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Review article

# A review of nanofibrous structures in lithium ion batteries

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## HIGHLIGHTS

- The state of the research of nanofibers in Li-ion batteries was comprehensively reviewed.
- Different fiber configurations and advantages thereof for each LIB part were analyzed.
- Frequently applied chemical modifications on electrospun nanofibers and effects on LIB capacity and stability were reviewed.

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## ABSTRACT

Materials for harvesting and storing energy have been extensively studied in the last decade. Many inorganic materials have already been developed and utilized in products for electrochemical energy-storage systems. The nature of these complex materials requires further investigation from several approaches in order to improve specific characteristics of batteries, such as storage capacity and environmental impact. Fiber scientists have also introduced original solutions using mostly inorganic novel materials. Nanofibers and nanofibrous materials have found applications in the three battery components of anodes, cathodes, and separators. Many methods produce nanofibers; out of these, electrospinning is seen as the most adaptable technique because of the versatility and scalability of the process. The present review collates recent studies on nanofibers for applications in Li-ion batteries, with a focus on the electrospinning technique. The advantages of the investigated fibrous materials are explored in detail.



## 1. Introduction

The demand for green energy materials and processes is increasing rapidly because of the inadequacy of fossil fuels, climate change, and deteriorating environmental conditions. Powering electrical engines with lithium ion batteries (LIBs) is one clean strategy to overcome problems of energy storage. LIBs are widely researched devices because they possess high energy densities, no memory effects, and relatively slow self-discharge rates, permitting one-cell battery designs and longer battery lifetimes [1,2]. For further enhancing the performance of LIBs, studies concentrate on changing either the chemical composition or macroscopic structure of the components [2–6].

LIBs contain four important components: anode (negative electrode), cathode (positive electrode), separator, and electrolyte. The operating principle relies on electrochemical reactions between separated electrodes, supported by the electrolyte as a conductive medium for Li ions. When charging, Li ions flow from the cathode and become part of the anode, which further transfers electrons towards the cathode and closes the circuit. The reverse occurs when discharging the battery. Fig. 1 gives a general schematic of LIB operation. Graphite, with a theoretical capacity of 372 mA h $g^{-1}$ and a low Li ion insertion potential (<0.1 V vs $Li^+$) is commercially used as an anode. Li oxides, such as $LiCoO_2$ or $LiMn_2O_4$, are preferred for cathodes, and the most commonly used commercial electrolyte is $LiPF_6$ in an organic solvent [1].

Fiber-based materials, as opposed to powder-form materials, have been reported as constituent parts of LIBs. Doped or blended nanofiber webs have been considered as electrodes and separators in LIBs. The enhanced characteristics of fibrous materials arise from the combination of compound characteristics and unique morphologies and structures formed in the fibers. The one-dimensional morphology, high surface area, adjustable density, and high

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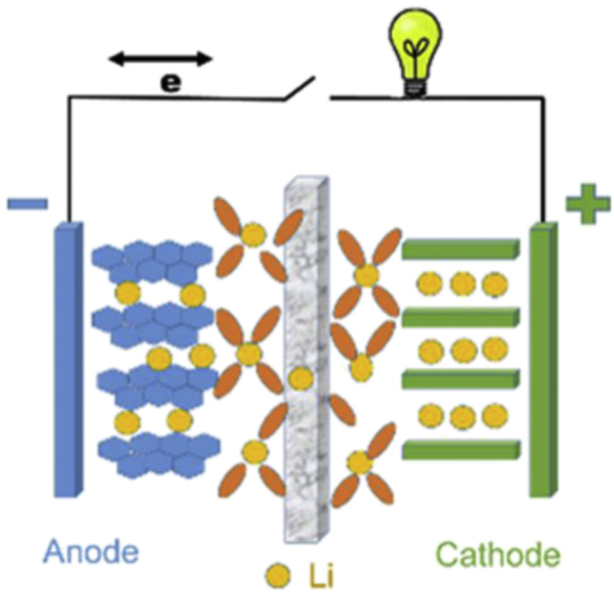


**Fig. 1.** Schematic of Li-ion battery (LIB).

porosity of fibers decreases the length of $Li^+$ diffusion pathways, and thus enhances the power capability and kinetic properties of the battery [7].

