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A Review on use of 3D Printing for Battery Manufacturing.

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Abstract
Mobile electronics are fundamentally dependent on energy storage. The demand for ever smaller, more powerful batteries continues to grow. With the goal of improving battery electrochemical performance, reducing manufacturing costs, and expanding their applications, significant research has been conducted on electrode materials, electrolytes, and cell structures over the years. As fossil fuels become more expensive and the number of internal combustion engines increase, there is an increasing interest in researching and developing batteries for electric and hybrid vehicles. In the meantime, 3D printing is changing our world and the technology is rapidly advancing, rapidly becoming the basis for next-generation 3D printed energy architectures, where batteries and super-capacitors could be printed in virtually any shape.

***Index Terms* - Batteries, 3D printing, Additive manufacturing, Solid State Batteries, Lithium-ion Batteries.**

I. Introduction

There is a growing interest in the research and development of batteries used in electric and hybrid vehicles due to the high demand for fossil fuels on the international market and the aggravation of environmental problems caused by the increase in the number of internal combustion engine vehicles [1]. Petrol and diesel fuel vehicles cause a large amount of carbon dioxide emission, which leads to some serious consequences on global warming [2]. To avoid worsening the above problems, recently, the government of the UK, France, Germany, Netherlands and other countries have announced a schedule to stop producing petrol vehicles, most of which are from 2025 to 2040 respectively [3].

1.1 EV's and Batteries

In the conceivable future, EV's will replace petrol vehicles to a large extent. The rechargeable battery is the core component of an EVs, which requires a high performance [4]. An electrochemical power source or battery is a device which enables the energy liberated in a chemical reaction to be converted directly into electricity. Batteries fulfil two main functions. First and foremost, they act as portable sources of electric power [5] and secondly, to store chemical energy and convert it to electrical energy.

1.2 Lithium-ion Batteries

There are numerous types of rechargeable batteries, including rechargeable Li-ion batteries (LIBs). LIBs have several advantages, such as, long life cycle, high power density, low self-discharge property, high gravimetric, and volumetric energy. Currently, lithium-ion batteries (LIB) are widespread and promising candidates for future application, such as electric vehicles and energy storage [6]. Nonetheless, they suffer from raw materials availability, safety concerns, and limited energy storage capacity. State-of-the-art lithium-ion cells consist of two porous electrodes (anode and cathode) and a separator, as depicted in Fig. 1 current collector, which consist of the active material, conductive agents, and binder [7]. The ion transfer requires a liquid electrolyte which is mainly composed of aprotic organic solvents and a conductive salt.

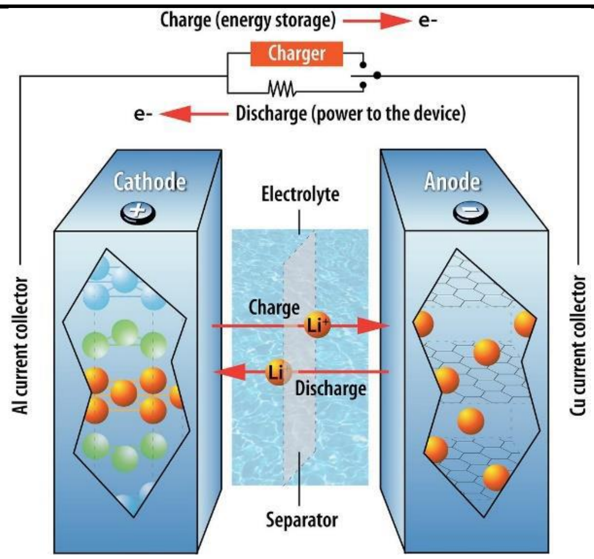

Figure 1. How the lithium-ion battery (LIB) works.

As observed in figure 1, Li-Ion batteries are nowadays representing the most used technology in electric vehicles, both thanks to high energy density and increased power per mass battery unit, allowing the development of some types of batteries with reduced weight and dimensions at competitive prices. Trough studies carried out by [8, 9, 10, 11] Li-Ion batteries used in electric vehicle industry were studied, highlighting increased power (800 … 2000 W/kg), and specific energy (100 … 250 Wh/kg), in comparison with Ni-MH batteries. Many of the issues that current LIBs are facing can be traced back to this liquid electrolyte. Safety concerns, in fact, arise from the flammability of the solvents. Side reactions of the solvents and the conductive salt led to capacity fading and aging [7].

