cycles. In terms of areal power and energy density, 3D 1T c-MoS\textsubscript{2} presented 12.6 mW cm\textsuperscript{−2} and 3.85 μWh cm\textsuperscript{−2}, respectively.

In another example of the potential of 1T-MoS\textsubscript{2}, Xu et al. used femtosecond laser direct writing to produce an MSC electrode of stacked 1T-MoS\textsubscript{2} films.\textsuperscript{[204]} The use of high-power density (usually higher than 10\textsuperscript{13} W cm\textsuperscript{−2}) and ultrashort (width of 35 fs) pulses produced a nonthermal effect, which prevented the 1T-MoS\textsubscript{2} phase transition to the semiconducting 2H-MoS\textsubscript{2}, thereby safeguarding the high electronic conductivity in the electrode. As shown in Figure 9a,b, 1T-MoS\textsubscript{2} films were produced via vacuum filtration and properly transferred and integrated onto a silicon substrate. The laser direct writing technique was then employed with femtosecond laser pulses to shape the interdigitated electrodes of \( \approx 12.5 \mu m \) in width and 833 nm apart, as shown in Figure 9c,d. Tested in H\textsubscript{2}SO\textsubscript{4}/PVA hydrogel electrolyte, the quasi-rectangular CV shape made the low ESR (i.e., 10 V s\textsuperscript{−1}), and superior performance of 1T-MoS\textsubscript{2} comparable with 2H-MoS\textsubscript{2} (Figure 9e). In addition, the CV plots of 1T-MoS\textsubscript{2} showed the differences depending on the laser pulse delay, i.e., for shaped femtosecond laser (t-fs laser) with different pulse delay of 5 or 10 ps.\textsuperscript{[204]} Similarly, the GCD curves in Figure 9f show the higher capacitance of the t-fs laser (5 ps) sample compared with the other delay times and the traditional nanosecond laser (ns laser). The 1T-MoS\textsubscript{2} presented an areal capacitance of 36 mF cm\textsuperscript{−2} with 93\% capacity retention up to 5000 cycles.

3.5.4. Transition Metal Oxides

Transition metal oxides (TMOs) have gained prominence as supercapacitors electrodes because some species present reversible solid-state redox reactions on their surface.\textsuperscript{[139]} These reactions commonly outperform the double layer capacitance—found in carbon-based materials—in terms of specific capacitance and energy density.\textsuperscript{[205]} Along with various chemistries, diverse morphologies, and abundant availability of some species TMOs are potential candidates for the next generation of supercapacitors and MSCs.\textsuperscript{[206]} However, the practical use of TMOs is hindered by low electronic conductivity, sluggish ion diffusivity, and large volume expansion. Several works have reported the use of carbon-based conductive agents to overcome this drawback of electronic conductivity. These carbon-based agents provide a scaffold with increased electronic conductivity and more active sites area for redox reactions.\textsuperscript{[207]}

![Figure 9](image-url)
In the work of Wang et al., 3D GO structure was first produced by extrusion process and subsequently reduced to rGO. As reported by the authors, this interdigitated rGO itself offered continuous path for electrons, better contact on the electrode–electrolyte interface, and support for pseudocapacitive metal-oxide species. Using the rGO as a 3D scaffold, NiO nanorods and MnO₂ nanosheets were individually studied and grown by electrodeposition onto the rGO structure. As per expectation, the specific capacitance of the specimen containing NiO was higher than the pristine rGO. This is ascribed to the pseudocapacitance contribution from NiO. Tested in 1 M KOH/PVA in symmetrical configuration the best-performing NiO nanorod in interdigitated rGO sample presented 166.6 mF cm⁻² at 0.6 mA cm⁻², whereas MnO₂ nanosheets-based material presented 70.4 mF cm⁻² at 0.5 mA cm⁻². In this work, the interdigitated rGO structure provided support to pseudocapacitive materials with capacitance retention higher than 80% up to 10,000 cycles. Overall, this work demonstrates carbon-based materials as supporting 3D scaffolds for pseudocapacitive materials toward higher capacitance materials.

