University of Massachusetts Amherst

From the Selected Works of Steve Acquah

August 14, 2020

3D Printing for Energy-Based Applications

Steve Acquah, *University of Massachusetts Amherst*

Available at: <https://works.bepress.com/steve-acquah/5/>

3D Printing for Energy-Based Applications

Steve F. A. Acquah

Contents

Introduction	2
Fundamentals of Additive Manufacturing	3
Fused Deposition Modeling	5
Digital Light Processing 3D Printing	6
Carbon Nanomaterials Materials in 3D Printing	7
Carbon Nanotubes	7
Fullerenes	9
Carbon Black	10
Graphene	12
Metal Nanoparticles and Nanowires	14
3D Printing Batteries and Energy Storage Devices	14
Fuel Cells	18
Solar Cells and Supporting Technologies	20
Conclusions and Further Outlook	23
References	23

Abstract

3D printing has transitioned from the commercial and educational sectors toward tools for materials science. The technologies available for 3D printing have evolved rapidly, facilitating the incorporation of new materials and functionalities into filaments and resins. As the cost of 3D printing decreases, and the technologies supporting high-resolution printing become industry standard, the push toward 4D printing, a subcategory of 3D printing, that enables the fabrication of components through multiple techniques and materials will transform the energy sector. 3D printing is no longer limited to the use of plastics, and the fabrication of metal, graphene, and hybrid architectures for use as electrodes is

S. F. A. Acquah (✉)

Department of Chemistry, Digital Media Lab, University of Massachusetts Amherst,
Amherst, MA, USA

© Springer Nature Switzerland AG 2020

O. V. Kharissova et al. (eds.), *Handbook of Nanomaterials and Nanocomposites for
Energy and Environmental Applications*,

https://doi.org/10.1007/978-3-030-11155-7_161-1

now possible. Energy storage and fuel cells have made advances using 3D printing-assisted methods to prototype and evaluate innovative designs and compositions. This chapter describes the techniques used to develop 3D-printed batteries looking at the limitations of extrusion-based printing and some of the new ideas that aim to provide low-weight and high-capacity ergonomically designed batteries. This chapter also explores the development of 3D-printed devices for wearable energy storage with a focus on the nanomaterials that have the potential to transform 3D-printed energy-based applications. The chapter will conclude with an overview of some of the emerging technologies for the impact of additive manufacturing techniques in the design of fuel cells and photovoltaics. The methods detailed in this chapter provide an introduction to the principles of energy-based applications supported by 3D printing and the design, the fabrication, and the tailoring of those applications. Further comprehensive information can be found in the references attributed to this chapter.

Keywords

3D printing · Additive manufacturing · Energy · Nanomaterials · Carbon black · Fullerenes · Carbon nanotubes · 4D printing

Introduction

3D printing has become a strong part of the revolution in education and research, transforming the approach to design prototyping in material fabrication. The global Coronavirus pandemic has highlighted the use of 3D printers in a global mobilization to produce personal protective equipment for frontline medical personnel and essential workers while also providing novel solutions for printing components for ventilators. 3D printing technology has advanced substantially in recent years, improving upon the quality of prints while minimizing mechanical and environmental factors that could result in warping, extruder clogging, and failed prints. While it is still too early to estimate the significant impacts of the Coronavirus on the additive manufacturing (AM) sector, before the crisis in 2018, 3D printers were recognized as the largest part of the 3D printing market with a 54.5% share of the market and sales revenues of nearly \$4.6 billion. Services were listed as the next highest percentage at 25.9%, around \$2.2 billion, while materials took 10.2% of the market, and software took 9.5%. 3D printers and materials were expected to have rapid growth, exceeding 50.7% of the market (\$13.9 billion) and 9.9% of the market (\$2.7 billion), respectively, by the year 2024 [1].

Additive manufacturing has helped to catalyze a movement of makers, supplementing STEM education with more hands-on activities. Research into AM technologies and materials has provided new ways to enable low-cost, rapid prototyping of designs. Researchers are already beginning to look beyond standard 3D printing materials like ABS and PLA and are focusing on multi-material filament compositions. These recent developments have helped to introduce 4D printing as a

new area of additive manufacturing. While being a subset of 3D printing, the idea behind 4D printing considers changes to the use of smart materials and processes that cause a change in a printed object. These changes can be due to heat, light, temperature, and other environmental stimuli to induce a transformation in the printed object over time (the fourth dimension) [2].

The push toward the use of 3D printing in the energy sector may be driven by the need to reduce costs and save time. Research into material compositions and fabrication processes to cut costs is essential, especially at a time of global economic uncertainty. The US Department of Energy (DOE) is one of the sources aiding research into 3D printing for energy-based applications. The use of 3D printing for energy-based applications, including storage and transfer processes, requires careful designs and precision to produce materials efficiently, and these considerations are heightened when modifying the thermoplastics used in 3D printing. There is a growing need for the incorporation of nanomaterials into 3D printing materials to provide enhanced functionality, with benefits in the mechanical and electrical properties of objects printed.

Fundamentals of Additive Manufacturing

One of the strengths of additive manufacturing (AM) as a sector is the breadth of the techniques available to produce objects. Fused deposition modeling, digital light processing, and stereolithography are the more familiar consumer-based printing techniques, but there are common threads between many other techniques that provide insight into potential applications in the energy sector.

For manufacturing, various technologies are suitable for the production of components with simple to complex geometries and provide a cheaper pathway to the mass production of specialized items with reduced timelines. The additional benefit of AM is that the technologies can be used to create objects using an extensive range of materials such as metals and alloys, polymers, ceramics, glass, synthetic stone, and even food [3]. Table 1 describes some of the techniques available. Selective laser sintering (SLS) is a process whereby small particles of polymers like the thermoplastic nylon, glass, or other ceramics are fused by heat from a laser to form 3D objects. During the process, the nylon powder is spread in thin layers on a build platform, and the laser selectively sinters the powder before an additional thin layer of powder is added, and the process repeats. The computer-controlled laser pulses down along the build platform, creating a cross-section of the object being printed in the powder. The advantage of this process is that there is very little post-processing required, and components made with nylon will be heat- and chemical-resistant. This would be useful for protective coverings for energy-based applications. While the process is straightforward, the name “laser sintering” has stirred much controversy [4]. Laser “sintering” is more of a historical term and a misnomer. In the interest of accuracy, it may be better to call it “laser melting” and combine it with the process for metals. Selective heat sintering (SHS) is a similar process where the distributing blades cover the build plate with a thin layer of powdered polymer,

Table 1 Comparison of additive manufacturing techniques for the energy sector

Additive manufacturing technology	Most common materials used	Energy-based applications	Considerations
Fused deposition modeling (FDM)	Thermoplastics – PLA, ABS	Complex structural designs, electrode fabrication, and sensors	Weakness between layers, low surface quality, and slow production time
Digital light processing (DLP)	Photopolymer (liquid)	High detail 3D energy storage devices. Conductive nanomaterials can be mixed with the photopolymer. Solid oxide fuel cell assembly	Limited to the use of photopolymers. Post-curing required
Stereolithography (SLA)	Photopolymer (liquid)	Complex geometries. Higher quality than DLP. Conductive nanomaterials can be mixed with the photopolymer. Solid oxide fuel cell assembly	Slower than DLP. High cost. Post-curing required
Selective laser sintering (SLS)	Nylon, ceramics	Supporting components that provide protection from high heat and chemicals	Particle size defines the quality. Granular surface
Selective heat sintering (SHS)	Thermoplastics (powder)	The rapid production of supporting components	Limited amount of materials, but cheaper setup than SLS
Selective laser melting (SLM)	Metals (powder) – Tungsten, cobalt, copper, aluminum, stainless steel, and titanium.	Rocket engine components. Very strong and durable prints. Rotors and impellers	Post-processing time can be long and supports difficult to remove
Electron beam melting (EBM)	Titanium, titanium alloys	Turbine blades and engine components. Removal of impurities from multicrystalline silicon	It can use metal powder or wire

but the heat source is a thermal printhead and is a cheaper process than SLS [5]. Selective laser melting (SLM) is technically a subcategory of SLS that uses metal powders, including tungsten, cobalt, copper, and aluminum. It is used to make strong and durable parts like rotors and impellers. Electron beam melting (EBM) is a technique that uses metal powder or wire in a vacuum, fusing the metal with an electron beam. It can be used to remove impurities from multicrystalline silicon [6].