1.3 Solid State Batteries

All solid-state batteries (ASSB), in contrast, are not only inherently safer due to the lack of flammable organic components, but also offer the potential for a dramatic improvement of energy density. Instead of a porous separator soaked with liquid electrolyte, ASSBs use a solid electrolyte, which acts as electrical insulator and ionic conductor at once. The use of a compact solid electrolyte acting as a physical barrier for lithium dendrites also enables the use of lithium metal as the anode material [12]. All solid-state batteries (ASSB), in contrast, are not only inherently safer due to the lack of flammable organic components, but also offer the potential for a dramatic improvement of energy density. Instead of a porous separator soaked with liquid electrolyte, ASSBs use a solid electrolyte, which acts as electrical insulator and ionic conductor at once (Fig. 2).

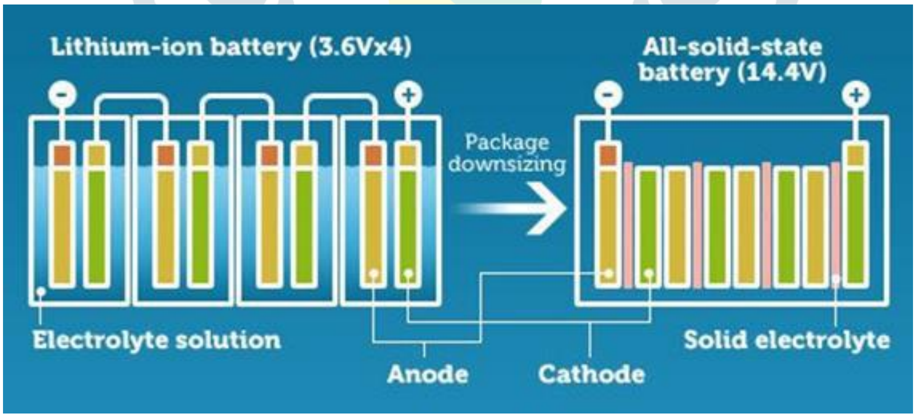

Figure 2. Diagram of (a) Lithium-ion Battery; (b) All Solid-State Battery [1].

A solid-state battery is a battery technology that uses solid electrodes and a solid electrolyte, instead of the liquid or polymer gel electrolytes found in lithium-ion or lithium polymer batteries. The SSB uses pure lithium metal as anode this provide large amount of power and extremely fast charging time with low risk of heating thanks to avoidance of flammable harmful liquid electrolyte. They use solid electrolyte which has higher energy density which could provide same output as lithium-ion battery but with much smaller size and weight.

Solid-state batteries have almost the same mechanism as lithium-ion batteries for extracting electricity from the batteries. Metal is used as the material for the electrodes, and electrical flow is generated by ions moving through the electrolyte between the cathode and anode. The big difference is that the electrolyte is solid. Also, when the electrolyte is a liquid, there is a separator that separates the cathode from the anode, preventing the liquid on the cathode side from mixing suddenly with the liquid on the anode side. But in the case of a solid electrolyte, the separator is unnecessary.

The key to research into solid-state batteries is the discovery and/or development of solid-state materials. In the past, no solid-state material had been discovered that could allow ions to move around inside and create a sufficient flow of electricity to the electrodes [13]. But the discovery of such materials has given momentum to the development of solid-state batteries. By changing from a liquid to solid electrolyte, the ions will move well in batteries, making it possible to create batteries with larger capacity and higher output than lithium-ion batteries.

Since the electrolyte will be changed from liquid to solid, a manufacturing process different from lithium-ion batteries is needed. For example, solid-state batteries can be based on oxides, sulphides, nitrides, etc., depending on the material. The solid electrolytes used in solid-state batteries based on sulphides, which is one of the mainstream types, are so sensitive to moisture that they degenerate even when exposed to moisture in the air. Therefore, the production of solid-state batteries, which require strict moisture control, will need dedicated facilities such as dry rooms [13].

As mentioned above, various companies are currently making efforts to commercialize solid-state batteries, which are expected to further enhance the performance of lithium-ion batteries. On the other hand, lithium-ion batteries are actively used in a wide range of fields.

