

## Review

# Electrode Fabrication Techniques for Li Ion Based Energy Storage System: A Review

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**Abstract:** Development of reliable energy storage technologies is the key for the consistent energy supply based on alternate energy sources. Among energy storage systems, the electrochemical storage devices are the most robust. Consistent energy storage systems such as lithium ion (Li ion) based energy storage has become an ultimate system utilized for both domestic and industrial scales due to its advantages over the other energy storage systems. Considering the factors related to Li ion-based energy storage system, in the present review, we discuss various electrode fabrication techniques including electrodeposition, chemical vapor deposition (CVD), stereolithography, pressing, roll to roll, dip coating, doctor blade, drop casting, nanorod growing, brush coating, stamping, inkjet printing (IJP), fused deposition modelling (FDM) and direct ink writing (DIW). Additionally, we analyze the statistics of publications on these fabrication techniques and outline challenges and future prospects for the Li ion battery market.

**Keywords:** electrode fabrication; energy storage; global market demand; lithium ion



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## 1. Introduction

The management of energy resources is a substantial concern for our civilization. To better satisfy the existing energy demand, one needs to have information about energy sources in terms of their quality, availability and environmental effects. Moreover, due to adverse climatic conditions, attention has moved towards the consumption of energy resources in terms of economics and sustainability. Thus, optimal energy resource management has become vital among energy planners and policy makers.

Fossil fuels, especially coal, oil and gases are the primary source of energy, providing ~85% of the primary energy supply. Industrialization, urbanization, increasing population and economic progression cause a huge increase in energy demand. According to the World Energy Outlook, in 2021, the annual energy consumption was 580 million joules, and it is expect to reach around 850 million joules by the end of 2050 [1]. While most countries are equipped with specific energy resources, they try to export some energy resources and import some in order to develop and improve their overall economy. Therefore, the trade gap between energy exports and imports remains in equilibrium. According to International Energy Agency (IEA) statistics during in 2020, China, the USA, India, Russia and Japan were the top five leading energy producer countries [1]. In accordance with the energy production, the final energy consumption follows in such a manner that the biggest share of ~37.0% is accounted for oil and petroleum products, followed by the electricity sector and natural gas consumption of ~22.8% and ~21.3%, respectively. However, the contribution of solid fossil fuels was only 2.1%. In 2019, the three most dominating sectors in the European Union were transport (~30.9%), households (~26.3%) and industry (~25.6%) [2]. Electricity is an expeditious, growing energy resource. In the next 25 years, it will progress more than other energy resources. Forecasting energy demand can influence overall revenue and cost

for distribution operators as well as for energy producers in terms of sustainability and profitability. This attracts power sectors to invest in energy storage for different application perspectives. Worldwide, the top and rapidly growing electricity exporters are Sweden (~93.2%), South Africa (~52.1%), Slovenia (~47.2%) and Austria (~43.7%). Similarly, other countries have also increased their investments in the new energy development sector [3]. Moreover, the top five countries for electricity import are USA (~10.1%), Italy (~5.9%), Germany (~5.7%), Brazil (~4.7) and Switzerland (3.9%) [4]. The average electricity import for 2019 based on 133 countries was 4.45 billion kWh. The largest import was reported in the USA and the smallest import was reported for Angola [4]. These data for electricity import and export indicate the need to consider energy management to improve the economy for any country.

The massive consumption of conventional fuel, in addition to growing energy demands, is responsible for energy crises. Moreover, rising energy demand ultimately leads to environmental changes, including global warming, contamination of air, soil and water [5–7]. To avoid this trend, we need to focus on sustainable or low-carbon energy resources such as solar, tidal, wind, wave, nuclear and energy storage, in the upcoming time. Although the world is moving towards renewable energy resources, they also have some drawbacks, such as irregular production. Therefore, they cannot be applicable for continuous usage. Thus, we need energy resources that can provide regular supply for commercial and household consumption. In addition, energy storage is one of the crucial requirements to fulfill the future energy demand due to limited source of nonrenewable energy. Energy storage devices are the back up for the electricity supply, as around >50 Megawatt (MW) is required to handle day-to-day inconsistent power demands. In addition to this, energy storage has the advantage of coping with the discontinuous supply from renewable resources since they produce a large amount of energy that smaller grids cannot accommodate. Expanding research concerning high power storage, as well as high energy density systems, is the only way to fulfill this demand at present.

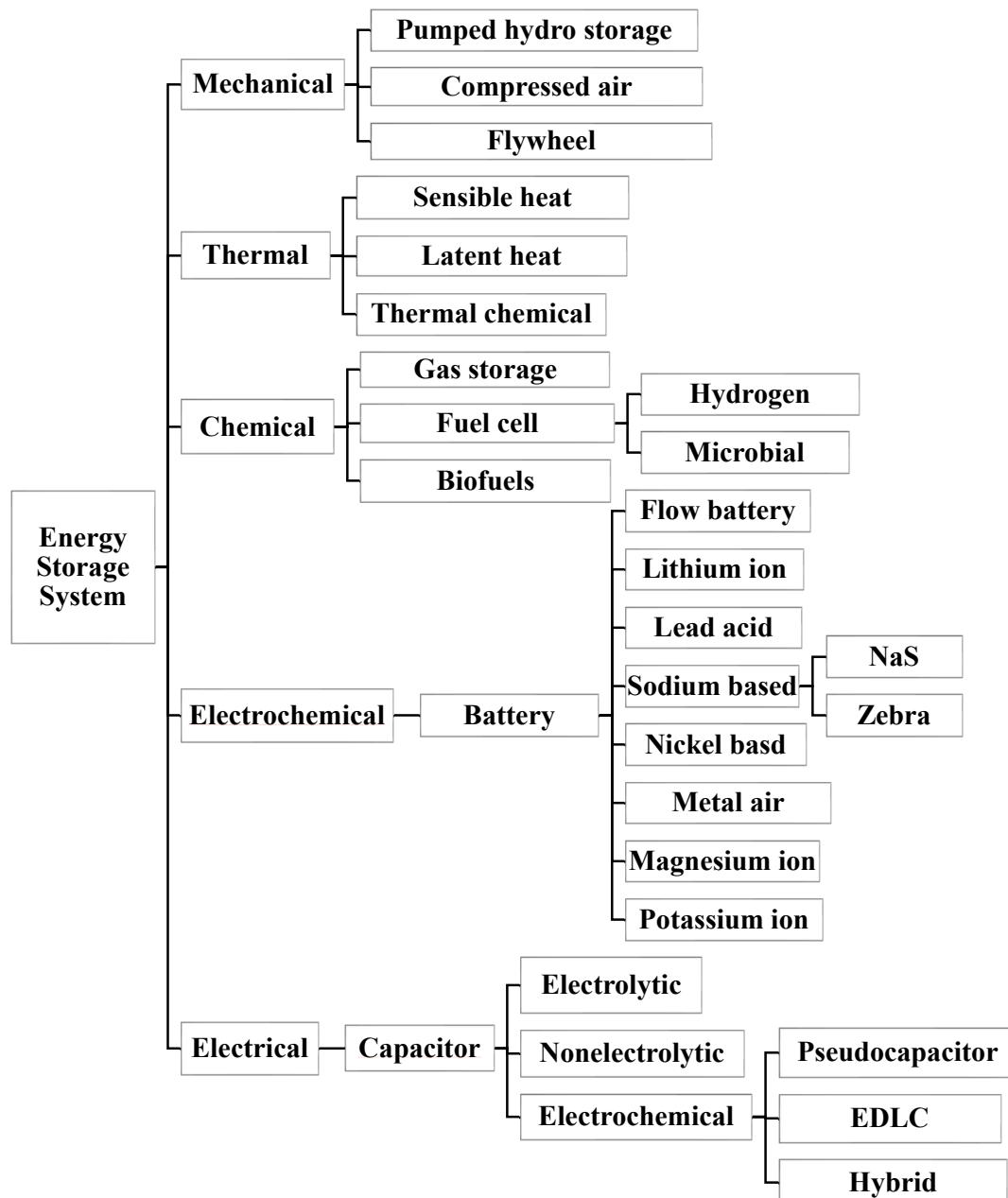
Electrochemical energy storage (ECES) is a proficient and promising energy storage systems. ECES plays a crucial role in clean energy technologies. There is strong competition between various ECES of lithium ion (Li ion), lead acid, sodium based (Na based), nickel based (Ni based), metal air, magnesium ion (Mg ion) and potassium ion (K ion) batteries. However, in terms of commercialization and long-term application, Li ion batteries are currently a majorly used resource among all ECES. In recent years, Mg ion and K ion-based energy storage have attracted attention as an alternative energy storage. One of the advantages for Mg ion batteries is that they can achieve 1000 cycles at a high 3C cycle rate [8]. The performance of K ion batteries can increase due to quick transport of electron and ions during charge–discharge cycling [9]. Nonetheless, regardless of the development of various electrode materials, a realistic application of other ECES is currently hindered due to their low specific capacity, poor performance and low voltage [10]. This is the case for Na ion batteries, for example, which have low specific capacity and low voltage. Even though they are comparatively cheap, they do not find much use in commercial applications as compared to LIB [11]. Thus, a huge effort is still required to replace Li ion batteries on the commercial scale. The advantages of Li ion-based energy storage system include higher specific energy, wide potential range, lightweight, cycle life, stability, etc. The majority of the materials used for Li ion energy storage are comparatively abundant, making this storage system more economically feasible. Thus, at present, none of the alternative energy storage systems are capable of competing with Li ion energy storage in large scale applications [12]. For this reason, we focus on Li ion energy storage systems in this study.