Fused Deposition Modeling

The most popular form of 3D printing in the consumer market is based on thermoplastic extrusion. The current method used in the 3D printers is credited to Scott Crump whose work in 1988 resulted in the development of the company Stratasys [3]. Fused deposition modeling (FDM) provides the entry point for additive manufacturing that is well supported in the industrial, educational, and research sectors with a strong network of “makers” that design 3D objects optimized for 3D printing. Commercial 3D printers typically use filaments that are 1.75 mm in diameter, and during printing (Fig. 1), the filament is unwound from a spool and fed into an extrusion assembly with the aid of motor-driven gears. The filament melts in a temperature-controlled chamber before being passed through the tip of the extruder nozzle onto the build plate.

The success of FDM for rapid development, unfortunately, does not widely transfer to the production of electrochemical energy storage (EES) devices because of the low electrical conductivity of thermoplastic filaments [7]. However, there are many recent advances in FDM for energy-based applications, including multi-material and conductive filaments.

Fig. 1 Diagram of an FDM printer

Digital Light Processing 3D Printing

In addition to FDM printing, the second most popular consumer 3D printing technology is digital light processing (DLP), which uses a projection of a digital mask to initiate localized photopolymerization. The concepts underlying DLP can be found in its predecessor, stereolithography (SLA). The SLA 3D printers use a build platform, an elevation system to move the platform up, a resin tank, a light source, and galvanometers. The build platform is first lowered into the resin-filled tank with a separation from the bottom of the tank to the build plate of one layer of height. The main difference between DLP and SLA is the source of light. SLA uses a UV laser with the beam directed to galvanometers, which in turn directs them to the specific coordinates represented by a cross-section of the object being printed. The beam from the laser hardens the photopolymer resin as it moves. DLP uses UV light from a projector, and the light source is stationary. This results in the entire layer hardening at the same time and makes DLP faster than SLA, but the use of UV laser with SLA means the printed objects are more precise. Figure 2 shows the typical components of a DLP 3D printer.

The advantage of DLP 3D printing for energy-based applications is the ability to mix various nanomaterials within the resin before polymerization. This avoids

Fig. 2 Diagram of a DLP 3D printer. (Image adapted from Acquah et al. [13])

having to process the nanomaterials in PLA and eliminates the problems associated with extrusion, including clogging of the extruder nozzle and multiple processing steps to produce novel filaments.

DLP printers are being used as a cost-effective tool to support research and development. The applications include piezoelectric acoustic sensors [8], 3D micro-supercapacitors (3D MSC) [9], solid oxide fuel cells [10], as well as the nanomechanical properties of the 3D-printed components [11].

Carbon Nanomaterials Materials in 3D Printing

Research into carbon nanomaterials has been advanced by the use of 3D printing to create controlled assemblies and conductive inks [12–14]. Carbon nanomaterials such as fullerenes, carbon nanotubes, graphene, and carbon black all have exceptional properties with regard to their mechanical, electronic, thermal, and optical nature. These materials can be processed with 3D printing filaments like PLA and ABS, as well as photopolymer resins.

Carbon Nanotubes

As an allotrope of carbon, these nanostructured tubes have been associated with potentially significant impacts in science and engineering. Carbon nanotubes (CNTs) come in many forms from a single-walled carbon nanotube (SWCNT), as shown in Fig. 3, to multi-walled carbon nanotubes (MWCNT).

Fig. 3 A model of a cross-section through a single-walled carbon nanotube. Image produced using Nanotube Modeler, JCrystalSoft

Fig. 4 Filament extrusion setup with a twin-screw extruder, water bath, filament puller, and winding device. (Reprinted (adapted) with permission. Arif et al. [23])

Although the theoretical representation of CNTs depicts them as being perfect singular or concentric tubes, similar to the tubes produced by the arc discharge process, the CNTs typically used in research and development are produced by the chemical vapor deposition (CVD) process which is beneficial for exploiting sidewall functional groups, which can then be chemically or mechanochemically transformed, used for cross-linking [15–18], and used as sensors [19].

Many additive manufacturing processes have begun to use CNTs embedded in their printing material feedstock, including selective laser sintering [20] and fused deposition modeling. There are now many polymer-CNT and polymer-carbon nanofiber composites designed for 3D printing that uses acrylonitrile butadiene styrene (ABS) [21], poly(lactic acid) (PLA) [22], and polyether ether ketone (PEEK) [23].

The problem with incorporating CNTs into polymer mixtures to produce polymer-CNT nanocomposites is that only low percentages can be used as there is a propensity for CNT agglomeration that causes points of failure. New approaches to help reduce the degree of agglomeration will be required to address the problem.

In one example, multi-walled carbon nanotubes (outer mean diameter of 10–15 nm and a length of about 0.1–10 μm) were used to reinforced polyether ether ketone (PEEK) composites. 3D printing was done by fused deposition modeling [23]. The mechanical and thermophysical properties of the electroconductive PEEK nanocomposites showed that the coefficient of thermal expansion (CTE) decreases by 18% with the incorporation of 3 wt% CNTs into the PEEK polymer. The CTE decrease is beneficial as it gives more dimensional stability to subsequent structures. The crystallization temperature and degree of crystallinity increased because of the uniform dispersion of CNT.

Making the filament is an important step and can be challenging to produce a uniform thickness for the filament. Errors during the process could cascade across the use of the filament during printing with potential problems with filament feeding and blocked nozzles. A filament production method was established with an extrusion system consisting of a twin-screw extruder, a customized filament puller, a water bath, and a winding device (filament spooler). The setup is shown in Fig. 4.

Accurate speed control was obtained with a potentiometer on the filament puller. The PEEK-CNT compound with 1 wt% CNT had good melt processability, but the PEEK-CNT compound with 3 wt% CNT was viscous and unusable for 3D printing.

The most important result was the determination of the percolation threshold. The electrical conductivity for the 1 wt% CNT filament was 9.1×10^{-7} S/cm.

PLA is a popular choice for the modification with nanomaterials, including carbon nanotubes, to make conductive composites [24]. One study used repeated melt blending [25] where CNTs were mixed with PLA granules at various weight percentages, with the extrusion of the mixtures to filaments targeted at a diameter 1.75 mm. The actual diameter of the filament was measured to be in the range of 1.40–1.75 mm. The production of filaments depends on ensuring there is a steady feed of material and preventing die swell. The PLA-CNT composite established a percolation threshold when CNT content was 2 wt % (~1.2 vol %). When the amount of CNT reached 2 wt %, the electrical conductivity (σ) of the composite film increased to the order of 10^{-6} S·m⁻¹; at 6 wt %, there was a further increase σ to the order of 10^{-2} S·m⁻¹. At this level, the thermoplastic composite behaves as a semiconductor in electrical devices; At 8 wt %, the σ increased to the order of 10^{-1} S·m⁻¹, which is suitable for many electrical applications.

