Electrospun Nanofibers as Separators in Li-ion in Batteries

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1. Introduction

One-dimensional (1D) nanostructures -having at least one dimension less than 100 nm- in the form of fibers, wires, rods, belts, tubes, spirals and rings have been a subject of intensive research due to their unique properties and intriguing applications in many areas. Among the various methods (melt-blowing, gel spinning, solution spinning, self-assembly) of producing nanofibers, electrospinning attracts much interest mainly due to being a simple and cost-effective method with relatively high production rate. This process utilizes a high voltage source to inject charge of a certain polarity into a polymer solution or melt, which is then accelerated toward a collector of opposite polarity. As the electrostatic attraction between the oppositely charged liquid and collector and the electrostatic repulsions between like charges in the liquid become stronger the leading edge of the solution changes from a rounded meniscus to a cone (Taylor cone). A fiber jet is eventually ejected from the Taylor cone as the electric field strength exceeds the surface tension of the liquid. The fiber jet travels through the atmosphere allowing the solvent to evaporate, thus leading to the deposition of solid polymer fibers on the collector (Figure 1).

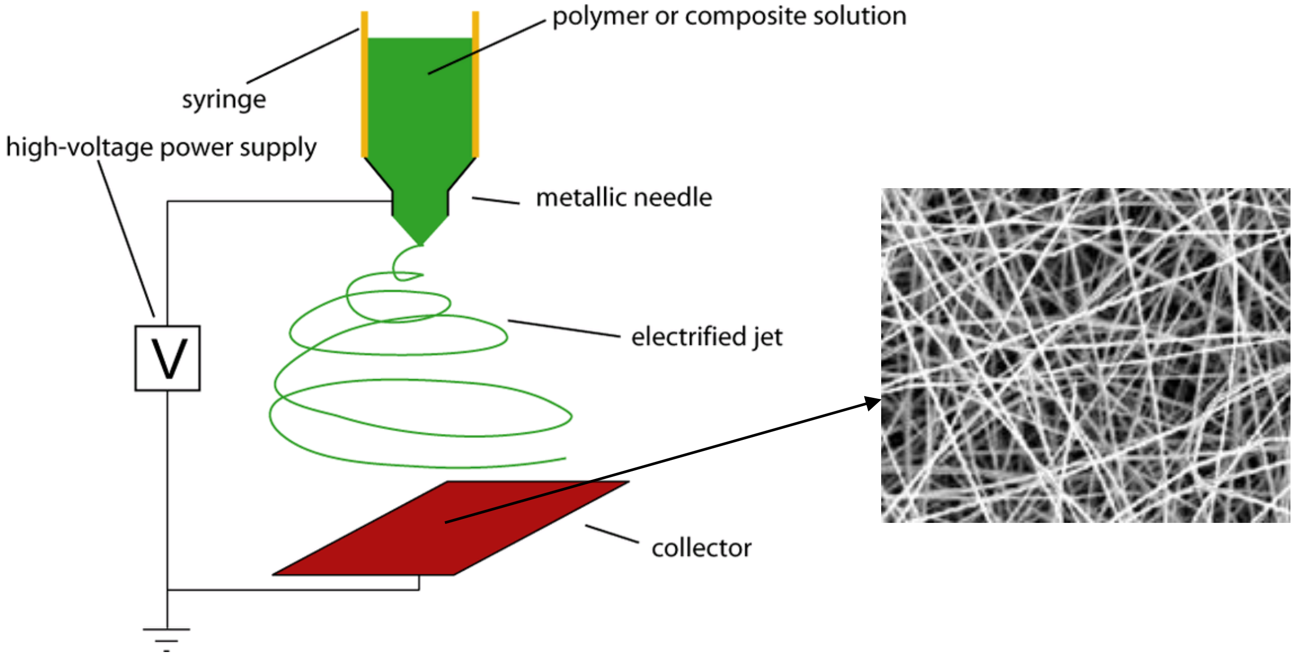

Figure 1. Schematic of a needle-type electrospinning setup

2. History

The process of electrospinning was patented by J. F Cooley and W. J. Morton in 1902 [1, 2]. Further developments toward commercialization were made by A. Formhals, and described in a sequence of patents from 1934 to 1944 [3, 4] Electrospinning from a melt rather than a solution was patented by C.L Norton in 1936 using an air-blast to assist fiber formation [5]. Between 1964 and 1969, Sir G. I. Taylor produced the theoretical underpinning of electrospinning [6-8]. Taylor's work contributed to electrospinning by mathematically modeling the shape of the cone formed by the fluid droplet under the effect of an electric field; this characteristic droplet shape is now known as the Taylor cone. In the early 1990s, Reneker and Rutledge demonstrated that many organic polymers could be electrospun into nanofibers [9]. Since then, the number of publications based on electrospinning has been increasing exponentially every year (Figure 2).