This review provides a general overview and classification of Li ion energy storage systems. Advantages, components and charge–discharge reactions, as well as electrolytes, separators and electrodes for Li ion energy storage, are briefly discussed. We also consider the techniques used for electrode fabrications, including electrodeposition, chemical vapor deposition (CVD), lithography, pressing, roll to roll, dip coating, doctor blade, drop casting,

nanorod growing, brush coating, stamping, inkjet printing (IJP), fused deposition modelling (FDM) and direct ink writing (DIW). The analysis of fabrication techniques includes the research articles published between 2003 and 2022. Additionally, we consider the challenges and prospects of Li ion energy storage technologies.

## 2. Materials and Methods

Energy storage systems (ESS) can be divided into five different groups [8,9,13,14], as displayed in Figure 1.



**Figure 1.** Classification of energy storage system (ESS) [8,9,13,14].

These include mechanical energy storage, thermal energy storage, chemical energy storage, electrochemical and electrical storage system and are based on different forms of stored energy [6,15].

ESS can be utilized for diverse applications according to time and magnitude scales, making these systems suitable for individual applications. A storage system must fulfill

certain standards including quick response time, long/short storage time, energy density, capacity reserves, portable/stationary, conversion rate, storage cost, environmental impacts, security, storage time limit and end use, i.e., standby or grid connections [6,16]. A brief description of each energy storage type is given below.

### 2.1. Mechanical Energy Storage System (MES)

Mechanical energy storage systems (MES) can easily store energy after transforming the energy from sources such as tidal, water current and waves. They include pumped storage, compressed air and flywheel storage technology, which are classified based on the working principal of forced springs, pressurized gas, potential energy and kinetic energy [17].

### 2.2. Thermal Energy Storage System (TES)

Thermal energy storage systems (TES) are suitable for heat or cold storage at specific temperatures in a certain storage medium [18]. Based on heat parameters, TES can be categorized into three different types: sensible heat, latent heat and thermal chemical storage systems.

### 2.3. Chemical Energy Storage System (CES)

Chemical energy storage systems (CES) involve the storage of chemical energy in terms of chemical bonds through chemical reactions. CES can be suitable for storing an enormous amount of energy storage for longer durations. The stored chemical energy can be released by means of an electron transfer to generate electricity [19]. CES can be grouped into gas storage, fuel cells (note that a fuel cell can be viewed, not as an energy storage, but as an energy conversion device) and biofuels based on the type of chemical reactions.

### 2.4. Electrochemical Energy Storage System (ECES)

Electrochemical energy storage systems (ECES) are batteries that convert chemical to electrical energy. The systems can be categorized into different types based on their chemical reaction, design and materials. ECES systems can be divided into flow batteries, Li ion, Na based, lead acid, Ni based, metal air, Mg ion and K ion batteries. In ECES, the electric current is generated through chemical reactions between the positive electrode and the negative electrode, separated by an electrolyte. This generated energy is accessible in a distinctive potential window and for a particular time [20].

### 2.5. Electrical Energy Storage System (EES)

Electrical energy storage systems (EES) are a capacitor-based energy storage mechanism. They can be grouped into electrolyte, nonelectrolyte and electrochemical, along with magnetic or current energy storage. Capacitors provide high current for short periods of time. In EES, metal plates are separated by a dielectric and the plates are charged from a DC source, providing a direct way to store energy [21].

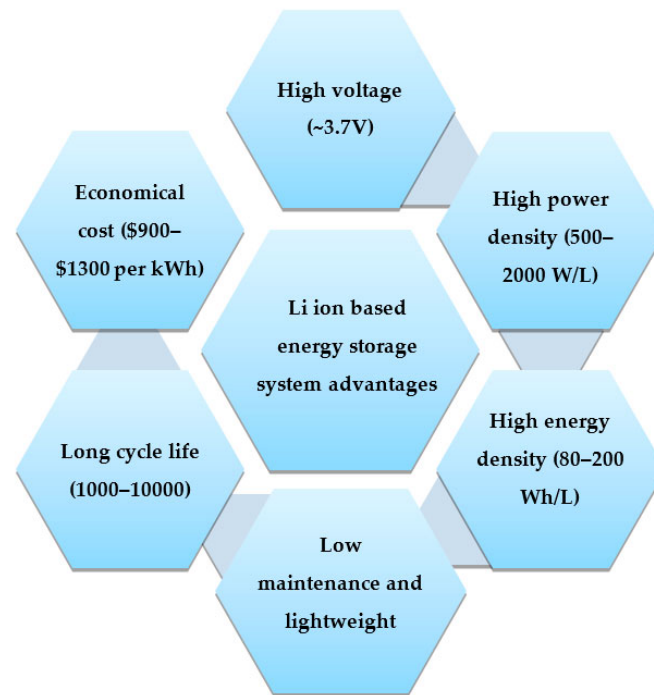
Here, we focus on electrochemical and electrical energy storage systems such as batteries and capacitors. These systems have advantages of high energy and power density, a long cycle life and are a clean energy supply. The operational capacities, in megawatts (MW), for some of the electrochemical and electrical energy storage systems have been reported by Sandia National Laboratories and the U.S. Department of Energy (DOE) [22], as summarized in Table 1. From these data, we can observe that there is a substantial usage of Li ion energy storage for all sectors. After considering the statistics, for the present study, we primarily focus on Li ion energy storage systems.

**Table 1.** Operational capacity for electrochemical and electrical energy storage systems [22].

Energy Storage System	MW Capacity	%
Li ion	1629	79.44
Na based (NaS and Zebra)	204.315	9.96
Flow batteries	71.87	3.5
Lead Acid	68.173	3.32
Capacitor	30.903	1.52
Ni based	30.385	1.48
Metal Air battery	15.987	0.78

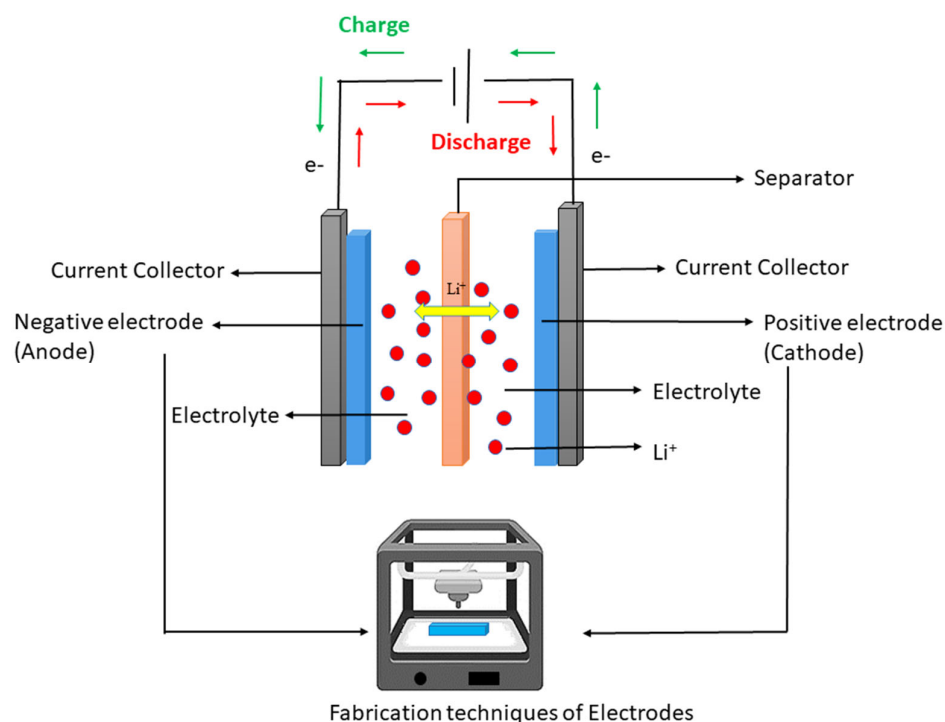
### 3. Li Ion-Based Energy Storage System

Li ion-based energy storage systems are the most dominating power resource used in various sectors including electronics, electric vehicles, wireless devices, etc. Compared to other technologies, this has a number of advantages in terms of energy and power density, voltage range, cycle life, overall cost and maintenance, along with the weight of device. Some of the major advantages are illustrated in Figure 2 [23–25].