Hundreds of papers have appeared in the literature, addressing nanofibrous anodes, separators, and cathodes in order of descending prominence (Fig. 2). Anodic nanofibers are considered to be excellent candidates to control dendrite growth, which minimizes the effects of volume change for silicate anodes in particular [8–12]. In cathodes, common difficulties arise from the relatively high internal resistance, particularly in lithium iron phosphate (LFP) cathodes, as well as degradation during cycling [13–16]. Separator studies mostly focused on improving mechanical strength, durability, and ionic conductivity [17,18]. The present review discusses nanofibrous LIB components separately, in the order of anodes, cathodes, and then separators, based on studies conducted in the last 10 years. The focus of this comprehensive review is on electrospun nanofibers with different configurations and active materials emphasizing carbon as supporting material for free-standing electrodes. Novel methods for nanofiber production and novel green carbon precursors as Li-ion electrodes were also considered.

## 2. Nanofiber production techniques

Many different fibrous structures can be obtained by different methods, including sol–gel templating [19], solution-liquid-solid or vapor-liquid-solid growth [20], hydrothermal synthesis [21], self-assembly [22], electrospinning [23], solution/melt blowing [24,25], and centrifugal spinning [26,27]. Among these, electrospinning is the most widely used technique; solution/melt blowing and centrifugal spinning are promising for large-scale industrial nanofiber production [26].

### 2.1. Electrospinning

Several studies have addressed the production of electrospun nanofibers, as the system permits the versatile and scalable production of nanofibers with structures such as core–shell, hollow, multilayer, aligned, or porous. Polymers, metals, ceramics, alloys, and composites can all be formed into nanofibers for different applications [28]. Although electrospinning was patented in the early 1900s as a fiber-production technique, it did not become a popular technology. With the growing importance of micro- and nanofibers, electrospinning was revived in the 1990s. The electrospinning apparatus to form fiber consists of a high-voltage supply, grounded collector, and spinneret components that produce the nanofibrous structure (Fig. 3A). The principle is based on the interaction of a charged fluid, such as a polymer solution or melt, with a strong electrical field (10–80 kV DC) [29–31]. The induced electrical charge in the viscoelastic fluid and the strong electric field forms a structure called a Taylor cone at the nozzle tip. When the electrical forces overcome the surface tension and viscosity of the fluid, the jet is ejected from the tip of the nozzle. The solvent evaporates during the motion of the fluid jet towards the collector,

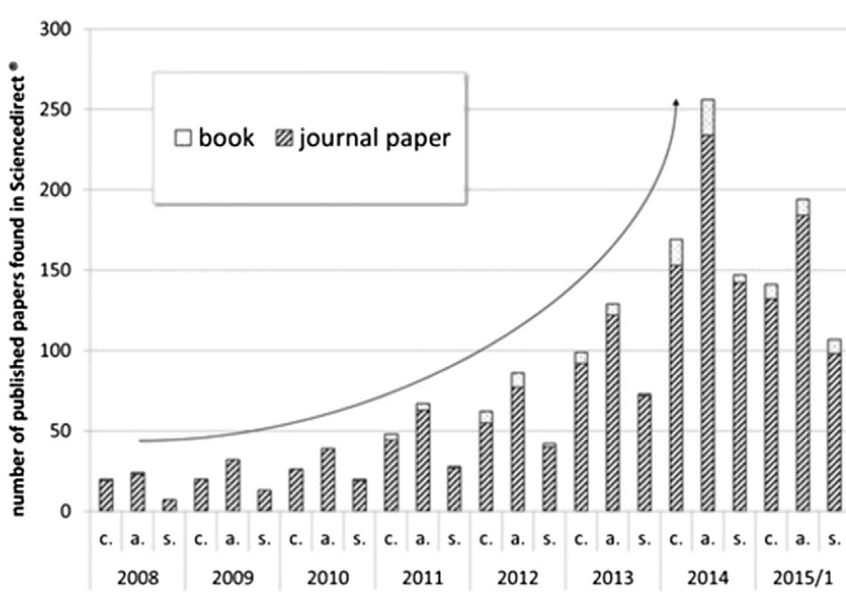


**Fig. 2.** Distribution of papers and book addressing nanofibrous cathode (c.), anode (a.), and separator (s.) for LIBs from 2008 to present.