The in situ dispersion of MWCNTs in 3D-printed polymer nanocomposites was demonstrated by Chavez et al. [26]. The MWCNTs were mixed with a clear resin to form a novel 3D print resin that was used on an SLA 3D printer. The mechanical and electrical characterizations revealed that the introduction of MWCNTs increased the elastic modulus of the resin by 77%. An electric field was used for in situ dispersion of the MWCNTs and increased the ultimate tensile strength of the MWCNT-resin reinforced nanocomposites by 42%. It was also shown that the scale and directionality of the electrical conductivity of MWCNT nanocomposites could be modified and controlled through the application of in situ electric fields when 3D printing using commercially available machines.

In summary, CNTs may find a new niche in 3D printing with research indications suggesting there may be a better level of control over dispersions in resins, powders, and filaments than would have been expected. These advancements have improved the mechanical and electronic properties of polymer nanocomposites. Still, with FDM 3D printing, the abrasive effects of the CNT filaments on the printer nozzles will have to be investigated.

Fullerenes

The archetypal fullerene C₆₀ (Buckminsterfullerene) (Fig. 5) transformed how carbon was considered in the formation of stable carbon structures, establishing its place as the third allotrope of carbon after diamond and graphite. Harold Kroto, Robert Curl, and Richard Smalley received the 1996 Nobel Prize in Chemistry for the discovery of fullerenes.

Fullerenes have a unique structure consisting of sp² carbons and highly symmetrical cages like C₆₀ and C₇₆ [27]. The 60-carbon atom molecule catalyzed a movement in chemistry, physics, biological sciences, and engineering to investigate the unique properties [28]. Fullerenes can undergo surface modifications to form fulleranol, enabling better dispersion in polymers [29, 30]. These modifications can

Fig. 5 A model of C_{60} (Buckminsterfullerene). Image produced using Nanotube Modeler, JCrystalSoft

be used to improve their utility, creating a pathway to highly effective n-type organic semiconductors and can be used in solar cells as electron acceptors and conductors [31, 32].

[6,6]-Phenyl-C61-butyric acid methyl ester (PCBM) is one of the more popular fullerene-based molecules used in energy-based applications and has been used in the development of 3D-printed photodetectors [33].

The arrival of graphene as one of the latest entries into the carbon nanostructured materials field has sidelined fullerenes. Still, the uniform nature of these nanomaterials and the solubility of their derivative may make fullerenes an attractive alternative for nanoscale 3D printing and polymer or resin-based additives for FDM, SLA, and DLP printers.

Carbon Black

As a well-known staple additive to conductive carbon composites, carbon black (CB) is a particulate form of industrial carbon that can be produced by the thermal decomposition of a hydrocarbon raw material or by thermal cracking. Carbon black has a semi-graphitic structure with hexagonal layers that are spaced further apart than what is typically found in graphite and without the vertical orientation. The particles of CB are closely packed, tightly bundled crystallites that have a few hexagonal layers [34].

Fig. 6 SEM images obtained for as-prepared 3DP PLA-CB (a, b) electrodes and the same kind of electrodes activated for 60 s (c, d) at a magnification of 40× (a, c) and 10,000× (b, d). (Reprinted (adapted) with permission. Vaneckova et al. [37])

The structural overtones in CB in relation to the semi-graphitic character have made it a potential alternative in conductive polymer composites. PLA-CB conductive composites have been produced as a rival to PLA-graphene composites for FDM and can be a viable alternative to the incorporation of metal nanoparticles. Studies have looked into the conductivity of PLA-CB [35, 36], and this conductive thermo-plastic composite, when used in FDM 3D printing, can be used to manufacture electrodes. Vaneckova et al. [37] constructed PLA-CB electrodes and activated them by using a simple electrochemical procedure. To evaluate the performance of the electrodes, cyclic voltammetric measurements, with Ruthenium(III) acetylacetonate as the electroactive probe, were performed. The faradaic peak separation values were between 80 and 85 mV. Scanning electron microscopy (SEM) imaging was conducted to investigate the surface characteristics of the electrodes. Figure 6a, b shows images of the as-prepared 3D-printed PLA-CB electrodes. Figure 6c, d presents images of the same kind of electrodes that were further treated to anodic activation for 60 s. The images suggest that the electrode surface morphology remained unaffected by the activation process.

In another example, a 3D-printed PLA-CB working electrode was used for the square-wave anodic stripping voltammetry (SWASV) determination of the trace concentration of Cu^{2+} in fuel ethanol. The work highlighted the benefit of the 3D-printed PLA-CB electrode, which, after chemical and electrochemical surface

treatment, exhibited good conductivity with low background currents and was an excellent substitute to other electrodes used in fuel bioethanol analysis [38].

3D-printed acrylonitrile butadiene styrene/carbon black, ABS-CB, electrodes were influenced by printing direction. Electrodes were printed in the horizontal and vertical directions. The electrodes printed in a vertical direction demonstrated enhanced electrochemical performance, suggesting that print orientation should be of significant consideration when 3D printing electronics [39].

In summary, the use of carbon black as a conductive additive for 3D printing has become the archetypal material for conductive filaments. The market is still growing, but it is likely that with improvements in FDM technology and filament processing techniques, alternative materials may become more popular.

Graphene

Research into graphene produced a wave of excitement in the scientific community, heightened in part by the 2010 Nobel Prize in Physics awarded for “groundbreaking experiments regarding two-dimensional material graphene.” Graphene is a single layer of carbon atoms densely packed into a benzene ring structure (Fig. 7) and describes the properties of many carbon-based materials, including carbon nanotubes, large fullerenes, and graphite [40]. Graphene exhibits superior room temperature electron mobility with values above $15,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [41]. It also has a unique nature to its charge carriers as it mimics relativistic particles and is better described by the Dirac equation instead of the Schrödinger equation. The properties of graphene make it a good additive for 3D printing [42].

Fig. 7 A model of a graphene sheet. Image produced using Nanotube Modeler, JCrystalSoft

For 3D printing applications, the mechanical properties of PLA-graphene filaments produced by FDM have been tested. The tests included the tensile strength, flexural strength, and parts manufactured from a spool of the PLA-graphene filament [43]. The tensile strength (σ_t) was greatly affected by the infill and layer thickness (linear in both cases) according to the model that they used for analysis where $R^2 = 0.9396$ and $RMSE = 1.63$. A tensile strength of 33.7 MPa (highest value) was obtained using a layer thickness of 0.27 mm and an infill of 78%. The results showed that tensile strength increased with increasing layer thickness and infill as generally expected by 3D printing. Flexural strength (σ_f) was determined to be greatly affected by the infill and layer thickness (linear in both cases) according to the model used for analysis where $R^2 = 0.9157$ and the $RMSE = 2.97$. The results showed the highest flexural strength as being 60.9 MPa when the layer thickness was 0.27 mm, and the infill was 78%. The general trend showed an increase in flexural strength with increasing layer thickness and infill, with higher σ_f /weight rates and σ_f /printing time when the infill reached 22% and a layer thickness of 0.27 mm.

PLA-graphene filaments were used to demonstrate the development of low-loss suspended microstrip microwave circuits [44] and biosensors for the analysis of biological fluids using FDM 3D printing to create the biosensing platforms [45]. In this research, an enzymatic glucose biosensor was produced on the PLA-graphene surface and applied to glucose sensing in blood plasma by chronoamperometry. The biosensor had a limit of detection (LOD) of $15 \mu\text{mol L}^{-1}$, an inter-day and intra-day precision that was lower than 5%, and ample recovery values of 90–105% for the analysis of plasma. This research highlighted one of the first applications of 3D-printed sensors and biosensors for the analysis of biological samples with analytical characteristics that were comparable to conventional modified electrodes.

