Advances in Textile Engineering

Chapter 2

Nanofibrous Membranes Applicable in Lithium Ion Batteries

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Abstract

This chapter aims to focus on the key role of the electrospun nanofibers in the recent progressions for the modification of the lithium ion battery's characteristics. The use of nanostructured materials as various components (including cathode, anode, separator and electrolyte) of the lithium secondary batteries can potentiate their various features. The development of the electrospun electrodes gives the possibility for the preparation of high capacity batteries with an excellent cycle stability. In addition, fabrication of separators through electrospinning method can lead to the electrospun separators with higher electrolyte uptake and proper ionic conductivity. Furthermore, nanofibrous membranes have the potential for use as solid-state electrolytes in lithium ion batteries. The ability of applying nanofibers in various components of the lithium ion batteries is promising for the fabrication of all-solid-state, flexible and lightweight nanofibrous batteries.

1. Introduction

Energy has always been a crucial aspect of human life. Saving and converting energy plays a key role in mankind survival. Nowadays, it has been shown an increased interest and need for the development of portable electrical sources. These power sources are considered as one of the most significant parts in a wide variety of applications including notebooks, mobile phones, electrical vehicles, medical tools, satellites and many more. A battery comprises of one or more electrochemical cells which are connected to each other in series or parallel. The electrochemical cell is consisted of a negative electrode (anode), a positive electrode (cathode), a separator and an electrolyte solution. In batteries, oxidation-reduction (redox) reactions occurring in the electrodes, lead to the conversion of the chemical energy to the electrical energy [1,2].

In general, batteries are divided into two categories including non-rechargeable batteries (primary batteries) and chargeable batteries (secondary batteries). The redox reaction is not reversible in primary batteries. So, the discharge process can be lasted till complete consumptions of all chemical compounds. However, the redox reaction is able to be restored by applying a potential between two electrodes in secondary batteries. Lead-acid, Nickle-cadmium, Nickle-metal hybrid and lithium ion (Li-ion) batteries are of the common secondary batteries. Li-ion batteries are the most promising chargeable batteries due to the highest energy density along with the lightest weight and the smallest size between the mentioned secondary batteries [1,2].

Li-ion batteries are also comprised of the anode, the cathode, the separator and the electrolyte solution (**Figure 1**). Lithium atom is the lightest weight metal. It can easily lose its electron and produce a lithium ion. The electron and the lithium ion move quickly due to the small size and low mass density. When the Li-ion battery is fully charged, the lithium atoms are placed in the anode. As lithium atoms tend to be in the form of lithium ions, lose their electrons. The produced lithium ions desire to move towards the cathode due to concentration gradient. However, this migration is pulled in by the attraction force between the Li ions and the electrodes, electrons and lithium ions are transferred to cathode through the cord and electrolyte, respectively. The discharge process can be continued until the consumption of all Li ions. The chemical reactions in the anode and cathode electrodes, during the discharge process is given in equation 1 and 2, respectively. In order to recharge the battery, it is sufficient to apply a higher potential to the battery [1,2].

$$LiC_{6} \rightarrow C_{6+}Li^{+} + e^{-} \qquad (1)$$
$$MO_{r} + Li^{+} e^{-} \rightarrow LiMO_{r} \qquad (2)$$



Figure 1: Schematically illustration of lithium ion batteries.

The characteristics of the Li-ion batteries such as potential, capacity and energy density depend on the ingredient features of the electrodes. In addition, safety and lifetime of the batteries are linked with the electrolyte and the electrolyte-electrode interface. Besides the raw material properties of the battery's components, the synthesis process plays a crucial role on battery performance. Recently, researchers have shown an increased interest in applying electrospun nanofibrous membranes as components of the Li-ion batteries to enhance the mentioned properties [1,2]. This chapter summarizes the recent research progresses towards the fabrication of the nanofibrous anode, cathode, separator and electrolyte.