Using a similar strategy, Yao et al. produced 3D graphene aerogel structure by DIW method from GO. After the annealing of 3D GO, as shown by Figure 10a, MnO₂ nanosheets were electrodeposited onto the 3D graphene scaffold. It is important to highlight that although the 3D graphene aerogel structure initially presented a surface area of 27 m² g⁻¹, after the MnO₂ electrodeposition the surface area of the material increased to 100 m² g⁻¹. The capacitance increase in the pseudocapacitive electrode (3D G/MnO₂) is shown in Figure 10b. Tested at 3 M LiCl in a three-electrode system, 3D G/MnO₂ electrode with mass loading of 45.2 mg cm⁻² delivered 11.55 F cm⁻² at 0.5 mA cm⁻² (Figure 10c,d). Moreover, the authors showed that by increasing the thickness of the scaffold (up to 4 mm thick) allowed a higher mass loading of MnO₂ (up to 182.2 mg cm⁻²). With higher mass loading of MnO₂, the thicker scaffold presented a linear dependence with areal capacitance (Figure 10e). This linear relationship indicates that although thicker electrodes presented higher charge transfer resistance values, they did not present diffusion limitation. This study demonstrates the potential of AM for fabricating scaffolds and depositing TMOs with high mass loading toward high-performance materials.

4. Conclusion

AM is a promising suite of emerging technologies for research and commercial initiatives. Aspects such as decreased waste, scalability, and the production of customized electrode shapes allow EES to easily integrate with commercial products. Furthermore, hierarchal 3D porous structures, produced by layer-by-layer deposition, may facilitate ion transport and yield higher power and energy densities due to increased surface area and improved electrolyte penetration. The utilization of AMTs to produce layered material-based electrodes is also beneficial.
because recurrent issues such as restacking or agglomeration can be addressed using 3D porous current collectors. However, these porous structures may lower mechanical properties in printed electrodes, hindering microelectronic applications and dendrite formation, as shown in the research by Wang et al.\textsuperscript{[210]} Future research could investigate AMTs that successfully print 3D-layered materials-based electrodes while retaining their mechanical properties.

FDM research should seek to increase the conductivity of additive materials used in filaments that directly impact battery rate capability and capacity. For techniques such as DIW, the formulation of functional inks must consider dynamic viscosity, solidification time, homogeneity, and orientation of active materials, which are crucial for printing microstructured EES electrodes. Overall, research of novel additive materials for filaments and formulation of functional inks that could maximize the printing process and the electrochemical performance of electrode materials is needed.

Research efforts are also needed to develop more precise AMTs. Although current AMTs do not exhibit precision at microscale, achieving precision at the nanoscale would increase pore accessibility and control ion diffusion and other electrochemical properties.\textsuperscript{[211]} Material heterostructures successfully combine material advantages and use these as building blocks, as described by Pomerantseva and Gogotsi\textsuperscript{[212]} Consequently, AMTs can be used to unite the best aspects of materials and manufacturing. EES research opportunities also are available for 4D materials, 3D-printed structures that respond to external stimuli. In summary, although this Review focused on AM electrode materials, AMTs could be used to produce an entire battery or supercapacitor cell, including the electrolyte and separator, and applications ranging from nanogenerators to 3D bioprinting hold promising opportunities for AM.

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Conflict of Interest

The authors declare no conflict of interest.

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Davi Marcelo Soares holds a master of science from the University of Campinas (Unicamp), Brazil, and currently is a Ph.D. candidate at Mechanical and Nuclear Engineering Department at Kansas State University, advised by Prof. Gurpreet Singh. His research focuses on layered materials for EES.
Zhongkan Ren obtained bachelor’s in materials chemistry from QUST, China, in 2014, master’s in mechanical engineering from Oregon State University, in 2016, and finished Ph.D. in mechanical engineering from Kansas State University, in 2020.

Hudson Zanin works with the University of Campinas to develop energy storage devices at Advanced Energy Storage Group. He has been working on advanced materials chemistry focused on electrode characterization under dynamic conditions. He has been working on supercapacitor and battery manufacturing.

Gurpreet Singh is Harold O. and Jane C. Massey Neff associate professor in the Mechanical and Nuclear Engineering Department at the Kansas State University. He received his master’s and Ph.D. from the University of Colorado at Boulder. Before joining Kansas State University, in 2009, he worked as a postdoctoral associate and guest researcher at Virginia Tech and National Institute of Standards and Technology, respectively.