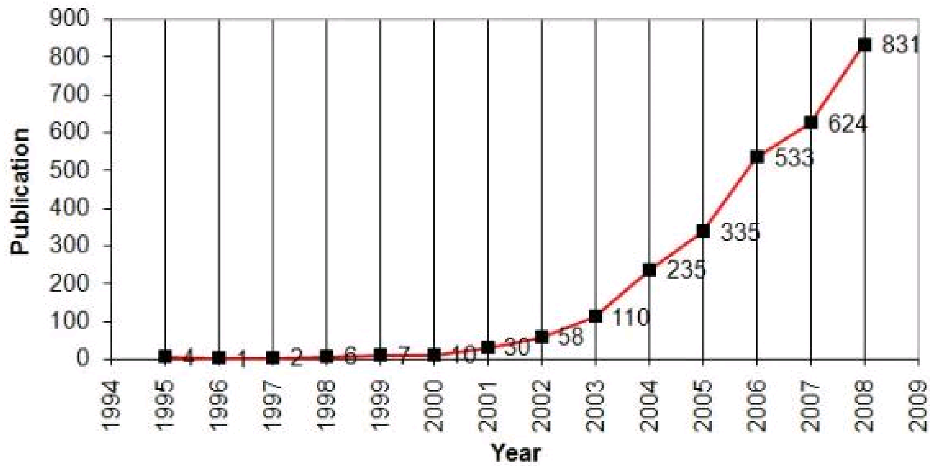

Figure 2. Number of publications per year (Source: Scopus)

3. From research to industry

Due its unique properties such as high porosity and high specific surface area, electrospun nanofibers have become the subject of many research projects for a wide range of applications (Table 1). Because of the growing popularity of the technology and benefits of electrospun nanofibers, companies like Electrospinz, Fuence, KES Kato, MECC, NanoNC and Yflow have introduced laboratory scale needle-type electrospinning equipments into the market. Besides, companies like Donaldson, eSpin Technologies, Fibertex, Finetex Technology, NTpia and Hills are using the technology in their products [10].

Table 1. Potential applications of nanofibers

Industry	Application	Benefits
Water	• Waste water cleaning • Poison removal • Industrial water treatment	• High efficiency • Fast function • Selectivity • Low cost / single use
Building	• Thermal insulation • Noise insulation • Solar panel	• High absorption coefficients • Clean energy generation • Transparent and colored panels
Environment	• Air filters for homes • Drink water cleaners • Water desalination • Noise absorption • Exhaust filters • Catalysts • Waste water cleaning	• High filtration efficiency • High permeability • Low cost / single use • Lightweight and effective

	• Industrial pollution filters	
Energy	• Battery separator and anode • Dye sensitized solar cell • Fuel cell catalyst support	• High capacity and power • Short charge time • Cheap, transparent, flexible, colored • High conversion efficiency
Automotive	• Noise absorption • Filters (engine intake, fuel, cabin air, exhaust) • Batteries for hybrid and electric cars	• Efficient and lightweight materials • Higher combustion efficiency • Cleaner environment • High charging rates, capacity and power
Health	• Wound care materials • Barrier garments • Respirators • Tissue engineering • Drug delivery materials	• Faster / more effective healing • Effective protection against infection • Cells grow as in natural environment • Biodegradability • Much smaller amount of drug