2. Electrospun Nanofibers as Anode

The electrochemical behavior of the Li-ion batteries is influenced by the chemical and physical properties of the anode. High energy density, coulomb efficiency and reversible capacity are characteristics of the ideal anode. Since 1991, carbon-based materials have been the best choice as the anode. High electronic conductivity, long cycle life and low cost are of other advantages of the carbon-based materials. In the most commercial batteries, the anodes are made of graphite (capacity~300 mAh.g⁻¹ & energy density~1-10 Wh.kg⁻¹) due to easily insertion of Li ions into the interspace between carbon layers during charging process. A growing body of literatures has focused on silicon-based anodes which showed high specific capacity around 3580 mAh.g⁻¹. Alloy anodes (e.g. $\text{Li}_4 \text{Ti}_5 \text{O}_{12}$) have also attracted a considerable attention due to their high specific capacity (400-2300 mAh.g⁻¹). However, the large volumetric change (~400%) during charging-discharging processes limited the practical applications of silicon- and alloy anodes. Moreover, transition metal oxides reveal appropriate capacity rate (600-1000 mAh.g⁻¹). Although, poor coulomb efficiency is a major drawback of the metal oxide anodes [2-5].

It has conclusively been demonstrated that nano-sized materials have more affinity for the attraction of the Li ions resulting from high specific surface area of the nanomaterials. The stronger adsorption of Li ions enhances electrode activity and boosts capacity rate in the anode terminal. In addition, diffusion length of the Li ions is decreased in nano-sized materials which leads to the improvement of the charge transfer. However, there are certain drawbacks associated with the use of the nanostructured anodes. Highly porous structure of the nanostructured anodes causes reduction of volumetric capacity. Moreover, low production rate and high cost are of other limitations [3,6].

Nano-sized anodes have been synthesized through different methods such as chemical vapor deposition, self-assembly, solution growth, electrospinning and many more. Electrospinning as a simple and cost effective route, provides a possibility for the fabrication of nano structures with tunable characteristics [3,6]. To date carbon nanofibers (CNFs) have been prepared from various electrospun sources for applying as anode in Li-ion batteries. Kim et al. [7] reported a high capacity rate of 450 mAh.g⁻¹ at 0.3 A.g⁻¹ for the CNF electrode, obtained from electrospun poly acrylonitrile (PAN). However, the as-fabricated CNF electrode showed poor cycle stability. In 2010, Ji et al. [8] presented superior cycle life and higher storage capacity (556 mAh.g⁻¹ at 0.05 A.g⁻¹) for CNF electrode prepared from electrospun PAN/poly pyrrole nanofibers. Tao et al. [6] used waste walnut shells for the fabrication of CNFs which presented 200 mAh.g⁻¹ at 0.1 A.g⁻¹. Poly (vinylidene fluoride) [9], polyimide [10], polyvinyl alcohol [11] and polyvinyl pyrrolidone [12] have also been reported as sources for the fabrication of CNF electrodes.

Ji et al. [13] examined that the storage capacity can be improved to 604 mAh.g⁻¹ at 0.05 A.g⁻¹ by introduction of Fe_2O_3 nanoparticles to the electrospun CNFs. In addition, incorporation of Sn nanoparticles to the electrospun CNFs showed enhancement of the whole electrochemical performances of the anode electrode applicable in Li-ion batteries [14]. Studies also have shown that insertion of manganese oxide [15], titanium dioxide [16], tin dioxide [17] and magnetite [18] nanoparticles into the CNF membranes can boost the electrochemical characteristics of the anode electrode.