1.4 Additive Manufacturing / 3D Printing

The evolution of industries depends on innovative and cutting-edge research activities associated with manufacturing processes, materials, and product design. In addition to the customary demands of low price and best quality, the market competition in current production industries is linked to requirements for products that are intricate, possess shorter life cycles, exhibit shorter delivery times, involve customization, and require less skilled workers. In fact, the current breed of products is very complicated and challenging to design. Accordingly, there is a strong incentive toward the design, development, and implementation of new and ingenious manufacturing processes [14]. In addition to 3D Printing, Additive Manufacturing makes scaled 3-dimensional physical objects directly from 3D-CAD data without using tools. [15]. Additive manufacturing (AM) can be described as a technique of blending materials by either fusion, binding, or solidifying materials such as liquid resin and powders. It builds part in a layer-by-layer fashion using 3D CAD modelling. The terminologies such as 3D printing (3DP), rapid prototyping (RP), direct digital manufacturing (DDM), rapid manufacturing (RM), and solid freeform fabrication (SFF) can be used to describe AM processes. AM processes fabricate components using 3D computer data or Standard Tessellation Language (STL) files, which contain information regarding the geometry of the object. AM is very useful when low production volumes, high design complexity, and frequent design changes are required. It offers the possibility to produce complex parts by overcoming the design constraints of traditional manufacturing methods [16]. During this CAD model is approximated by triangles and tessellations, and then sliced into layers by suitable slicing software [17].

Parts created using additive manufacturing are layered without the use of formative tools, offering several advantages over existing manufacturing processes [18].

1.5 3D Printing batteries

In the 3D-printing manufacturing process, the printable inks (or filaments) of electrode materials are first prepared and then directly printed according to the predetermined electrode and cell designs including the sizes, shapes, and architectures, and finally packaged with or without electrolyte filling. This 3D printing process is more convenient, customizable, and intelligent in comparison to the conventional tape casting and deposition techniques. The 3D-printed batteries possess the following advantages:

- The batteries have much-enhanced design freedom in the micron-sized dimensions, with option of almost any desired shapes due to the ability to fabricate complex architectures;
- Both higher areal and volumetric energy densities due to the higher areal-loading densities and the larger high-aspect ratio of the 3D electrodes;
- A higher power density due to the shorter ion or electron diffusion pathways of the 3D-structural electrodes;
- Relatively lower manufacturing costs because 3D printing can dramatically reduce material wastage and save potential production time, as well as have the capability of eliminating the assembly and packaging steps through direct integration of batteries and micro-scale electronics [19].

1.6 3D Printing Techniques for Battery Manufacturing

3D printing technologies can be divided into seven categories according to their technical processes:

1. Material extrusion (e.g., direct ink writing [DIW], fused deposition modelling [FDM]),
2. Powder bed fusion (e.g., selective laser sintering [SLS], direct metal laser sintering [DMLS]),
3. Vat photopolymerization (e.g., stereolithography [SLA], digital light processing [DLP], two-photon lithography [TPL]),
4. Material jetting (e.g., inkjet printing [IJP], aerosol jet printing [AJP]),
5. Sheet lamination (e.g., laminated object manufacturing [LOM]),
6. Binder jetting, and
7. Directed energy deposition [DED].

There have been several high-quality reviews on 3D printing technologies that each give a comprehensive description of their characteristic properties [20-22].

1.7 DfAM and Manufacturing of Batteries

Cathodes, anodes, electrolytes, and separators contribute significantly to the overall performance of batteries, which includes key parameters such as energy density, volume energy density, power density, cycle life, and safety.

Individual battery modules require several specific properties, such as mechanical strength, high electronic, and ionic conductivity. Therefore, it is necessary to select and combine suitable 3D printing techniques and materials such that they can together meet the specific requirements. Developing functional nanomaterials into printable materials for appropriate 3D printing techniques is undeniably of great significance with regard to advances in batteries and other energy storage technologies. [23].

In comparison with the preparation of printable inks for DIW and IJP, designing printable active materials using the FDM and SLA techniques is more difficult and complex. For the FDM technique, the feedstock composite that has a thermoplastic matrix embedded with active materials must first be blended and then extruded to form a filament with suitable dimensions through an extruder [24].

For the SLA technique, the curable ink containing the active materials, photo initiators, and prepolymers should be first prepared in a suitable amount that can fill the printing tank [25]. While some battery modules were indirectly built from the printed templates using SLA technology, there are currently no studies showing direct printing of the active materials using SLA [26].

3D-printed electrodes are constructed by either printing directly or requiring post-treatment processes, such as solvent evaporation, freeze-drying, annealing, physicochemical treatments, and photo-/thermo-curing. Due to the high electrical conductivity, electrochemical activity, and mechanical stability of printed active materials, these post-treatment procedures are commonly used. It should be pointed out that some of these post-treatment processes may lead to shrinkage and/or distortion of the printed architectures and manufacturing complexity, thereby decreasing the printing repeatability and reproducibility [27].

The architectures of 3D-printed modules largely determine the battery configurations and have a significant influence on the electrochemical performance. As schematically shown in Figure 4B, the four types of 3D-printed module architectures are thin films, porous frameworks, surface patterns, and fibers.