A powder-bed AM process was used to produce graphene-based 3D structures [46]. A graphene oxide (GO)/hydroxyapatite (Hap) nanocomposite (GHN) was synthesized with varying GO to Hap percentages (wt.%), to develop a printable powder. 3D porous structures were printed with the GHN powder, and it was noted that at a layer thickness of 125 μm and a core binder saturation level of 400%, the compressive mechanical strength of the samples produced with higher amounts of graphene were significantly improved.

Graphene has been used for the fabrication and characterization of graphene-based (PLA) and ABS conductive filaments, with graphene loadings of up to 5.6% wt. for ABS-graphene and 0.8% wt. for PLA-graphene [47]. This research highlighted that at a high graphene loading level of 7.4% wt., graphene sheets that have aggregated may clog the printer's nozzle, resulting in the 3D printing failure. For ABS-graphene, at 0.4 wt%, the electrical conductivity was $1.78 \times 10^{-7} \text{S} \cdot \text{m}^{-1}$ and then rose to $3.04 \times 10^{-7} \text{S} \cdot \text{m}^{-1}$ at 2.3 wt%. When graphene loading reached 3.8 wt%, the conductivity significantly increased to $6.4 \times 10^{-5} \text{S} \cdot \text{m}^{-1}$. There was a decrease in the conductivity to $2.5 \times 10^{-7} \text{S} \cdot \text{m}^{-1}$ upon testing a printed a 10 mm $\times$ 10 mm $\times$ 1 mm model due to the possible internal voids among adjacent stacked filaments. This may help explain why printing orientation is an essential consideration for electronic applications.

For energy-based applications, freestanding lithium-ion anodes and solid-state graphene supercapacitors were made via additive manufacturing (FDM) using a bespoke PLA-graphene filament [48]. The proof of concept was demonstrated using a printable 3D graphene-based PLA filament that was 3D-printed to optimize efficiency. This 3D electrode platform was analyzed for its ability to create hydrogen by the hydrogen evolution reaction.

In summary, PLA-graphene, in a similar way to PLA-CB, defines a new era in conductive thermoplastic filaments for 3D printing technology that will support applications for sensors, electrodes, and energy storage devices.

Metal Nanoparticles and Nanowires

The use of metal nanoparticles and nanowires as integral components of 3D printing material additives is of great importance. While their utility is advantageous when compared to other additives for conductive filaments, there are still some considerations that need to be overcome to achieve high-quality conductive 3D networks for the FDM, SLA, and DLP3D printing techniques. Particle size is a major factor, and with inkjet inks, there is a general rule that the maximum pigment particle size should be $<1/10$ of the orifice diameter to prevent bridging and blockage, with the possibility of a larger ratio depending on the nozzle type [49]. The considerations for FDM 3D printing focus more on the diameter of the filament, but there are still nanoparticle size considerations for additives. For good electrical conductivity with metals, highly conductive metals which are stable to oxidation, such as silver ($\sigma = 6.3 \times 10^7 \Omega^{-1}\text{m}^{-1}$) and gold ($\sigma = 4.42 \times 10^7 \Omega^{-1}\text{m}^{-1}$), are the best but expensive. Alternatives such as copper ($\sigma = 5.96 \times 10^7 \Omega^{-1}\text{m}^{-1}$), aluminum ($\sigma = 3.78 \times 10^7 \Omega^{-1}\text{m}^{-1}$), and nickel ($\sigma = 1.43 \times 10^7 \Omega^{-1}\text{m}^{-1}$) may be used [50]. FDM, SLA, and DLP would all require the determination of the percolation threshold to ensure sufficient networks between the nanoparticles and nanowires are established. The other major problem is that these metals may be abrasive to 3D printer nozzles. For other additive manufacturing techniques such as selective laser melting (SLM) and electron beam melting (EBM), the melting process forms good electrical contacts.

3D Printing Batteries and Energy Storage Devices

It is difficult to imagine a time when there was no dependence on batteries and other energy storage devices. These devices power everything from smartphones to modes of transportation, and within educational and industrial research labs, there is a continuing effort to produce ever smaller and longer-lasting batteries. Researchers are working with 3D printers to advance current battery technology; it would create a paradigm shift whereby before manufacturers designed their products around the batteries, now the manufacturers can save space and incorporate the design of the batteries into the products. This is a benefit, but it can also cause concern with the development of non-standardized batteries when the specific products they were designed for reaches their end of life.

Fig. 8 (a) Individual components of the 3D-printed coin cell. (b) Assembled 3D-printed coin cell. (Reprinted (adapted) with permission. Reyes et al. [51])

Reyes et al. [51] developed a 3D-printed lithium-ion battery by producing the anode, cathode, and separator materials. Their battery obtained an ionic conductivity of 0.085 mS cm^{-1} , which was similar to polymer and hybrid electrolytes. Their method involved identifying the degree of PLA swelling with solvents while increasing the ionic conductivity, infusing lithium salts and measuring how much the ionic conductivity changed. They finally determined the amount of conductive carbon filler and any changes in morphology that may affect the ability to 3D print. They reported pure PLA as having a low ionic conductivity of $8.2 \times 10^{-11} \text{ mS cm}^{-1}$. Electrochemical impedance spectroscopy (EIS) was used to measure the ionic conductivity. It was determined that a 1:1 (by volume) solution of propylene carbonate (PC) and ethyl methyl carbonate (EMC) had a better volume change (29%) in PLA with an ionic conductivity (0.031 mS cm^{-1}) and did not result in making the PLA brittle. It was used to test the ionic conductivity with lithium electrolytes. PLA infused with LiClO_4 had the second-highest ionic conductivity (0.085 mS cm^{-1} , 20°C) but, more importantly, retained its mechanical integrity and ionic conductivity after a period of 24 h. After optimization of the anode and cathode, the final composition for each electrode was 6/24/70 vol % lithium titanate/graphene/PLA and 4/16/80 vol % lithium manganese oxide/MWNT/PLA.

A 3D-printed full-cell was produced and tested with the current collectors, anode, cathode, and separator, all enclosed in a printed coin cell. Figure 8a shows the individual components of the cell, and Fig. 8b shows the assembled cell. The 3D-printed anodes, cathodes, and separators were infused with 1 M LiClO_4 in 50/50 vol EMC/PLA prior to assembly. A conductive filament with a resistivity of $0.006 \Omega \text{ cm}$ and printing temperature of $130\text{--}160^\circ\text{C}$ was used for 3D printing the current collectors, and pure PLA was used for the separators.

The electrochemical performance for full-cells was performed within a cutoff voltage range $3.0\text{--}2.0 \text{ V}$ at a mass-normalized current of 20 mA g^{-1} . The resistivity values showed that the use of two printed current collectors increased the resistivity from $10^2 \Omega \text{ cm}$ for the half-cells to $10^4 \Omega \text{ cm}$ for the printed full-cell. The volumetric capacity of the full 3D-printed coin cell was 0.25 mAh cm^{-3} .

Fig. 9 Separated view of the internal 3D-printed components of a 3D-printed bangle battery with an integrated LED. Assembled 3D-printed bangle battery powering an LED. (Reprinted (adapted) with permission. Reyes et al. [51])

An LED bangle with an integrated battery was produced (Fig. 9.). The battery anode and cathode were printed as curved electrodes that combined to form the bangle with the use of a Celgard polymer separator. The bangle battery powered a green LED for ~60 s.

This chapter has highlighted PLA as a popular commercial 3D printing filament and has become a foundation for creating the next-generation multi-material 3D printing filaments. Some examples of these filaments include wood [52] and anti-bacterial PLA that uses silver [53, 54]. PLA is not an ionic conductor, which is an initial step that needs to be overcome before a conductive filament can be produced. Jahangir et al. [55] investigated the mechanisms involved in the combination of PLA polymer with the printing of silver NPs, and polymer-metal hybrid materials for 3D printing will support the development of electrodes [56]. A significant advantage of 3D printing is that the architecture of electrochemical energy storage (EES) devices can be highly controlled, providing micro-size precision, which is not possible in conventional manufacturing methods [7].