**Figure 2.** Advantages of Li ion-based energy storage system [23–25].

Li ion is the key element in Li-based energy storage. During discharge, Li ions move from the negative electrode (anode) towards the positive electrode (cathode) after ionization, passing through the electrolyte. At the positive electrode, these Li ions change their oxidation states. During charging, this process is completely reversible. Micro permeable separator pores are small enough for Li ions to be able to move through. A schematic representation of this system is shown in Figure 3.

The components used in the Li ion-based energy storage system include the electrolyte, separator and electrodes, i.e., positive electrode and negative electrode.



**Figure 3.** Schematic illustration of Li ion-based energy storage system.

### 3.1. Electrolyte

Electrolytes should provide high Li-ion mobility and diffusion rates in the system. The following lithium ion containing solvents are often used:  $\text{LiPF}_6$ ,  $\text{Li}_2\text{SO}_4$ ,  $\text{LiCl}$ ,  $\text{LiNO}_3$ ,  $\text{CH}_3\text{COOLi}$ ,  $\text{LiTFSI}$ ,  $\text{LiClO}_4$ , etc. Earlier electrolytes contained dissolved Li salts in organic solvents [26]. However, in recent years, the attention shifted towards other electrolytes that showed high dielectric constant at a wide range of temperatures, such as propylene glycol [27]. Carbonates including dimethyl carbonate, ethylene carbonate or ethyl methyl carbonate are also under consideration. These mixtures are stable with respect to positive electrode surfaces. They also have a wide range of electrochemical stability with high solvation for Li salts. Most liquid electrolytes, e.g., dimethyl carbonate, ethylene carbonate or ethyl methyl carbonate and  $\text{LiPF}_6$  used in Li based energy storage are due to their high conductivity at room temperature [28]. Moreover, ethers based on electrolytes, e.g., tetrahydrofuran, polymethoxy ethers, diethyl ether, etc., are alternative substitutes due to their low viscosity and high ionic conductivity [29]. Additives are another alternative that are used to avoid dendrite growth. Small concentrations of additive can significantly improve the property of electrolyte, e.g., 12-crown-4 additive in  $\text{LiBF}_4$  electrolyte, succinimide additive in  $\text{LiPF}_4$  electrolyte, etc. have positive effects on electrolyte properties. Such combinations are referred to as functional electrolytes. Based on the application, SEI modification and overcharging protection additives can be categorized into distinct types [29]. Polymer based electrolytes are another option due to their advantages over liquid electrolytes in terms of safety, e.g., polysiloxane, poly(vinylene carbonate) (PVC), Poly(ethylene oxide), etc. [30]. Even though polymer electrolytes have higher thermal stability, their conductivity of Li ions is comparatively lower. This is due to the low mobility of ions or the high viscosity of electrolyte.

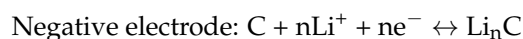
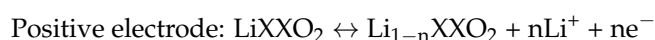
### 3.2. Separator

A separator is positioned in between two electrodes (negative and positive) to avoid their direct contact. Separators should have negligible/low electronic conductivity, high ionic current, higher stability toward electrolytic chemicals, higher wettability and mechanical stability and adequate physical strength to endure assembly procedure. In case of short-circuit in energy storage device, this separator can break the flow of ions and inhibit

thermal runaway. This can happen due to melting or pore filling of separator that might lead to instantaneous reactions inside the device. Most separators used in batteries are microporous polymeric films or nonwoven fabrics for, e.g., celgard and glass fiber [31]. More details on separators can be found in the review by Arora and Zhang [31].

### 3.3. Electrodes

Electrodes play an important role in electricity generation via chemical reactions. A positive electrode is crucial to determine battery characteristics in terms of their capacities and potential differences. The negative electrode plays a significant role in terms of electric current flow through external circuit. A high capacity and long cycle life of the negative electrode contribute to the high energy density in Li ion batteries [32]. Common positive electrode materials for Li based energy storage are LCO, LMO, LFP, LTO, etc., and negative electrode materials are  $\text{TiO}_2$ , carbon, graphite, Si, Sn, etc. The reaction occurring during the charging and discharging processes are specified below [33]:



During charging, Li ions are stored in the negative electrode; during discharging, Li ions flow back to the positive electrode and pass through the electrolyte. In the reaction of charging–discharging, the electrons generated from Li ions result in current that can be utilized in DC applications.

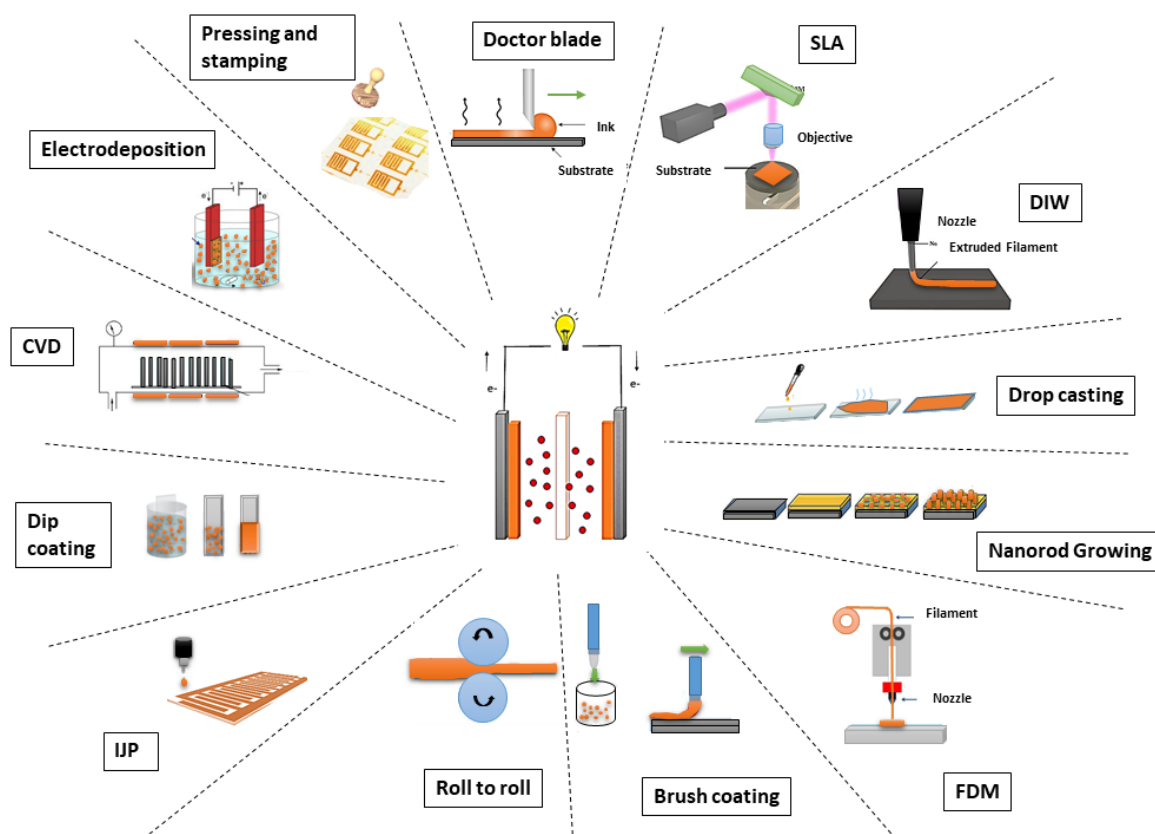
Even though there are several works already published on Li ion-based energy storage, only a few analyzed the fabrication technologies of the electrodes. In the present study, we narrowed our focus down to Li ion-based energy storage systems in terms of the different electrode fabrication techniques.

Based on the literature, the majority of standard electrode fabrication techniques for Li energy storage are discussed in the next section. Unfortunately, a complete comparison by considering all the properties is often challenging; in some cases, the data provided in the literature on different electrode systems, i.e., single electrode; half-cell; complete cell, contain no complete descriptions of the procedure/materials. Inconsistencies in data hinder the comparison of different sources. This review pinpoints a useful depiction of the techniques used for electrode fabrication in Li ion-based energy storage.