Large volumetric change during Li insertion and extraction in the silicone-based anodes have been a serious limitation for many earlier studies. This volume change leads to the poor mechanical properties and low cycle life. Studies have shown that silicone-loaded nanotubes and nanofibers provide a specific structure which is able to absorb the applied stress and prevent the cracks [19,20]. Xue and coworkers [21] reported enhancement of the cycle stability for the CNF anode loaded with Si/C nanoparticles. Hwang et al. [22] demonstrated proper cycling durability and high storage capacity of 721 mAh.g⁻¹ for a core-shell nanofibrous anode (Si as the core and C as the shell). Wang et al. [23] showed low changes in the morphology of the anode prepared by the electrospun Si/C nanofibers. In addition, porous C/Si composite nanofibers has shown long cycle life with a high capacity rate of 1100 mAh.g⁻¹ at 0.2 A.g⁻¹ [24].

Several studies thus far have linked alloys such as silicon, tin and antimony-based alloys

with CNFs to improve electrochemical performances of the anode. Jang et al. [4] reported a stable structure with high capacity storage of 560 mAh.g⁻¹ for the CNFs filled with Co-Sn alloy. An enhancement in the mechanical stability along with proper capacity rate was also illustrated by incorporation of Cu-Sn [25], Sn-Sb [26], Ni-Sn [27], Ag-Fe-Sn [28] and many more alloys into the CNF anodes.

3. Nanofirbous Membanes as Cathode

Cathode material in Li-ion batteries depends on the applied anode in the electrochemical cell. When a lithium metal is used as anode in Li-ion batteries, it is not needed to apply a lithiated cathode. However, it is essential to utilize lithiated cathode when the anode is carbon-based. Cathode material significantly influences the battery performance. Transition metal oxides and phosphates are the main choices as the cathode of Li-ion batteries. In 1980, Goodenough et al. introduced Lithium cobalt oxide (LiCoO₂) as cathode which has been the most successful cathode in commercial Li- ion batteries. However, low stability and high capacity fading have hindered its further applications. Olivine LiMPO₄ (M=Fe, Mn, Ni and Co) provides appropriate electrochemical characteristics including proper cycle life and specific capacity. Generally, olivine cathode materials presented low cycle stability and capacity rate [29-32].

Lithium layered metal and vanadium oxides are the main promising classes of cathode materials. Layered oxides have shown more stability in various temperatures and higher capacity storage. Li-riched metal oxides $(xLi_2MnO_3.(1-x)LiMO_2 (M = Ni, Co, Mn))$ and NCM $(LiNi_xCo_yMn_zO_2 (x+y+z=1))$ are classified as layered oxides. Notably, poor cycle life and the capacity loss are the main drawbacks of the layered metal oxides as cathode of Li-ion batteries which need to be improved. Lithiated vanadium oxides including LiVO_3, LiV_2O_5, Li_{1+x}V_3O_8 and many more, have illustrated a high discharge capacity rate (~400 mAh.g^{-1}). However, migration of vanadium ions leads to the high capacity fading [29-32].

Much of the current literatures on the cathode of the Li ion batteries pay particular attention to the synthesis of the nano structure cathodes. Morphological and electrochemical features of the electrospun LiCoO_2 [29-32], Olivine LiMPO_4 , Lithium layered metal oxides [33] and lithiated vanadium oxides [34,35] have been widely studied. Reduction of the Li ion path length and so increasing the diffusion rate improve cycle life and the electrochemical performance [31]. Chen et al. [30] prepared nanofibrous LiCoO_2 by annealing of the PVP/ LiCoO_2 at 700 °C for 12 hours. Liu and Taya [32] fabricated nanofibrous LiCoO_2 membranes by electrospinning of lithium acetate/cobalt acetate/PVP solutions. The resulted electrospun LiCoO_2 showed higher storage capacity compared with the common LiCoO_2 cathodes. Zhang and coworkers [2] suggested electrospun LiFePO_4/C cathode for compensation of low electrical conductivity of LiFePO_4 and so improvement of the cycle stability. The LiMn_2O_4 porous hollow nanofibers presented a stable cycling behavior over 400 cycles [36]. In addition, electrospun