3D-printed batteries were typically limited to FDM 3D printers, but another approach to battery technology through additive manufacturing can be found in the work of Saleh et al. [57] where 3D-printed hierarchically porous microlattice electrode materials were made, resulting in a 400% increase in specific capacity, an areal capacity increase of 100%, and an elevated electrode volume utilization when directly compared to a solid Ag block electrode.

The 3D-printed battery electrodes were produced by assembling individual droplets one-by-one into 3D structures (Fig. 10.). The process is novel because complex geometries that would be difficult to produce can be made with the droplet technique. Electronic devices and low-weight and high-capacity batteries can be printed using this method [57].

Other 3D printing techniques have been used, including super inkjet printing (SIJP) by Ho et al. [58]. In this method, silver nanopaste and n-tetradecane were mixed to form a paste to form an ink for printing. Sintering was used to control the

Fig. 10 (a) Schematic of the fabrication of 3D micro-architected battery electrodes by assembling nanoparticles in 3D space at microscale using the aerosol jet printing process. Heat removes the binders and sinters the nanoparticles to form the 3D microlattice with hierarchical porosity. (b) Schematic of the formation of the 3D microlattice. (c) Representative SEM images of the 3D microlattice fabricated by the process described in (a) and (b). The FIB image shows a representative section of the truss member of the microlattice. Porosity at a length scale of 100 microns or more is seen from printing, while porosity at a length scale of about a micron is seen within the truss members. (Reprinted (adapted) with permission. Saleh et al. [57])

conductivity and porosity with highly conductive structures sintered at 250 °C for 1 hour. The microbatteries were printed on glass slides, and two staggered arrays of 19×19 pillars (722 pillars total) were printed on a 9 mm^2 silver electrode pad using the SIJP. The batteries were constructed by immersing a pair of silver structures into an aqueous electrolyte made up of potassium hydroxide (KOH) and dissolved zinc oxide (ZnO) powder. During operation, the surface of the silver oxidizes (positive electrode), while zinc “electroplates” form zinc ions in the electrolyte onto the surface of the silver (negative electrode), creating a charged zinc-silver oxide microbattery.

In summary there is a strong research focus on 3D printing electrodes and components for energy storage devices. FDM, SLA, and DLP techniques with modified printing materials have been used to create porous and microlattice structures, enhancing the efficiencies of the electrodes produced.

Fuel Cells

Fuel cells in the simplest case are electrochemical cells that consist of an anode, a cathode, and an electrolyte that provides ion mobility.

Microtubular solid oxide fuel cells (MT-SOFCs) are very promising electrochemical power sources. They address the need for portable power sources with high volumetric power density and rapid thermal cycling while being smaller in size and enabling a fast start-up. Huang et al. [59] produced a 3D-printed MT-SOFC with good power output, extended stability, and thermal cycling stability. The 3D-printed MT-SOFC achieved 4000 h of long-term operation at a constant current of 18.5 A (fuel utilization (F_u) = 64.38%) and performed more than 1000 cycles of rapid thermal cycling without cell failure. The 3D printing technology helped to ensure homogeneous dispersion of the YSZ and NiO particles preventing bulk NiO or YSZ formation.

Microbial fuel cell (MFC) technology, where a bioelectrochemical system processes an electric current using bacteria and an oxidant (typically oxygen), continues to provide a pathway to sustainable energy sources. 3D printing technologies are being used to enhance the efficiency of these fuel cells. You et al. [60] demonstrated a complete MFC from different materials using 3D printing, with the advantage of optimizing the various components and increasing the efficiency of the redesigned unit (Fig. 11). They started by first comparing the performance of 3D-printed materials that could be used for MFC membranes and anodes with conventional materials. They then investigated the strengths and limitations of each material. Finally, they demonstrated the practicality of monolithic MFC fabrication.

The filaments used to make the membranes were selected from the Poro-Lay series filaments, Lay-Fomm 60 (functional component – polyurethane), Lay-Felt (functional component – proprietary), and Gel-Lay (functional component – polyamide), all from Formfutura, Netherlands. The control cation exchange membrane was CMI-7000 (Membrane International, USA) has a thickness of 0.45 mm, and the 3D-printed membranes had a 2 mm thickness designed to reduce leakage from the

Fig. 11 The 3D printable components of a microbial fuel cell with the highlighted (a) 3D-printed membrane and (b) the anode. (Reprinted (adapted) with permission. You et al. [60])

anodic chamber (Fig. 11a). All of the printed membranes were submerged in water for 3 days, with water replaced twice a day. A conductive polylactic acid (PLA) filament (ProtoPlant, USA) was used for the anode material comparison and was designed to be printed as a rectangular mesh. A cuboid style analytical single-chamber MFC with an anodic chamber volume of 25 mL was used for the experiments. Each tested membrane with an area of 30 cm² was placed between the anode and cathode frames. A hot-pressed activated carbon cathode electrode was placed on the membrane as the cathode electrode.

The MFCs produced were filled with sewage sludge (Saltford, UK), and synthetic wastewater [61] was used every 3–4 days as feedstock. 9 k Ω external resistors were connected to all MFCs, and the resistance values were changed to match the internal resistance value for each MFC after polarization measurements. Then after a period

of 5 weeks when all the MFCs gave a reproducible output, $700\ \Omega$ was connected to all the MFCs apart from the MFCs with 3D-printed anodes (Fig. 11b.), whose load was $3\ \text{k}\Omega$. The electricity-generating performance of all MFCs increased, as the anode biofilms matured over time. Polarization measurements were performed, and the best performing membrane material was Gel-Lay, which produced a max power (P_{MAX}) of $240 \pm 11\ \mu\text{W}$. This result was 1.4-fold higher than the control CEM which exhibited a P_{MAX} of $177 \pm 29\ \mu\text{W}$. The next high-performing membrane was Lay-Felt, which showed a P_{MAX} of $186 \pm 3\ \mu\text{W}$, better than the control. Lay-Fomm was lower than the control with a $P_{\text{MAX}} = 137 \pm 25\ \mu\text{W}$. MFCs which had conductive PLA anodes and the same control membranes, CEMs, gave the lowest P_{MAX} of $43 \pm 1\ \mu\text{W}$. In general, 3D-printed membranes are porous materials that are non-(ion) selective, meaning that charge transfer through the membranes is aided by the porosity of materials.

Solar Cells and Supporting Technologies

From the discovery of the photovoltaic effect by Edmond Becquerel in 1839 to the production of dye-sensitized solar cells (DSSCs), an economically sound alternative to the dominance of photovoltaic devices, the race has been on to boost the efficiency of photon-to-electron conversion. It is the conversion of solar energy directly into electricity as a clean, sustainable energy resource, which is helping to address the energy crisis and reduce the environmental impact of the continued use of fossil fuels.

3D printing has also been envisioned for solar applications with encouraging results that may steer the development of cheap and efficient photovoltaic (PV) devices and supporting technologies such as solar concentrators. One type of printed PV devices is the large-scale roll-to-roll production of cells placed on flexible substrates [62], but the use of multicrystalline silicon in solar cells is currently the most widespread technology. Multicrystalline silicon is a fundamental component of the conventional solar cell market, but it does suffer from impurities with silicon, with oxygen being one of the largest contributing factors. The casting process in the presence of oxygen causes the impurities with the high-temperature use of quartz crucibles, leading to the precipitation of SiO_2 . A series of experiments were done using electron beam melting for the removal of oxygen impurities from silicon to improve solar cell performance [6].