## 4. Electrode Fabrication Techniques for Li Ion-Based Energy Storage System

Electrode fabrication techniques are schemes that involve the production of controlled material deposition as a single or multiple layers or films. Among these, a few techniques have been used for 2D and 3D fabrication through a specific nozzle design and heat input system that result in defined material deposition. These fabrication techniques play a significant role for the cost, sustainability, time and near-net shape production in different patterns for both small and large scales. The proper choice of fabrication technology ultimately provides a more economical route for the energy storage system. Therefore, fabrication techniques for better production technology need to be investigated. Figure 4 shows several fabrication techniques and their principles for Li ion-based energy storage that are reported in the literature. There are already many deposition techniques reported in the literature; however, it is difficult to find distinctive methods for their classification. Every technique has qualities contain both advantageous and disadvantages features. The selection of favorable techniques is usually based on individual application and resource availability. In many cases, the combination of two or more techniques can be applied in material deposition. In addition, the reformation or controlling of the film properties are likely to be based on the deposition technique selection; this means that two different processes cannot produce materials with the same properties. The same material, but used in different applications, might be produced by different deposition techniques. The

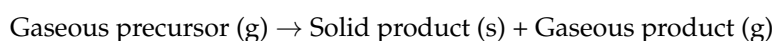
deposition technology is determined by the factors involving materials behavior, substrate property, application area, safety, overall cost, stability, manufacturing factor, material, equipment availability, etc. [34]. In this section, we discuss the following technologies: chemical vapor deposition (CVD), lithography, pressing, roll to roll, dip coating, doctor blade, drop casting, nanorod growing, brush coating, stamping, inkjet printing (IJP), fused deposition modelling (FDM) and direct ink writing (DIW).



**Figure 4.** Electrode fabrication techniques for Li ion-based energy storage system.

#### 4.1. Chemical Vapor Deposition (CVD)

Chemical vapor deposition (CVD) is a deposition procedure that produces high quality thin films in vacuum. CVD is based on the chemical interaction between a precursor and a gas mixture, resulting in the coating of a desired material on a substrate. The control over the interfacial reaction between the substrate and coating as well as between the gaseous product and the substrate is an important factor to consider during the material deposition [34]. The CVD technique is used for various applications such as conductors, conductive oxides, passivation layers, etc. In the CVD technique, the following chemical reaction takes place:



The solid product, in the form of thin films, obtained from the process can be used directly in applications. This technique is feasible for material deposition on larger areas. CVD is one of the techniques used for the electrode fabrication for Li ion energy storage, as shown in Figure 4. Ren et al. [35] used CVD technique for the deposition of multiwalled carbon nanotubes (MWCNT) array, with a thickness of 18 nm, used as one of the electrodes in a Li ion storage system.

#### 4.2. Doctor Blade (Tape Casting)

The doctor blade technique, also referred to as tape casting, is a method used for thin film production for larger surface areas. Originally, this method was developed in 1940 for piezoelectric materials/capacitors thin sheets [36]. The doctor blade technique is based on the principle in which a uniform/homogeneous slurry made of active material, binder and dispersant is spread onto a substrate and dried at a certain temperature to form a uniform film. The doctor blade technique is suitable for coatings with thicknesses ranging from twenty to several hundred-microns. It is a cost-effective process. One of the major drawbacks of the doctor blade technique is the wastage of large amounts of material; for example, ~5% of the solution is lost during the process—the optimization of parameters is crucial for the technique [37]. This process is much slower when compared to other techniques, and it takes a longer time to dry the produced films. The doctor blade technique is one of the techniques that is used for electrode fabrication in Li ion energy storage system, as shown in Figure 4. Liu et al. [38] used the doctor blade technique for deposition of a MnO–C, carbon black and poly-vinyl difluoride (80:10:10 ratio) mixture on a Cu foil substrate. After heat treatment, they used the prepared film as one of the electrodes electrochemical studies.

#### 4.3. Drop Casting

In the drop casting technique, a drop of suspension ink containing active material particles with binder and solvent is dropped onto the surface of the electrode. After drop casting, the electrode should dry completely before application. Small amounts of active material are required, but this technique has limitations for larger surfaces and eventually, industrial production [39]. However, drop casting is an electrode fabrication technique used for small-scale production, as shown in Figure 4. Senthilkumar et al. [40] prepared activated carbon (AC) electrode and bismuth oxide ( $\text{Bi}_2\text{O}_3$ ) electrode via the drop casting method. They prepared a slurry by mixing AC/ $\text{Bi}_2\text{O}_3$ , carbon black and polyvinylidene fluoride (PVDF) binder in N-methyl-2-pyrrolidone (NMP). This slurry was drop casted onto a stainless-steel substrate and dried overnight. The prepared electrode was then used in Li ion storage device.

#### 4.4. Nano Rod Growing

Chemical synthesis by using shape control ligands or different combination of precursors can result in nano rod growth. The synthetic process requires control of both kinetic and thermodynamic parameters [41]. Nano rods are ideal for several applications, including energy storage, due to their anisotropic shape. The increase in surface plasmon leads to enhanced electric field in nano rods as compared to that of spherical particles. A slight deviation from kinetic and thermodynamically optimized conditions can cause huge variations of the final product. This is a technique used for electrode fabrication in Li ion energy storage, shown in Figure 4. Deng et al. [42] used this approach to produce niobium oxide as the electrode in Li ion energy storage. They immersed the carbon cloth in a precursor of niobium for 24 h and then annealed it at 400 °C for 1 h. After that, the carbon cloth was placed in a Teflon reactor containing a mixed solution of hydrochloride acid and ethanol. The reactor was sealed with an autoclave and heated to 200 °C for 24 h. After the completion of this solvothermal process, a nanorod was formed on the carbon cloth. This was used as the electrode in Li ion energy storage.

#### 4.5. Brush Coating

Brush coating is a low cost, simple fabrication technique used for both nano and micro sized 1D materials. It utilizes a shear force. During shearing, one challenge is nano-film morphology control. The withdrawal rate and temperature need to be controlled [43]. Brush coating is the simplest technique used for electrode fabrication in Li ion energy devices. The working principle is shown in Figure 4. Hao et al. [44] implemented the brush coating to prepare lithium manganese oxide ( $\text{Li}_2\text{Mn}_4\text{O}_9$ ) electrodes via deposition of a

mixed slurry of the active material (75 wt%), acetylene black (20 wt%) and polyvinylidene fluoride (5 wt%) in NMP solvent. The slurry was deposited on stainless steel substrate to form a film for the Li ion storage system.

#### 4.6. Roll to Roll (RTR)

The roll to roll (RTR) technique is a cost-effective process. RTR deposition involves gravure or offset printing and flexography, or a combination of the processes. This technique is suitable for water-based materials and processing of short time deposition on a flexible substrate. After deposition of films, the substrate is unwound from the roll. Further treatments, including drying, heating, curing and deposition of another layer, can be done [37,45]. The RTR technique has the high rate of production, and its manufacturing cost can be reduced by automatic fabrication towards larger quantities. Although the capital cost for setting up the instrument is comparatively higher, this cost can be recovered by cost-effective production on a larger scale [46]. RTR is useful for larger scale production of electrodes in Li ion energy storage, as shown in Figure 4. Ping et al. [47] used the RTR technique for deposition of electrode film prepared from a slurry of mesocarbon microbeads (MCMB) mixed with polyvinylidene fluoride binder in NMP. After deposition of the slurry onto a Cu foil, heat treatment was performed at 80 °C. This film was further used as an electrode in the Li ion energy storage system.

#### 4.7. Dip Coating

The dip coating method was first reported in a seminal work by Schott in 1940 [48]. From the 1950s onwards, this method was applied in automotive production of rear mirrors. The principle of the dip coating method comprises the immersion of the substrate in a solution containing active material; subsequently, the substrate is withdrawn. The film formed after drying and curing can be used for further applications. This simple and cost-effective coating technique permits the deposition of different oxide and hybrid materials on larger areas as well as on substrates of complex shapes. Major drawbacks of the dip coating technique are the slow rate and possibility of blocking that influences the eventual outcomes. Dip coating is amongst the techniques used for electrode fabrication in Li ion energy storage, as shown in Figure 4. Zhou et al. [49] synthesized graphene oxide (GO) by Hummer's method. Later, they dispersed GO in distilled water via ultra-sonication to the prepared suspension. They used the dip coating method to deposit the suspension on the carbon cloth. This was applied as an electrode in the Li ion energy storage system.