However, the relatively low production rate of needle-type electrospinning process was the main problem for the transition of the technology from laboratory to industry. The mechanical complexity of the design and the clogging of the needles during the process are two big obstacles to use multi-needle system for the industrial scale production of nanofibers. On the other hand, the electrospinning from free surface of liquid was named as a needleless electrospinning by Yarin [11]. However before that, the needleless modification for continuous production of nanofibers –so called the Nanospider™ technology- was patented and owned by Elmarco [12]. In this process, the spinning electrode is partially submerged into a polymer solution containing bath. With the rotation of the electrode, a very thin film of polymer solution covers the surface of the electrode, and once high voltage is applied between collecting and spinning electrode, electrostatic forces overcome the surface tension of the polymer solution and nanofibers are ejected from the Taylor cone (Figure 3). In Nanospider™ technology there is no syringe, capillary, nozzle or needle. Therefore, it is mechanically very simple and there is no clogging issue. The main advantages of the technology are: (i) continuous mass production, (ii) high production capacity, (iii) high web and nanofiber uniformity, and (iv) ease of upkeep. For further information about the technology and products please refer to [13].

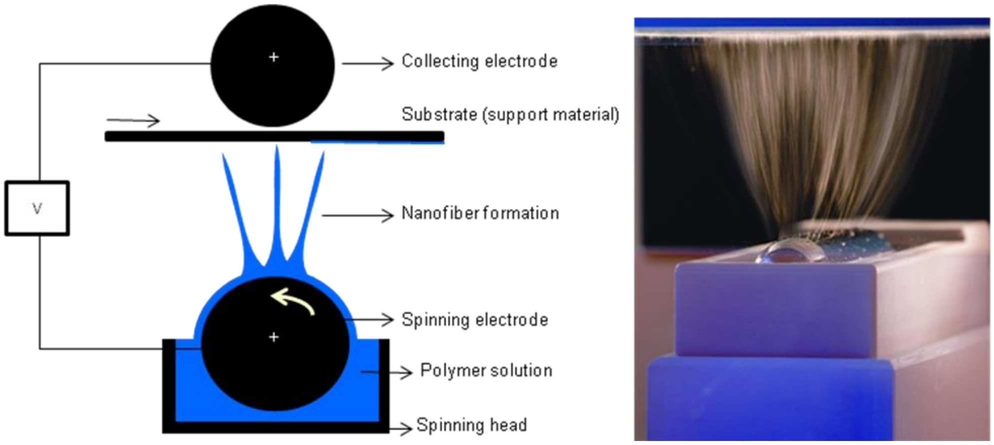

Figure 3. Schematic illustration and picture of Nanospider™ technology

4. Materials

In general, most polymers can be electrospun provided a suitable solvent is chosen for preparing the polymer solution. The quality of nanofibers strongly depends on polymer properties (molecular weight), solution parameters (surface tension, viscosity, conductivity) and process parameters such as electric field. Some polymers like polypropylene (PP) and polyethylene (PE) can be electrospun via melt electrospinning process but this typically generates thicker fibers. Electrospinning is not limited to the polymer field and has been extended into sol-gel systems to fabricate oxide nanofibers like TiO_2, SiO_2, Al_2O_3, ZnO, $Li_4Ti_5O_{12}$, ZrO_2 and $MgAl_2O_4$. Even some metal precursors have been added to polymer solutions to yield metal nanofibers of Fe, Cu, Co, Pt and Ni. In addition, nanofibers from biopolymers like gelatin, chitosan and cellulose, and polyacrylonitrile (PAN) derived carbon nanofibers can also be produced by this technology.

5. Nanofibers for Li-ion Batteries

Today, lithium-ion battery is a necessity as an energy storage device for mobile phones, notebooks, portable audio and gaming devices, hybrid electric vehicles (HEV), etc. Li-ion battery and separator manufacturers are highly concentrated in Asia. China has emerged as the largest Li-ion battery producer with over 50% of the output. The top 3 battery separator players (Exxon Mobil/Tonen, Celgard and Asahi Kasei) dominate over 85% of the market and made large manufacturing capacity investments over the last two years. Li-ion separator market is expected to continue growing in 2010 and beyond (Figure 4).