Flexible microelectrodes have been produced by a three-axis micropositioning stage attached to a micronozzle [63]. This work highlighted the patterning of silver microelectrodes by the omnidirectional printing of concentrated nanoparticle inks with minimum widths of 2 micrometers onto plastic. It marked an essential step in flexible microelectrode applications, creating new pathways for the design of 3D photovoltaic structures. It is possible that with future advancements in 3D printers, flexible conductive filaments with nanoscale resolution could support the principles detailed in this research.

Fig. 12 (a) Schematic illustration of the external light trap. By concentration, light is funneled through a small aperture and is trapped. Also shown in green is the reflection from a metallic reflective front contact. (b) A rendered 3D model of the light trap. The front quarter of the light trap is removed for visibility. A concentrator is placed on top of a square cage with the solar cell at the bottom (cell area shown in red). Most of the reflected light from the solar cell is recycled within the cage. (Reprinted (adapted) with permission. van Dijk et al. [65])

The dye molecules in DSSCs are adsorbed at the surface of nanocrystalline oxide semiconductors such as TiO_2 . The thin films produced have some considerations to meet, including a large enough surface area for dye adsorption, and mesoporous channels for the electrolyte. The 3D printing technique “two-photon polymerization” was used to manufacture TiO_2 thin films with 3D micro-designs for use in DSSCs [64]. The films are better than conventional “random assembly”-produced films as they incorporate light scattering designs that enhance the photocurrent in the cell by up to ~25%. The concept of improved light scattering and solar concentrators has also been explored by 3D printing for the assembly of functional parts that support solar cell applications. van Dijk et al. [65, 66] worked on light traps produced by 3D printing. These traps were circular, square, and hexagonal compound parabolic concentrator arrays. The tests showed that the silver-coated thermoplastic 3D-printed traps, when positioned on top of an organic solar cell, provided a substantial improvement in the external quantum efficiency (EQE). Figure 12a shows how sunlight can be trapped by funneling the light through an aperture in a light trap. The cross-sectional area of the hole is smaller than that of the solar cell used for testing so that the light trap can retro-reflect the light that would have been lost. The light trap has two components: a parabolic concentrator and a cage (as shown in Fig. 12b). The photons that pass the cell and are not absorbed, and the

Fig. 13 (a) A 3D-printed compound parabolic concentrator (CPC) before and after chemical smoothening, the insets show the enlarged surface. (b) The silver-coated CPC with a focal ring of sunlight at the center. (c) The separated cage and CPC that can be combined to an external light trap. (d) View of the CPC from the entrance side, showing the reflection in the parabolic curve. Two wrinkles in the concentrator are encircled in red. (Reprinted (adapted) with permission. van Dijk et al. [65])

photons that are reflected by the surface of the solar cell are retro-reflected by the light trap.

The light trap was 3D-printed using ABS filament on a FDM 3D printer. ABS was used to enable the printed parts to be vapor smoothened by exposure to saturated acetone vapor (see Fig. 13a). After smoothening, the cage and the compound parabolic concentrator (CPC) were coated with silver to enable the focusing of sunlight. (See Fig. 13b for the coated print.) Figure 13c shows the square cage and the circular concentrator that was stacked to form the completed light trap. The fabrication process was unfortunately difficult as some undesired unevenness in the parabolic shape has distortions, which are highlighted in the projected image inside of the CPC as displayed in Fig. 13d. The problem could be addressed by a number of solutions, including 3D printing at higher resolution with FDM or printing with SLA or DLP resin-based systems which would substitute the post-processing acetone vapor step for a UV curing cycle.

The 3D-printed parabolic concentrator and a light cage when used with a thin-film nc-Si:H solar cell gave a 15% enhancement in the energy conversion efficiency of the cell when compared to the same cell without the light trap attached.

In summary, 3D printing for solar applications is still in its infancy, but there are already solutions being investigated to improve current solar cell technologies. This is a research area that would certainly benefit from advanced manufacturing techniques including 4D printing.

Conclusions and Further Outlook

3D printing is a revolutionary technology which, within a short timeframe, has transitioned into a consumer-based technology that is helping to drive STEM education through hands-on design and fabrication. 3D printers are also being used as research tools for rapid prototyping and cost-saving. Advances in the multi-material 3D printing filaments and resins have provided a unique opportunity to develop 3D-printed components for energy-based applications tailoring the properties of the printed objects to the nanoscale. There have been many successful approaches to printing electrodes, and the use of carbon nanomaterials such as carbon black and carbon nanotubes has created new avenues for manufacturing complex assemblies that were previously difficult to envision.

The outlook for 3D printing in the energy sector is good, with the price of the technology decreasing with innovations in printer design and function increasing as the push toward 4D printing continues. Market reports indicated that the use of 3D printing technology up to the year 2025 was strong prior to the onset of the Coronavirus. Cost-saving initiatives will likely be put in place over the next few years that will continue to strengthen the research and development into 3D-printed energy-based applications.

References

1. BCC-Research (2019, November) Global Markets for 3D Printing. 140
2. BCC-Research (2020, March) 4D Printing: an emerging market
3. Bogue R (2013) 3D printing: the dawn of a new era in manufacturing? *Assem Autom* 33 (4):307–311. <https://doi.org/10.1108/aa-06-2013-055>
4. Bourell DL (2016) Sintering in Laser Sintering. *JOM* 68(3):885–889. <https://doi.org/10.1007/s11837-015-1780-2>
5. Rajamani D, Balasubramanian E (2019) Investigation of sintering parameters on viscoelastic behaviour of selective heat sintered HDPE parts. *J Appl Sci Eng* 22(3):391–402. [https://doi.org/10.6180/jase.201909_22\(3\).0001](https://doi.org/10.6180/jase.201909_22(3).0001)
6. Asghar H, Shi S, Jiang DC, Tan Y, Rehman JU, Gilani ZA, An GY, Guo XL, Li PT (2018) Improvement of solar cell performance after oxygen removal by Electron beam melting. *SILICON* 10(5):1887–1891. <https://doi.org/10.1007/s12633-017-9694-y>
7. Cheng M, Deivanayagam R, Shahbazian-Yassar R 3D Printing of electrochemical energy storage devices: a review of printing techniques and electrode/electrolyte architectures. *Batteries Supercaps* 17. <https://doi.org/10.1002/batt.201900130>
8. Tiller B, Reid A, Zhu BT, Guerreiro J, Domingo-Roca R, Jackson JC, Windmill JFC (2019) Piezoelectric microphone via a digital light processing 3D printing process. *Mater Des* 165:7. <https://doi.org/10.1016/j.matdes.2019.107593>