#### 4.8. Electrodeposition

Electrodeposition is a flexible technique for 2D and 3D material coating. This method is also known as electroplating, and it was developed for alloys and metal coating. These days, electrodeposition covers the deposition of alloys, metals, polymers and semiconductor materials with respect to various dimensions and sizes [50]. Based on a reaction mechanism, the electrodeposition of electrodes for energy storage can be divided into cathode electrodeposition and anode electrodeposition. Electrodeposition is a process in which the controlled deposition of a material takes place on a conducting substrate via an electric current flow through an ion containing solution. This process involves a phase change and electron transfer [51]. The major drawback of this technique is a problematic disposal of waste products, a long time required to create a thick layer, as well as a high equipment cost. Electrodeposition can play a significant role for thin film deposition that can be used for energy storage system. Jin et al. [52] performed anodic electrodeposition to fabricate a manganese oxide film on a carbon fiber substrate. The electrodeposition was carried out at 1.0 V in a precursor solution of manganese acetate. Thus, deposited manganese oxide film was utilized as an electrode in a Li ion energy storage system.

#### 4.9. Coating, Pressing, and Stamping

Coating, pressing and stamping are low cost, concise methods typically used for micro-energy storage systems. Stamping can directly provide desired electrodes by transferring active material of a required pattern. We notice that stamp molds are not easy to handle, and elimination of uncured parts can ultimately damage the electrode. In this method, to assure that ink is transmitted to the substrate, the adhesion between the substrate and ink should be stronger than that between the mold and the ink [53]. These are ones of the most basic and simple techniques, compared to other methods used for electrode fabrication of Li ion energy storage (Figure 4). Babu et al. [54] prepared lithium titanium oxide by mixing the active material, acetylene black and polyvinylidene fluoride binder (80:10:10 ratio) in NMP. They used this slurry for coating on a stainless-steel substrate. This film was further used as an electrode in a Li ion energy storage system.

#### 4.10. Inkjet Printing (IJP)

Inkjet Printing (IJP) is a material deposition technique used for 2D material printing. IJP can produce high-resolution patterns due to its tremendous printing proficiency for multi materials. Polymer jetting and binder jetting are the two different inkjet deposition techniques. Photosensitive polymers deposited through polymer jetting and are later cured by light. However, the binders ejected on top of a powder bed in binder jetting technique form a cross section referred to as 3DP. The limitations of inkjet printing come from parameter optimization, specific printed patterns and droplet formation. Frequent challenges of IJP technique are clogging of the nozzle, wetting property, homogeneity and size of the film [55]. The IJP technique was used for electrode fabrication due to its controllable thin film producing capacity. Sundriyal et al. [56] used the IJP technique to print electrode materials and conducting layers on a substrate such as commercial paper. After optimizing properties for suspension of AC, GO, MnO<sub>2</sub>, and GO-MnO<sub>2</sub>, these suspensions were deposited through the IJP technique and used as an electrode for a Li ion energy storage system.

#### 4.11. Direct Ink Writing (DIW)

Direct ink writing (DIW) is an additive manufacturing method for the direct extrusion of slurry-based inks for 3D printed batteries. The technology is also referred to as robocasting; the material paste gets extruded via small nozzle. The technique was developed to build a complex structure of ceramic green bodies in 1996. In recent years, DIW has been used to print battery components including negative electrode, gel electrolyte, positive electrode and packaging. The electrodes printed by DIW are popular due to their affordable manufacturing, ease of operation and flexibility of materials. The printing principle includes preparation of viscoelastic inks based on gels with a shear thinning property. The design principle for the printable ink is the most crucial factor for the DIW technique. Furthermore, ink rheology, printing speed and printing resolution also play a significant role for the DIW process. Therefore, through the optimization of parameters, resolutions of up to 1  $\mu\text{m}$  can be reached. One critical problem with this technique that needs to be solved is the mechanical stability of grown films. Therefore, substantial improvements of the DIW technique are needed [57]. DIW is used in the fabrication of electrodes for micro energy storage, as shown in Figure 4. Izumi et al. [58] used DIW to print a cathode from the mixture of lithium titanium oxide as active material and poly(vinylidene difluoride) binder in NMP solvent. The fabricated electrode system was used as an electrode in Li ion energy storage.

#### 4.12. Fused Deposition Modelling (FDM)

In fused deposition modelling (FDM), extrusion of a thermoplastic filament deposits through a moving heated nozzle on a substrate, where it readily solidifies. Many thermoplastic materials typically include poly(lactic acid) (PLA), acrylonitrile butadiene styrene (ABS), polycarbonate (PC), high-impact polystyrene (HIPS), polyamides (PA) and ther-

moplastic polyurethane (TPU). These materials can be printed in the resolution range of 50–200  $\mu\text{m}$  [59]. Even though the printing resolution of FDM is low as compared to that of other 3D printing technologies, FDM became popular due to its speed, cost, dimension range and lower requirement of post-processing treatment. Flexible and user-friendly fabrication of the materials via regulation of the printing parameter facilitate the FDM technique for production of hollow and porous structured objects with superior mechanical strength [60]. Presently, the printing of multi-material objects with multi-nozzle printing technology is also possible. For instance, graphene-polymer filaments were printed layer by layer to fabricate conducting devices [61]. Due to its speed and printing flexibility, FDM has gained attention for electrode printing that can be used in energy storage systems. Reyes et al. [62] used the mixture of poly(lactic acid), dissolved in dichloromethane (DCM), active and conductive materials to produced electrode through extrusion. This FDM deposited electrode was used in a Li ion energy storage system.

#### 4.13. Stereolithography (SLA)

Stereolithography (SLA or SL) is a 3D printing technologies used for creating objects in a layer-by-layer route using photochemical processes by means of light. This forms chemical monomers and oligomers cross-linked together as in polymers [63]. This also involves post-processing heat or photo curing treatment used for solidifying the monomers into the required structure. Generally, this technique is used to create porous battery electrodes because of its high-resolution capacity [64]. Although the surface quality of the product obtained from SLA has a good quality as compared to other processes, it has some limitations in the case of multi-material deposition. In recent times, SLA is used to fabricate polymeric membrane materials and phosphonium polymerized ionic liquid objects [65]. SLA seems to be an ideal technique for assembly of luminescent solar concentrators, since luminescent nanomaterials can disperse into methyl methacrylate resin [66]. Stereolithography is one of the technologies used for electrode fabrication in energy storage systems (Figure 4). For example, Cohen et al. [67] used lithography to prepare an electrode on a silicon wafer substrate and utilized this electrode in Li ion energy storage devices.

Table 2 shows the application of different fabrication technologies for a Li based energy storage system. This table includes information about fabrication technologies, electrolyte, solvent and electrodes, separator and working potential ranges, as well as resulting specific capacity and cycle retention of a particular Li ion energy storage system.

**Table 2.** Summary and examples of the electrode fabrication technology for Li ion-based energy storage system.

Sr.	Tech.	Electrodes	Electrolyte and Solvent	Separator	Voltage (V)	Capacity	Cycle Retention (%)	Ref.
1	CVD	MWCNT-LTO//MWCNT-LMO	1 M LiPF <sub>6</sub> in mixture of EC, DEC, and DMC (1:1:1 w/w)	-	0–1.5	138 mAh/g at 0.01 mA	97% (1000 cycle)	[35]
		MWCNT//LTO	1 M LiPF <sub>6</sub> in EC and DEC (1:1 by volume)	Polypropylene membrane	0–3.0	-	92% (3000 cycle)	[68]
2	Doctor blade	AC//MnO	1 M LiPF <sub>6</sub> in mixture of EC, DMC and DEC (1:1:1 by volume)	Polypropylene film (Celgard 2400)	0–4.0	637 mA h/g at 100 mA/g	92.5% (3500 cycle)	[38]
		EEG//TiO <sub>2</sub> @EEG	1 M LiPF <sub>6</sub> gel based	-	0–3.0	58 F/g at 0.4 A/g	68% (1000 cycle)	[69]
		AC//carbon coated $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	1 M LiPF <sub>6</sub> in PC	Whatman GF/D glass microfiber filter	0.6–3.0	750 mAh/g at 0.13 A/g	99% (100 cycle)	[70]
3	Drop casting	AC//Bi <sub>2</sub> O <sub>3</sub>	KI added in 1 M Li <sub>2</sub> SO <sub>4</sub>	Polypropylene sheet	0–1.6	99.5 F/g	72% (1000 cycle)	[40]

Table 2. Cont.