- Thin films are the most common and commercially available architectures for electrodes, which are usually constructed by the IJP among the various 3D printing techniques [28].
- 3D porous frameworks are another common type of architecture for 3D-printed electrodes, which can be constructed by DIW, FDM, and SLA printing techniques [29].

1.8 Role of Printing Designs on Battery Performance

Evaluation criteria of performance based on the gravimetric, areal, or volumetric parameters are discussed first. Gravimetric performance is traditionally used to evaluate electrode materials in basic research, while area and volumetric performances are indicators of practical potential, especially for 3D-printed batteries that aim for "small and powerful".

The currently available commercial batteries are regulated in large sizes and restricted in the usual form factors via the conventional tape casting manufacturing process. 3D printing technology can unlock the form factor limitation and promise to print any sizes and shapes, because of its unique advantage in geometrically complex shape or configuration designs [30].

By using 3D electrode architectures, batteries' capacity, energy density, and power density can be increased due to the high area-loading density and high aspect ratio of 3D electrodes. Moreover, a selective pursuit of areal energy densities or power densities can be easily achieved by accurately designing the tailorable thickness and porosity of 3D-printed electrodes [31].

In terms of volumetric performance, a screen-printed planar Zn/MnO2 micro battery achieved a high volumetric energy density of 17.3 mWh/cm3, outperforming lithium thin-film batteries (≤10 mWh/cm3) [32]. Another printed flexible dual-ion micro battery can deliver an ultrahigh volumetric energy density of 291 mWh/cm3 at 1 C and an ultrahigh volumetric power density of 1,756 mW/cm3 at 5 C [33].

In addition to the arbitrary configurations and enhanced performance of 3D-printed batteries, 3D printing designs are also useful for solving scientific and technological problems in batteries. Solid-state batteries are among a class of promising next-generation safe batteries without the use of organic-based flammable liquid. However, one of the greatest challenges is the development of solid-state electrolytes that have high ionic conductivity and suitable mechanical properties.

1.9 Future Scope and application

In general, 3D printing technology is suitable for micro batteries that often need to achieve high areal or volumetric energy and power densities in a narrow space. Moreover, the arbitrary architectures of micro batteries are more difficult to be fabricated by conventional tape coasting methods. However, 3D-printed batteries are still in the research and development stage, and further optimization is needed to improve manufacturing costs, throughput, repeatability, and reproducibility.

There are many start-ups that consider manufacturing of batteries using additive manufacturing. The manufacturing process and application is stated below.

1. Sakuú (Keracel):

Sakuú manufactures solid state batteries with help of multi process additive manufacturing. Sakuú produces next generation SSBs with potential to power electric vehicles (EV's). They have already created a 3D printed 3Ah lithium metal solid state battery which is better than current lithium-ion batteries. They achieved this by creating

multilateral system capable of combining binder jet and powder bed 3D printing technologies to process multiple ceramics and metals within the same part layer. By using this technology, they can print each layer much thinner and could double batteries energy even with same volume or same capacity at half cost.
The milestone is promising for the development of Sakuú's second-generation fully 3D printed SSB, which is on track to begin being shipped in 2023. The company is anticipating another "substantial leap" in energy-density for its 3D printed battery, which is claimed to be the world's first. With twice the energy-density and 30% less weight than existing lithium-ion cells, the firm's second-gen batteries could be deployed within energy storage, micro-reactors, and electronics applications. They are expecting to complete by the start of next year, the pilot line will reportedly be able to produce up to 2.5 MWh of solid-state batteries every year.

2. Blackstone Technology:

Blackstone Resources presented its manufacturing process for lithium-ion batteries from the 3D printer at an event at its plant in Döbeln, Saxony. According to the company, this allows the power storage layers of the battery cells to become thicker, which should increase the energy density by 20 per cent – Blackstone calls this "Thick Layer Technology". Blackstone's 'Thick Layer Technology' is intended as a much more flexible and cost-effective alternative, covering a wider range of cell formats while using environmentally friendly materials. Owing to the dynamic nature of the 3D printing process, Blackstone states that it can even tailor the size and shape of the cells to the customer's requirements. Additionally, by fabricating batteries with 3D printing, Blackstone can reduce the number of materials that don't store any energy, like aluminum and copper, by up to 10%. They claim to manufacturing cost could come to 65$/kWh as compared to conventional method which cost around 140$/kWh.
Ulrich Ernst, founder and CEO of Blackstone Resources, adds, "The patented process relies on an environmentally friendly, purely water-based process and reduces waste materials by 50%. In this way, we are making an important and sustainable contribution to the transport turnaround and in the fight against climate change."