9. Park SH, Kaur M, Yun D, Kim WS (2018) Hierarchically designed Electron paths in 3D printed energy storage devices. *Langmuir* 34(37):10897–10904. <https://doi.org/10.1021/acs.langmuir.8b02404>
10. Xing BH, Yao YX, Meng X, Zhao WM, Shen MH, Gao SY, Zhao Z (2020) Self-supported yttria-stabilized zirconia ripple-shaped electrolyte for solid oxide fuel cells application by digital light processing three-dimension printing. *Scr Mater* 181:62–65. <https://doi.org/10.1016/j.scriptamat.2020.02.004>
11. Gojzewski H, Guo Z, Grzelachowska W, Ridwan MG, Hempenius MA, Grijpma DW, Vancso GJ (2020) Layer-by-layer printing of photopolymers in 3D: how weak is the Interface? *ACS Appl Mater Interfaces* 12(7):8908–8914. <https://doi.org/10.1021/acsami.9b22272>
12. Fu K, Yao YG, Dai JQ, Hu LB (2017) Progress in 3D printing of carbon materials for energy-related applications. *Adv Mater* 29(9). <https://doi.org/10.1002/adma.201603486>
13. Acquah SFA, Leonhardt BE, Nowotarski MS, Magi JM, Chambliss KA, Venzel TES, Delekar SD, Al-Hariri LA (2016) Carbon nanotubes and graphene as additives in 3D printing. In: *Carbon nanotubes – current progress of their polymer composites*. InTech. <https://doi.org/10.5772/63419>
14. Muth JT, Vogt DM, Truby RL, Menguc Y, Kolesky DB, Wood RJ, Lewis JA (2014) Embedded 3D printing of strain sensors within highly stretchable elastomers. *Adv Mater* 26(36):6307–6312. <https://doi.org/10.1002/adma.201400334>
15. Koli V, Dhodamani A, More K, Acquah SFA, Panda DK, Pawar S, Delekar S (2017) A simple strategy for the anchoring of anatase titania on multi-walled carbon nanotubes for solar energy harvesting. *Sol Energy* 149:188–194. <https://doi.org/10.1016/j.solener.2017.03.036>
16. Steven E, Saleh WR, Lebedev V, Acquah SFA, Laukhin V, Alamo RG, Brooks JS (2013) Carbon nanotubes on a spider silk scaffold. *Nat Commun* 4:8. <https://doi.org/10.1038/ncomms3435>
17. Acquah SFA, Ventura DN, Rustan SE, Kroto HW (2013) Interconnecting carbon nanotubes for a sustainable economy. *Syntheses and applications of carbon nanotubes and their composites*. Intech Europe, Rijeka. <https://doi.org/10.5772/51781>
18. Ventura DN, Stone RA, Chen KS, Hariri HH, Riddle KA, Fellers TJ, Yun CS, Strouse GF, Kroto HW, Acquah SFA (2010) Assembly of cross-linked multi-walled carbon nanotube mats. *Carbon* 48(4):987–994. <https://doi.org/10.1016/j.carbon.2009.11.016>
19. Ventura DN, Li S, Baker CA, Breshike CJ, Spann AL, Strouse GF, Kroto HW, Acquah SFA (2012) A flexible cross-linked multi-walled carbon nanotube paper for sensing hydrogen. *Carbon* 50(7):2672–2674. <https://doi.org/10.1016/j.carbon.2012.02.011>
20. Zhang YH, Cui YH, Wang S, Zhao XW, Wang FM, Wu GH (2020) Effect of microwave treatment on bending properties of carbon nanotube/wood plastic composites by selective laser sintering. *Mater Lett* 267:4. <https://doi.org/10.1016/j.matlet.2020.127547>
21. Shofner ML, Lozano K, Rodriguez-Macias FJ, Barrera EV (2003) Nanofiber-reinforced polymers prepared by fused deposition modeling. *J Appl Polym Sci* 89(11):3081–3090. <https://doi.org/10.1002/app.12496>
22. Torres J, Coteló J, Karl J, Gordon AP (2015) Mechanical property optimization of FDM PLA in shear with multiple objectives. *JOM* 67(5):1183–1193. <https://doi.org/10.1007/s11837-015-1367-y>
23. Arif MF, Alhashmi H, Varadarajan KM, Koo JH, Hart AJ, Kumar S (2020) Multifunctional performance of carbon nanotubes and graphene nanoplatelets reinforced PEEK composites enabled via FFF additive manufacturing. *Compos Pt B-Eng* 184:10. <https://doi.org/10.1016/j.compositesb.2019.107625>
24. Postiglione G, Natale G, Griffini G, Levi M, Turri S (2015) Conductive 3D microstructures by direct 3D printing of polymer/carbon nanotube nanocomposites via liquid deposition modeling. *Compos Pt A-Appl Sci Manuf* 76:110–114. <https://doi.org/10.1016/j.compositesa.2015.05.014>
25. Yu WW, Zhang J, Wu JR, Wang XZ, Deng YH (2017) Incorporation of graphitic nano-filler and poly(lactic acid) in fused deposition modeling. *J Appl Polym Sci* 134(15):11. <https://doi.org/10.1002/app.44703>

26. Chavez LA, Regis JE, Delfin LC, Rosales CAG, Kim H, Love N, Liu YT, Lin YR (2019) Electrical and mechanical tuning of 3D printed photopolymer-MWCNT nanocomposites through in situ dispersion. *J Appl Polym Sci* 136(22):7. <https://doi.org/10.1002/app.47600>
27. Goodarzi S, Da Ros T, Conde J, Sefat F, Mozafari M (2017) Fullerene: biomedical engineers get to revisit an old friend. *Mater Today* 20(8):460–480. <https://doi.org/10.1016/j.mattod.2017.03.017>
28. Acquah SFA, Penkova AV, Markelov DA, Semisalova AS, Leonhardt BE, Magi JM (2017) Review-the beautiful molecule: 30 years of C-60 and its derivatives. *ECS J Solid State Sci Technol* 6(6):M3155–M3162. <https://doi.org/10.1149/2.0271706jss>
29. Penkova AV, Acquah SFA, Dmitrenko ME, Sokolova MP, Mikhailova ME, Polyakov ES, Ermakov SS, Markelov DA, Roizard D (2016) Improvement of pervaporation PVA membranes by the controlled incorporation of fullerene nanoparticles. *Mater Des* 96:416–423. <https://doi.org/10.1016/j.matdes.2016.02.046>
30. Penkova AV, Acquah SFA, Sokolova MP, Dmitrenko ME, Toikka AM (2015) Polyvinyl alcohol membranes modified by low-hydroxylated fullerene C-60(OH)₁₂. *J Membr Sci* 491:22–27. <https://doi.org/10.1016/j.memsci.2015.05.011>
31. Wallace GG, Chen J, Li D, Moulton SE, Razal JM (2010) Nanostructured carbon electrodes. *J Mater Chem* 20(18):3553–3562. <https://doi.org/10.1039/b918672g>
32. Penkova AV, Acquah SFA, Piotrovskiy LB, Markelov DA, Semisalova AS, Kroto HW (2017) Fullerene derivatives as nano-additives in polymer composites. *Russ Chem Rev* 86(6):530–566. <https://doi.org/10.1070/rcr4712>
33. Park SH, Su RT, Jeong J, Guo SZ, Qiu KY, Joung D, Meng FB, McAlpine MC (2018) 3D printed polymer photodetectors. *Adv Mater* 30(40). <https://doi.org/10.1002/adma.201803980>
34. Accorsi J, Yu M (1998) Carbon black. In: Pritchard G (ed) *Plastics additives: an A-Z reference*. Springer, Dordrecht, pp 153–161. https://doi.org/10.1007/978-94-011-5862-6_18
35. Kim JH, Hong JS, Ahn KH Design of electrical conductive poly(lactic acid)/carbon black composites by induced particle aggregation. *J Appl Polym Sci* 11. <https://doi.org/10.1002/app.49295>
36. Liu ZW, Ling FW, Diao XY, Fu MR, Bai HW, Zhang Q, Fu Q (2020) Stereocomplex-type polylactide with remarkably enhanced melt-processability and electrical performance via incorporating multifunctional carbon black. *Polymer* 188:11. <https://doi.org/10.1016/j.polymer.2019.122136>
37. Vaneckova E, Bousa M, Lachmanova SN, Rathousky J, Gal M, Sebechlebska T, Kolivoska V (2020) 3D printed polylactic acid/carbon black electrodes with nearly ideal electrochemical behaviour. *J Electroanal Chem* 857:8. <https://doi.org/10.1016/j.jelechem.2019.113745>
38. Joao AF, Squizzato AL, Richter EM, Munoz RAA (2020) Additive-manufactured sensors for biofuel analysis: copper determination in bioethanol using a 3D-printed carbon black/polylactic electrode. *Anal Bioanal Chem*. <https://doi.org/10.1007/s00216-020-02513-y>
39. Bin Hamzah HH, Keattch O, Covill D, Patel BA (2018) The effects of printing orientation on the electrochemical behaviour of 3D printed acrylonitrile butadiene styrene (ABS)/carbon black electrodes. *Sci Rep* 8:8. <https://doi.org/10.1038/s41598-018-27188-5>
40. Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, Grigorieva IV, Firsov AA (2004) Electric field effect in atomically thin carbon films. *Science* 306(5696):666–669. <https://doi.org/10.1126/science.1102896>
41. Geim AK, Novoselov KS (2007) The rise of graphene. *Nat Mater* 6(3):183–191. <https://doi.org/10.1038/nmat1849>
42. Jeon H, Kim Y, Yu WR, Lee JU (2020) Exfoliated graphene/thermoplastic elastomer nanocomposites with improved wear properties for 3D printing. *Compos Pt B-Eng* 189:13. <https://doi.org/10.1016/j.compositesb.2020.107912>
43. Camargo JC, Machado AR, Almeida EC, Silva E (2019) Mechanical properties of PLA-graphene filament for FDM 3D printing. *Int J Adv Manuf Technol* 103(5–8):2423–2443. <https://doi.org/10.1007/s00170-019-03532-5>