Sr.	Tech.	Electrodes	Electrolyte and Solvent	Separator	Voltage (V)	Capacity	Cycle Retention (%)	Ref.
4	Nanorod growing	AC//Nb <sub>2</sub> O <sub>5</sub>	1 M LiPF <sub>6</sub> in EC and DMC (1:1 by volume)	-	1–3.5	220 mA h/g at 1 C	73% (2500 cycle)	[42]
		MnO <sub>2</sub> NW//Fe <sub>2</sub> O <sub>3</sub> NT	PVA/LiCl gel in DI	NKK TF40	0–1.6	91.3 F/g at 2 mA/cm <sup>2</sup>	84% (5000 cycle)	[71]
5	Brush coating	Li <sub>2</sub> Mn <sub>4</sub> O <sub>9</sub> //AC	1 M LiNO <sub>3</sub> in NMP	-	0–1.4	54.6 F/g at 100 mA/g	80% (1000 cycle)	[44]
6	RTR	AC/LiFePO <sub>4</sub> //MCMB	1 M LiPF <sub>6</sub> in EC/DEC mixture (1:1 v/v)	polypropylene microporous sheet (C2400, Celgard)	2.0–3.8	23.80 mAh/g	92.9% (100 cycle)	[47]
		AC//Graphite	1 M LiPF <sub>6</sub> in EC/DMC	Glassy fibrous separator	1.5–4.5	120 mF	84% (300 cycle)	[72]
		AC//HOG-Li	1 M LiPF <sub>6</sub> in EC/DMC	-	2.0–4.2	73.1 mAh/g at 20 mA/g	84.2% (1000 cycle)	[73]
		G-LTO//G-SU	1 M LiPF <sub>6</sub> in EC, DMC and DEC with a volume ratio (1:1:1 v/v)	-	0–3.0	75 mAh/g at 1 A/g	87% (500 cycle)	[74]
7	Dip coating	V <sub>2</sub> O <sub>5</sub> /Pin@ACC//rGO@ACC	5 M LiNO <sub>3</sub> /PVA in DI	Filter paper saturated with LiNO <sub>3</sub> /PVA	0–1.8	275.5 F/g at 0.4 A/g	91.1% (5000 cycle)	[49]
8	Electro deposition	MCNP//FCNP MnO <sub>2</sub>	LiCl/PVA gel electrolyte in DI	-	0–1.8	-	81.2% (10,000 cycle)	[52]
9	Coating, Pressing and stamping	(RHDPC-H <sub>3</sub> PO <sub>4</sub> ) and (RHDPC-KOH)//LTO	1 M LiPF <sub>6</sub> in EC and DEC mixture with 1:1 v/v	Microporous glass fiber separator (Whatman1823-090, UK)	0–3.0	80 F/g and 120 F/g at 2 A/g	92% (2000 cycle)	[54]
		Graphene//LTO/C	1 M LiPF <sub>6</sub> in EC and DEC	Celgard 2500	1.0–3.0	58 F/g at 10 A/g	65% (1000 cycle)	[75]
		AC(MSP-20)//T-Nb <sub>2</sub> O <sub>5</sub> @Carbon core	1 M LiPF <sub>6</sub> in EC and DEC mixture with 1:1 v/v	-	1–3.5	180 mA h/g at 0.05 A/g	Without significant fading(1000 cycles)	[76]
		LiMn <sub>2</sub> O <sub>4</sub> /Graphene//AC	1 M LiPF <sub>6</sub> in EC/DEC/DMC (1:1:1 vol %)	Celgard 2400 polypropylene membrane	0–2.3	43.7 F/g at 2C	90.6% (500 cycle)	[77]
		AC//LTO/AC	1 M LiPF <sub>6</sub> in EC/DEC (1:1 v/v)	Celgard 2400	1.0–2.5	128 mA h/g at 100 mA/g	67% (160 cycles)	[78]
		AC//TiO <sub>2</sub>	1 M LiPF <sub>6</sub> in EC/DEC (1:2 molar ratio)	Glass fiber paper	0–3.2	117 mAh/g	85.47% (400 cycles)	[79]
		N-ACs//Si/C	1.2 M LiPF <sub>6</sub> in EC/DMC	-	2–4.5	79 mA h/g at 0.4 A/g	76.3% (8000 cycle)	[80]
		G-MoO <sub>2</sub> //G-MoO <sub>2</sub> Graphene	1 M LiPF <sub>6</sub> in DMC	Glass-fiber separator	0–3.0	173.2 F/g at 50 mA/g	91.2% (500 cycle)	[81]
10	IJP	GO//MnO <sub>2</sub> /AC	PVA/LiCl in DI	Gel	2.0	1.586 F cm <sup>-2</sup>	89.6% (9000 cycles)	[56]
		Ni//MnO <sub>2</sub>	CH <sub>3</sub> COOLi/PVA in DI	-	0–0.8	52.9 mF cm <sup>-2</sup>	77.4% (500 cycles)	[82]
		LTO//LTO	-	-	1.0–2.0	153 mAh g <sup>-1</sup> at 10.4 μA cm <sup>-2</sup>	300 cycles	[83]
		LCO//LCO	-	-	-	110 mAh g <sup>-1</sup> at 75 mA g <sup>-1</sup>	95% (100 cycles)	[84]
		LiFePO <sub>4</sub> //LiFePO <sub>4</sub>	-	Glass-fiber separator	0.062–0.930	125 mAh g <sup>-1</sup> at 9C	-	[85]
		LiFePO <sub>4</sub> //LiFePO <sub>4</sub>	-	Celgard 2400	2.0–4.0	110 mAh g <sup>-1</sup> at 750 mA g <sup>-1</sup>	96.4%	[86]
		SWCNT//SWCNT	PVA/LiCl in DI	Gel	-	15.34 F cm <sup>-3</sup>	96.5% (5000 cycles)	[87]

Table 2. Cont.