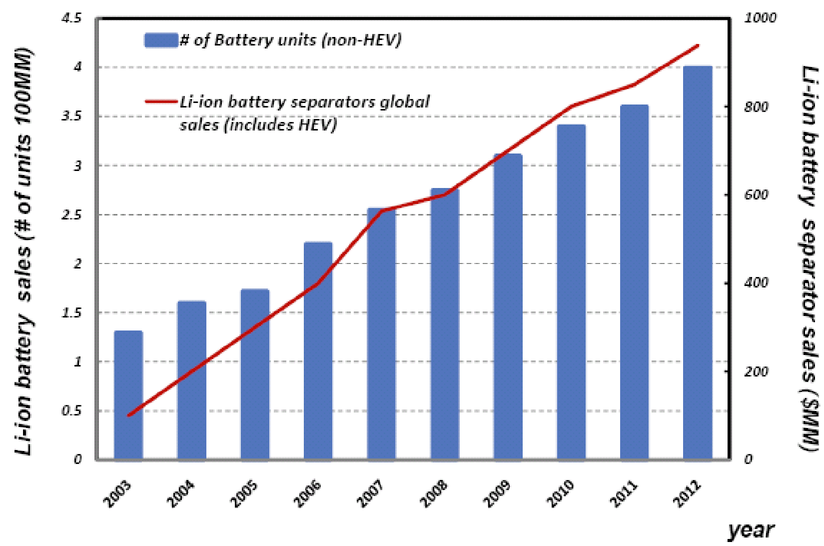

Figure 4. Market size and growth trends for Li-ion batteries and separators

Separator is a thin (~10 mm) porous membrane (pore~1mm) typically made from polyethylene (PE) or polypropylene (PP) foil. It avoids direct contact between anode and cathode to prevent electrical shortage, overheating and/or explosion. The current separators have a safety function such that at overcharge, polyethylene melts and pores get closed, ultimately, shuts down the lithium ion transportation. However, there are still challenges like slow Li ion transportation between anode and cathode, which decreases the power density and increases internal resistance of the cell.

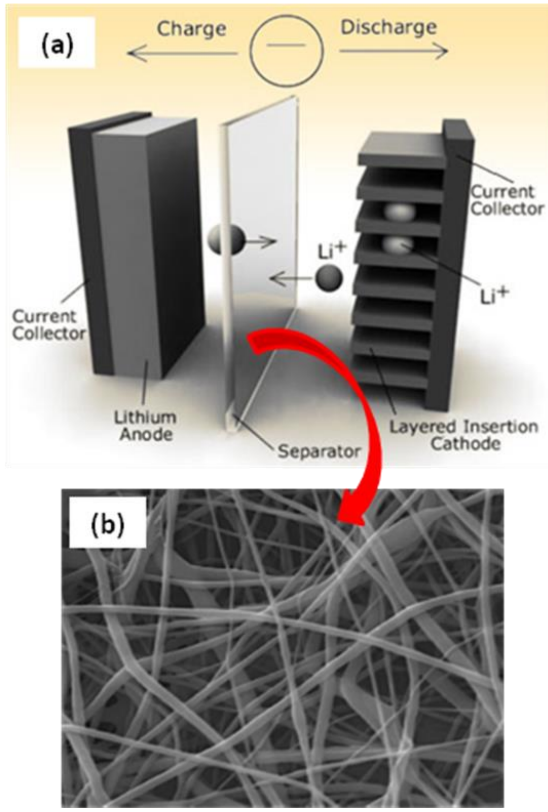

Figure 5. a) Schematic illustration of Li-ion battery cell and b) PVDF-HFP nanofiber membrane (5000X magnification)

In order to overcome these challenges, common PP and PE separator membranes can be replaced or coated with PVDF, PVDF-HFP and PAN nanofibers (Figure 5). Separator made from nanofiber membrane could have higher porosity and permeability and better wettability by electrolyte. More important, the nanofiber layer with porosity above 90% can reduces the resistance to ionic current and allows higher transport of Li ions. As a result, a significant increase in battery power density, faster charging and increase of battery life can be provided by nanofibers. Elmarco has been performed intensive R&D in improving or replacing current separators with nanofiber membrane. Initial test results demonstrated that nanofibers significantly improve battery properties.

References

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