3. Photocentric:

The British 3D printer and material manufacturer Photocentric, is also investing in research and development of 3D printed solid state battery technology. The company uses its patented 'Visible Light Polymerization [VLP]' 3D printing technology, where a low energy light source is used to polymerize liquid resin. By using this technology, they intend to 3D print battery electrodes and using the freedom of geometry that the process provides, intends to deliver significant improvements in battery manufacture and then they assemble them into the cells. These electrodes are then undergone some thermal post processing to dehydrate them to make sure that there is no moisture left on surface or inside the structure. 3D printing allows to design the entire battery: from the electrode architecture to the full battery cell

- The process for fabricating 3D printed battery electrodes:
- The use of slurry consisting of a photopolymer binder, an electrode active material and a conductive additive
- The electrode structure is created by using visible light photopolymerization
- The LCD screen displays pixels which in turn cure voxels of photopolymer creating a 3D structure layer by layer
- The 3D printed electrodes are washed, post exposed and dehydrated before being assembled

Photocentric has received a grant funding by the Advanced Propulsion Centre under their Technology Developer Programme (TDAP) to develop 3D printed batteries. It is hoped that this technology will enable orders of magnitude improvements in battery performance and be used in a future Giga factory based in the UK. And with using their technology of visible light polymerisation in combination with the LCD screen-based 3D printers they could enable the low-cost mass manufacture of batteries.

IV. Conclusion and Perspective

3D printing of advanced batteries has drawn considerable attention as an innovative technology that can disruptively change the design and architecture at all levels of materials, modules, and devices. The aim of this review is to provide readers with a comprehensive overview of 3D-printed batteries from the perspectives of printing techniques, printable materials, and design considerations at both the module and full-cell device levels, as well as a comprehensive understanding of their application potential. Over the past few years, technological advances have been witnessed in optimizing a suitable printing technique for achieving 3D battery products, battery modules of both electrodes and electrolytes, architectures and configurations of full cells. Together with these technological advancements, there have been pursuits for in-depth understanding of the governing principles involved in 3D printable materials, components, and printing techniques and the resultant battery performance. There is no doubt that such pursuits will continue in the coming years.

Figures

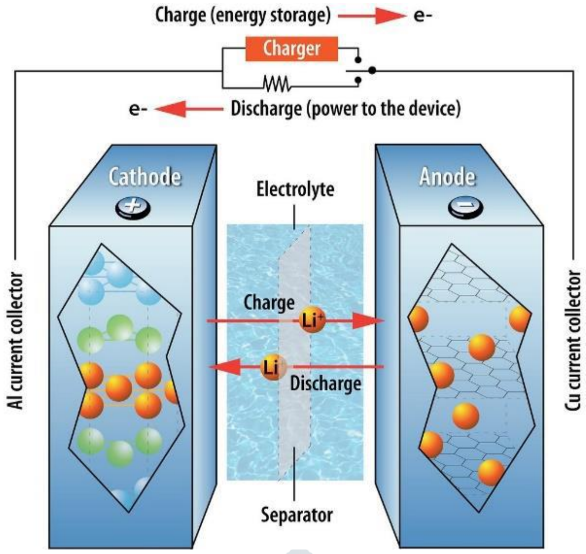

Figure 1. How the lithium-ion battery (LIB) works.

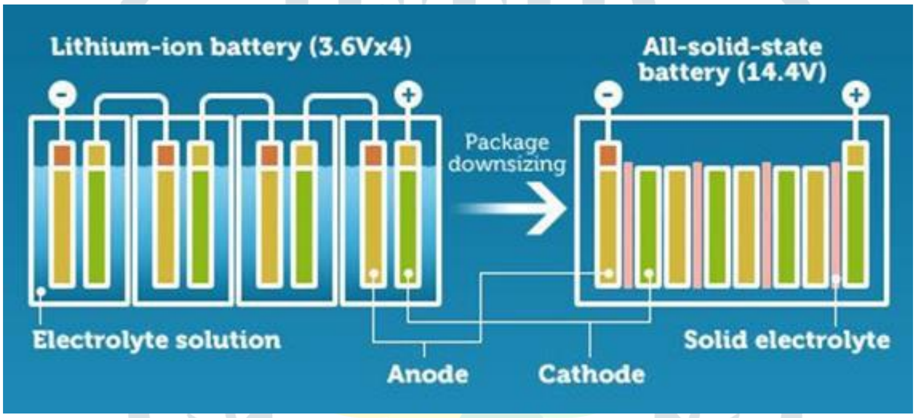

Figure 2. Diagram of (a) Lithium-ion Battery; (b) All Solid-State Battery [1].

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