Sr.	Tech.	Electrodes	Electrolyte and Solvent	Separator	Voltage (V)	Capacity	Cycle Retention (%)	Ref.
11	DIW	LTO//AB	-	Porous PP film	1.0–3.0	~80 mAh g <sup>-1</sup> at 1C	90% (200 cycles)	[58]
		LMFPC//LMFPC	-	Celgard membrane	2.0–4.5	150.21 mAh g <sup>-1</sup> at 10 C	1000 cycles	[88]
		LMO//LMO	-	PP/PE/PP membrane (Celgard)	3.0–4.2	0.83 mAh cm <sup>-2</sup> at 1 C	-	[89]
		LFP/LTO//CNT	-	LiPF <sub>6</sub> in EC/DEC solution	1.0–4.0	89 mAh g <sup>-1</sup> at 50 mA g <sup>-1</sup>	81% (30 cycles)	[90]
		LFP/LTO//CNT	-	Celgard 2400	1.0–4.3	102 mAh g <sup>-1</sup> at 0.2 C	92.2% (100 cycles)	[91]
		LFP//MWCNT	-	-	2.5–4.2	80 mAh g <sup>-1</sup> at 4 C; 132 mAh g <sup>-1</sup> at 1 C	51.8% (115 cycles)	[92]
		PE-CNT	1 M LiPF <sub>6</sub> in xylene, NMP	Celgard 2325	-	80 mAh g <sup>-1</sup> at 1C	-	[93]
		LTO//LTO	-	-	-	140 mAh g <sup>-1</sup> at 0.5 C	100 cycles	[94]
		Li//LFP	1 M LiTFSI in DMM/DOL	-	0.05	140 mA h g <sup>-1</sup> at 0.2 C	85% (3000 cycles)	[95]
		LTO//LFP	1 M LiTFSI in PC	Ceramic-filled polymer composites	0.5–3.0	33 mAh g <sup>-1</sup> at 0.2 mA cm <sup>-2</sup>	-	[96]
		LTO//LFP	1 M LiClO <sub>4</sub> in EC/DMC (1:1 v/v)	-	1.8	1.5 mAh cm <sup>-2</sup> at 5 C	-	[97]
		Li//GO	1 M LiTFSI in DMM/DOL	-	1.5–3.0	812.8 mAh g <sup>-1</sup>	43.4% (50 cycles)	[98]
		Li//Ni/rGO	-	-	1.25	1000 mA h g <sup>-1</sup> at 100 mA g <sup>-1</sup>	-	[99]
		LTO//LFP	Al <sub>2</sub> O <sub>3</sub> /PVDF in glycerol	Celgard 2325	-	154 mAh g <sup>-1</sup> at 0.2 C	-	[100]
		LTO//LiCoO <sub>2</sub>	1 M LiPF <sub>6</sub> in 1:1 ratio of EC/DEC	-	1.0–2.1	150 mAh g <sup>-1</sup> at 0.2 C	-	[101]
		Li//MnO <sub>2</sub>	PVDF-co-HFP/Pyrr <sub>13</sub> TFSI/LiTFSI/TiO <sub>2</sub> in NMP	Porous polymer film	-	127.3 mAh g <sup>-1</sup>	98.6% (100 cycles)	[102]
		LTO/GO//LTO/GO	1 M LiPF <sub>6</sub> in EC and DEC	Gel polymer electrolyte	2–4	185 mAh g <sup>-1</sup> at 10 mA g <sup>-1</sup>	100% (10 cycle)	[103]
		Li//S/BP <sub>2000</sub>	1 M LiTFSI in DMM/DOL	Celgard 2400	-	1009 mAh g <sup>-1</sup> at 5.5 mg cm <sup>-2</sup>	87% (200 cycles)	[104]
12	FDM	LFP/CNT//LFP/CNT	1 M LiPF <sub>6</sub> in EC and DEC	-	2.5–4.2	150 mAh g <sup>-1</sup> at 0.1 C	51.8% (115 cycles)	[92]
		LTO//LFP	1 M LiPF <sub>6</sub> in EC and DEC	Celgard 2400	1.0–2.5 and 2.0–4.3	128 mAh g <sup>-1</sup> at 0.2 C	-	[91]
		LTO//LMO	1 M LiClO <sub>4</sub> EMC and PC (50/50 vol %)	25 µm PP disk	2.0–3.0	3.91 mAh cm <sup>-3</sup>	-	[62]
		Graphene//Li	1 M LiPF <sub>6</sub> in EC and DEC	Celgard 2400	0.01–3.0	40 mAh g <sup>-1</sup> at 120 C	-	[105]
		Graphene//Pt	1 M LiCl	-	-1.0 to -0.5	248 mAh g <sup>-1</sup> at 40 mA g <sup>-1</sup>	93% (1000 cycles)	[106]
		Graphite//PLA/Li	1 M LiPF <sub>6</sub> in EC and DEC	PVDF-co-HFP	0.01	215 mAh g <sup>-1</sup> at 18.6 mA g <sup>-1</sup>	-	[107]
		LTO/NGP//LMO/MWCNT	1 M LiClO <sub>4</sub> in EMC and PC (50/50 vol %)	Al <sub>2</sub> O <sub>3</sub>	2.0–3.0	7.48 mAh cm <sup>-3</sup> at 1 C	-	[62]
		LTO//LFP/GO/MWCNT	1 M LiPF <sub>6</sub> in EC and DEC	Celgard	2.6–3.8	80 mAh g <sup>-1</sup> at 2 C	-	[108]
		LTO//LFP	1 M LiPF <sub>6</sub> in EC and DEC	-	1.4–3.2	~2.9 µAh cm <sup>-2</sup> µm <sup>-1</sup> at 1 C	80% (1000 cycles)	[109]
		LTO//LFP	1 M LiPF <sub>6</sub> in EC and DEC	-	1.9–3.2	500 mAh cm <sup>-2</sup> at 0.1 C	-	[67]
		LTO//LFP	1 M LiClO <sub>4</sub> in EC:DMC	-	1.5–4.2	1.4 µAh cm <sup>-2</sup> at 2–4 µA	97.7%	[110]
		LTO//LFP	1 M LiPF <sub>6</sub> in EC and DEC	-	1.5–4.2	1.4 µAh cm <sup>-2</sup> at 2–4 µA	97.7%	[110]
		LTO//LFP	1 M LiPF <sub>6</sub> in EC and DEC	-	1.5–4.2	1.4 µAh cm <sup>-2</sup> at 2–4 µA	97.7%	[110]
		LTO//LFP	1 M LiPF <sub>6</sub> in EC and DEC	-	1.5–4.2	1.4 µAh cm <sup>-2</sup> at 2–4 µA	97.7%	[110]
		LTO//LFP	1 M LiPF <sub>6</sub> in EC and DEC	-	1.5–4.2	1.4 µAh cm <sup>-2</sup> at 2–4 µA	97.7%	[110]
		LTO//LFP	1 M LiPF <sub>6</sub> in EC and DEC	-	1.5–4.2	1.4 µAh cm <sup>-2</sup> at 2–4 µA	97.7%	[110]
		LTO//LFP	1 M LiPF <sub>6</sub> in EC and DEC	-	1.5–4.2	1.4 µAh cm <sup>-2</sup> at 2–4 µA	97.7%	[110]
		LTO//LFP	1 M LiPF <sub>6</sub> in EC and DEC	-	1.5–4.2	1.4 µAh cm <sup>-2</sup> at 2–4 µA	97.7%	[110]
13	Lithography (SLA)	NiSn//LMO	1 M LiClO <sub>4</sub> in EC:DMC (1:1 mass ratio)	-	1.4–3.2	~2.9 µAh cm <sup>-2</sup> µm <sup>-1</sup> at 1 C	80% (1000 cycles)	[109]
		LTO//LFP	1 M LiPF <sub>6</sub> in EC and DEC	-	1.9–3.2	500 mAh cm <sup>-2</sup> at 0.1 C	-	[67]
		LTO//LFP	1 M LiClO <sub>4</sub> in EC:DMC	-	1.5–4.2	1.4 µAh cm <sup>-2</sup> at 2–4 µA	97.7%	[110]

A complete comparison between the fabrication techniques, considering all properties, is challenging in some cases. Based on some basic parameters, a comparison has been done, as shown in Table 3. For this comparison, we have considered the following parameters:

- Fabrication speed, i.e., if the process is fast or slow;
- If it is possible to fabricate on a bigger surface or larger area;
- Thickness of produced film, i.e., in nanometer (nm) or micrometer (µm) range;
- Fabrication cost, i.e., if its high or low cost;

- Wastage of material during the deposition process.

**Table 3.** Comparison of electrode fabrication techniques used in Li ion energy storage.

Technology	Fabrication Speed (Fast/Slow)	Possibility of Fabrication on Larger Area	Film Thickness Range (nm) or ( $\mu\text{m}$ )	Fabrication Cost	Material Wastage (More/Less)	Refs.
CVD	Fast	Yes	nm	High	Less	[34]
Doctor blade	Slow	Yes	$\mu\text{m}$	Low	More	[37]
Drop casting	Fast	No	nm	Low	Less	[39]
Nanorod growing			nm	-	Less	[41]
Brush coating	Fast	Yes	nm and $\mu\text{m}$	Low	More	[43]
RTR	Fast	Yes	$\mu\text{m}$	Low	More	[45,46]
Dip coating	Slow	Yes	nm and $\mu\text{m}$	Low	More	[48]
Electrodeposition	Slow	No	nm	High	More	[51]
Coating, pressing and stamping	Fast	Yes	$\mu\text{m}$	Low	Less	[53]
IJP	Fast	Yes	nm	High	Less	[55]
DIW	Fast	No	$\mu\text{m}$	High	Less	[57]
FDM	Fast	No	$\mu\text{m}$	High	Less	[60]
SLA	Fast	No	$\mu\text{m}$	High	Less	[64,66]

Different fabrication techniques have different preparation and application aspects. From the point of view of applications, some fabrication techniques are more suitable for small-scale production; others are more suitable for the industrial scale.

### 5. Publication Statistics for Li Ion Based Electrode Fabrication Techniques

In many earlier published papers dedicated to Li ion batteries, the focus was on slurry preparation, tape casting on collector, assembling of cell components, packing of electrodes in a metal containers and, finally, electrolyte injection. Most fabrication processes, however, are not suitable for miniaturization. Thus, more advanced fabrication techniques should be applied to produce miniature Li ion-based electrodes. Additive manufacturing (AM) technology is capable of fabricating complex structures with low wastage of material; thus, the overall process could be economically sustainable. Therefore, it is not surprising that, in recent years, the research focus has shifted from the conventional top-down approach towards bottom-up fabrication techniques. In AM processes, the prepared electrode inks can be printed in the form of a designed electrode of various sizes, shapes and architectures. Moreover, AM can produce porous structures if necessary. Overall, AM opens a new set of possibilities for the speedy manufacturing of batteries or micro batteries with distinct structural design and high performance.

Figure 5 shows the number of research articles published on electrode fabrication between the years 2003–2022 and schemed through data from the open source search engine, ‘scopus’ [111]. The relevant data are filtered by addressing the keywords such as “CVD, doctor blade, drop casting, nano-rod growing, brush coating, roll to roll, dip coating, electrodeposition, coating, pressing, stamping, ink jet printing (IJP), direct ink writing (DIW), fused deposition modeling (FDM), lithography” in combination with “Li ion energy storage device”.

When a year-to-year comparison is made from the data obtained for various methods of fabrication, we observed a subsequent literature growth in the areas of both conventional and modern fabrication methods for the manufacturing of Li ion-based energy storage systems. Further, we observed that ~92% of the published articles highlighted the application of technologies that majorly included electrodeposition, lithography, CVD and the doctor blade technique. The exponential growth is observed for the number of articles published per year on the processes considering electrodeposition, CVD, lithography and dip coating fabrication techniques. In this study, we excluded articles that are not in English and not published in peer-reviewed journals.

In the years ranging from 2016 to 2022, there was a continuous increase in publications concerning IJP, DIW and FDM. One of the major reasons for this trend might be the

popularity of additive manufacturing (AM) techniques and their advantages in comparison to conventional fabrication techniques. Although a plethora of publications dedicated to the additive manufacturing techniques were found, we narrowed our investigation down to 209 publications based on the following benchmarks:

- Articles published from 2016–2022.
- Final application solely dedicated to Li ion-based storage system.
- Considering AM techniques, including lithography, IJP, DIW and FDM.