44. Sorocki J, Koryciak S, Piekarz I, Gruszczynski S, Wincza K, Ieee (2017) Investigation on additive manufacturing with conductive PLA filament for realisation of Low-loss Suspended Microstrip Microwave Circuits. 2017 International conference on electrical, Electronics and System Engineering. Ieee, New York
45. Cardoso RM, Silva PRL, Lima AP, Rocha DP, Oliveira TC, do Prado TM, Fava EL, Fatibello-Filho O, Richter EM, RAA M (2020) 3D-printed graphene/poly(lactic acid) electrode for bioanalysis: biosensing of glucose and simultaneous determination of uric acid and nitrite in biological fluids. *Sens Actuator B-Chem* 307:9. <https://doi.org/10.1016/j.snb.2019.127621>
46. Azhari A, Toyserkani E, Villain C (2015) Additive manufacturing of graphene-hydroxyapatite nanocomposite structures. *Int J Appl Ceram Technol* 12(1):8–17. <https://doi.org/10.1111/ijac.12309>
47. Wei X, Li D, Jiang W, Gu Z, Wang X, Zhang Z, Sun Z (2015) 3D printable graphene composite. *Sci Rep* 5(1):11181. <https://doi.org/10.1038/srep11181>
48. Foster CW, Down MP, Zhang Y, Ji X, Rowley-Neale SJ, Smith GC, Kelly PJ, Banks CE (2017) 3D printed graphene based energy storage devices. *Sci Rep* 7(1):42233. <https://doi.org/10.1038/srep42233>
49. Rae A, Hammer-Fritzinger D (2006) Creating metal and nonmetal nanosystems using conductive jettable inks. *Solid State Technol* 49(4):53–55
50. Kamysnyy A, Magdassi S (2019) Conductive nanomaterials for 2D and 3D printed flexible electronics. *Chem Soc Rev* 48(6):1712–1740. <https://doi.org/10.1039/c8cs00738a>
51. Reyes C, Somogyi R, Niu S, Cruz MA, Yang FC, Catenacci MJ, Rhodes CP, Wiley BJ (2018) Three-dimensional printing of a complete Lithium ion battery with fused filament fabrication. *ACS Appl Mater* 11(10):5268–5279. <https://doi.org/10.1021/acsaem.8b00885>
52. Guessasma S, Belhabib S, Nouri H (2019) Microstructure and mechanical performance of 3D printed Wood-PLA/PHA using fused deposition modelling: effect of printing temperature. *Polymers* 11(11). <https://doi.org/10.3390/polym11111778>
53. Walker JS, Arnold J, Shrestha C, Smith D (2020) Antibacterial silver submicron wire-poly(lactic acid) composites for fused filament fabrication. *Rapid Prototyping J* 26(1):32–38. <https://doi.org/10.1108/rpj-04-2019-0100>
54. Bayraktar I, Doganay D, Coskun S, Kaynak C, Akca G, Unalan HE (2019) 3D printed antibacterial silver nanowire/poly(lactide) nanocomposites. *Compos Pt B-Eng* 172:671–678. <https://doi.org/10.1016/j.compositesb.2019.05.059>
55. Jahangir N, Cleeman J, Hwang HJ, Malhotra R (2019) Towards out-of-chamber damage-free fabrication of highly conductive nanoparticle-based circuits inside 3D printed thermally sensitive polymers. *Addit Manuf* 30. <https://doi.org/10.1016/j.addma.2019.100886>
56. Fafenrot S, Grimmelsmann N, Wortmann M, Ehrmann A (2017) Three-dimensional (3D) printing of polymer-metal hybrid materials by fused deposition modeling. *Materials* 10(10). <https://doi.org/10.3390/ma10101199>
57. Saleh MS, Li J, Park J, Panat R (2018) 3D printed hierarchically-porous microlattice electrode materials for exceptionally high specific capacity and areal capacity lithium ion batteries. *Addit Manuf* 23:70–78. <https://doi.org/10.1016/j.addma.2018.07.006>
58. Ho CC, Murata K, Steingart DA, Evans JW, Wright PK (2009) A super ink jet printed zinc-silver 3D microbattery. *J Micromech Microeng* 19(9). <https://doi.org/10.1088/0960-1317/19/9/094013>
59. Huang WH, Finnerty C, Sharp R, Wang K, Balili B (2017) High-performance 3D printed microtubular solid oxide fuel cells. *Adv Mater Technol* 2(4):5. <https://doi.org/10.1002/admt.201600258>
60. You J, Preen RJ, Bull L, Greenman J, Ieropoulos I (2017) 3D printed components of microbial fuel cells: towards monolithic microbial fuel cell fabrication using additive layer manufacturing. *Sustain Energy Technol Assess* 19:94–101. <https://doi.org/10.1016/j.seta.2016.11.006>
61. Winfield J, Ieropoulos I, Greenman J (2012) Investigating a cascade of seven hydraulically connected microbial fuel cells. *Bioresour Technol* 110:245–250. <https://doi.org/10.1016/j.biortech.2012.01.095>

62. Vak D, Hwang K, Faulks A, Jung YS, Clark N, Kim DY, Wilson GJ, Watkins SE (2015) 3D printer based slot-die coater as a lab-to-fab translation tool for solution-processed solar cells. *Adv Energy Mater* 5(4):8. <https://doi.org/10.1002/aenm.201401539>
63. Ahn BY, Duoss EB, Motala MJ, Guo XY, Park SI, Xiong YJ, Yoon J, Nuzzo RG, Rogers JA, Lewis JA (2009) Omnidirectional printing of flexible, stretchable, and spanning silver micro-electrodes. *Science* 323(5921):1590–1593. <https://doi.org/10.1126/science.1168375>
64. Knott A, Makarovskiy O, O'Shea J, Wu YP, Tuck C (2018) Scanning photocurrent microscopy of 3D printed light trapping structures in dye-sensitized solar cells. *Sol Energy Mater Sol Cells* 180:103–109. <https://doi.org/10.1016/j.solmat.2018.02.028>
65. van Dijk L, Paetzold UW, Blab GA, Schropp REI, Di Vece M (2016) 3D-printed external light trap for solar cells. *Prog Photovoltaics* 24(5):623–633. <https://doi.org/10.1002/pip.2702>
66. van Dijk L, Marcus EAP, Oostra AJ, Schropp REI, Di Vece M (2015) 3D-printed concentrator arrays for external light trapping on thin film solar cells. *Sol Energy Mater Sol Cells* 139:19–26. <https://doi.org/10.1016/j.solmat.2015.03.002>