We excluded publications that discussed AM techniques in the following contexts:

- Publications where AM techniques were classified in terms of Selective Laser Sintering (SLS), Multi Jet Fusion (MJF), Digital Light Process (DLP), Electron Beam Melting (EBM), PolyJet and Direct Metal Laser Sintering (DMLS); and those that are not used for the application of Li ion-based energy storage.

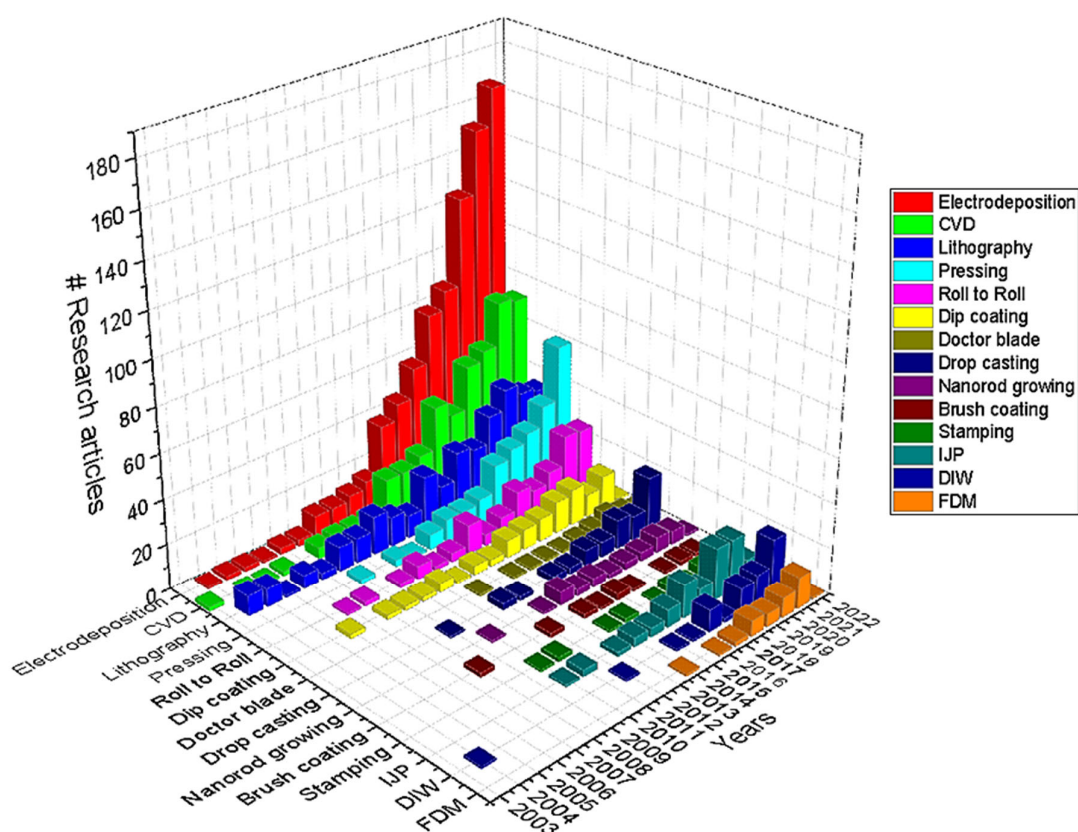


Figure 5. The number of research articles vs. years for different electrode fabrication techniques [111].

## 6. Challenges and Future Prospects for Li Ion Based Energy Storage

Many experts anticipated that the growth of Li ion battery technologies will take over most of the energy storage market in the upcoming 10 years [112,113]. For instance, the demand for Li ion batteries due to portable electronics including laptops, tablets, cameras, phones, etc., is expected to be around 100 GWh by the year 2030. Likewise, there will be a huge demand in other sectors. A detailed analysis of the anticipated demands can be found in Ghassan et al. [114].

Even though there is active research aiming to substitute lithium, there are very few options; this can indicate success with Li ion-based energy storage devices. In particular, one active research area is electrochemical hybrid systems with modified electrode material and electrolytes. Another important topic is the cost and life cycle assessment (LCA), which has a huge impact on the global energy storage market. The development of energy storage technologies is important for the energy transition and will ultimately contributing to

sustainable development goals. Starting from raw material, component fabrication, cell assembly, manufacturing, packing, collection and ending with effective recycling/recovery, this entire chain contributes to the global market growth and environmental disputes. Detailed prospects for the environmental effects of Li ion-based energy storage still need to be evaluated.

## 7. Summary

Electrodes are the most crucial elements of Li ion-based energy storage systems. In recent years, several attempts have been made to improve electrode materials to achieve higher capacity and better cyclic stability of energy storage devices. Fabrication technologies for electrodes, such as CVD, doctor blade, drop casting, nano-rod growing, brush coating, roll to roll, dip coating, electrodeposition, coating, pressing, stamping, ink jet printing (IJP), fused deposition modeling (FDM), direct ink writing (DIW) and lithography for Li ion-based energy storage have been discussed and illustrated with examples. Electrode fabrication technologies are important; they will eventually contribute to the overall cost, functional characteristics and lifetime of energy storage system. Considering the increasing usage of renewable energy generation and the acute need for more energy storage facilities, the impact of Li ion batteries will continue to grow. The technological development of all related aspects, including materials, fabrication techniques, production process, waste generation and life cycle will be of high significance.

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## Abbreviations

$\mu\text{m}$	Micrometer
ABS	Acrylonitrile butadiene styrene
AC	Activated Carbon
Ag NPs	Silver nanoparticles
$\text{Al}_2\text{O}_3$	Alumina
AM	Additive manufacturing
BP2000	Black Pearls 2000
CES	Chemical energy storage
$\text{CH}_3\text{COOLi}$	Lithium acetate
CNTs	Carbon/carbon nanotubes
CVD	Chemical Vapor deposition
DI	De-ionized water
DIW	Direct ink writing
DEC	Diethyl carbonate
DMC	Dimethyl carbonate
DMM	1,2-dimethoxymethane
DOL	1,3-dioxolane
EC	Ethylene Carbonate

ECES	Electrochemical energy storage
EES	Electrical energy storage
EG	Exfoliated Graphene
EMC	Ethyl methyl carbonate
ESS	Energy storage system
EU	European Union
F/g	farad per gram
FDM	Fused deposition modelling
GO	Graphene Oxide
IEA	International Energy Agency
IJP	Inkjet printing
K	Potassium
kWh	kilowatt hour
KOH	Potassium hydroxide
K <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	Potassium pyrophosphate
LFP	Lithium iron phosphate (LiFePO <sub>4</sub> )
Li	Lithium
LiCl	Lithium chloride
LiClO <sub>4</sub>	Lithium perchlorate
LCO	Lithium cobalt oxide (LiCoO <sub>2</sub> )
LiNO <sub>3</sub>	Lithium nitrate
LiPF <sub>6</sub>	Lithium hexafluorophosphate
Li <sub>2</sub> SO <sub>4</sub>	Lithium sulfate
LiTFSI	Lithium bis(trifluoromethanesulfonyl)imide
LMFPC	LiMn <sub>1-x</sub> Fe <sub>x</sub> PO <sub>4</sub>
LMO	Lithium manganese dioxide (LiMnO <sub>2</sub> )
LTO	Lithium titanium oxide (LiTiO <sub>2</sub> )
mA	milliampere
mAh/g	milliampere hours per gram
MES	Mechanical energy storage
Mg	Magnesium
MW	Megawatt
MWNTs	Multiwalled carbon nanotubes
Na	Sodium
NGP	Nano graphene platelets
Ni	Nickel
NiCl <sub>2</sub>	Nickel chloride
NiSn	Nickel tin
NMP	N-methyl-2-pyrrolidone
NW	Nano-wire
PC	Propylene carbonate
PE	Polyethylene
PE-CNT	Polyethylene-Carbon nano-tubes
PP	Polypropylene
Pt	Platinum
PVA	Poly(vinyl) alcohol
PVDF	Polyvinylidene fluoride
PVDF-co-HFP	Poly(vinylidene fluoride-co-hexafluoropropylene)
Pyr13TFSI	N-propyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide
rGO	Reduced graphene oxide
RTR	Roll to roll
SLA	Stereolithography
SnCl <sub>2</sub>	Tin(II) chloride
SWCNT	Single-walled carbon nanotube
TES	Thermal energy storage
TiO <sub>2</sub>	Titanium dioxide
ZEBRA	Zeolite battery research Africa project

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