 $LiNi_1/3Co_1/3Mn_1/3O_2$ and $LiNi_3/8Co_1/4Mn_3/8O_2$ nanofibers have shown a proper discharge capacity (~170 mAh.g⁻¹) and retained the capacity about 90 % after 50 cycles [33]. Yu et al. [34] suggested mesoporous V₂O₅ nanofibers with the storage capacity of 370 mAh.g⁻¹ and high cycle stability as cathode material. An et al. [37] fabricated carbon encapsulated hollow porous nanofibers of V₂O₅ as cathode of Li ion batteries which showed high specific capacity with an excellent cycling stability.

4. Electrospun Separators

Separator is a thin and porous membrane, located between the anode and the cathode, which prevents the electronic contact of two electrodes. In addition, separators maintain the liquid electrolyte and enable migration of Li ions between two electrodes during chargedischarge process. Separators play a key role in the battery performance. Energy density, cycle stability and safety of the battery are influenced by the separator's features. An ideal separator should offer sufficient chemical, electrochemical, dimensional and mechanical stabilities, high electrolyte uptake (EU %), appropriate ion conductivity (1-10 mS.cm⁻¹), low thickness (20-25 μ m), high porosity (ϵ >60 %), small pore sizes (<1 μ m) and so on. In the most commercial batteries, microporous polyolefin membranes (e.g. poly ethylene (PE), poly propylene (PP) and their blends) are used as separator. Polyolefin membranes provide appropriate mechanical and chemical stability against the electrodes and the electrolyte. However, low wettability (EU~50 %) of the membranes resulting from low porosity (~40 %) leads to the poor ionic conductivity (0.8 mS.cm⁻¹) and reduced cycle stability of the battery. In addition, large pore sizes in the polyolefin mats may cause penetration of electrode components and internal short circuits. Notably, preparation of a polyolefin mat with small pore sizes seems to be impossible considering the average diameter of the polyolefin fibers ($\sim 1 \mu m$) [38,39].

To modify the features of the polymer membranes, several polymers have been applied to synthesis of the polymer membranes such as PVDF, PAN and poly methyl methacrylate (PMMA). Numerous studies have shown that the membrane electrolytes based on the PVDF ($\varepsilon \sim 57$ % and EU ~ 152 % and $\sigma \sim 1.5$ mS.cm⁻¹) and PAN (EU ~ 70 % and $\sigma \sim 1.5$ mS.cm⁻¹) provide proper electrochemical stability, high electrolyte uptake and good ionic conductivity at room temperature. Although, mechanical strength fading and reduction of ionic conductivity upon long storage are of undesirable effects of the PVDF and PAN membranes, respectively [40,41].

Non-woven fabrics and inorganic composites are two promising classes of the separators. Non-woven fabric mats are commonly made from bonding (physical, chemical or mechanical bonding) of various natural or synthetic fibers including celluloses, polyamide, polytetrafluoroethylene, PVDF, etc. Non-woven fabric mats provide a porous structure containing large pore sizes. This form of separators are typically applied as a support membrane

for the gel electrolytes. Inorganic composite separators are referred to porous membranes formed by bonding of the ceramic particles such as alumina, silica and zirconia. Excellent wettability and thermal stability are the main characteristics of the inorganic composite mats. However, handling of such separators is still a challenge for the assembly of the battery due to poor mechanical strength of the ceramic mats. In addition, tuning the thickness of the inorganic composites is problematic because of the affinity of the ceramic particles to aggregation [38, 42].

One of the most significant current discussions in modification of the separator properties, is fabrication of nanofibrous polymer membranes through electrospinning method. Highly porous structure (~ 90 %) of the electrospun membranes provides proper permeability and wettability with suitable pathways for the migration of Li ions which lead to lithium secondary batteries with higher power density and rate capability. The morphological and electrochemical characteristics of the PVDF, PAN, polyethylene terephthalate (PET) and (PMMA) nanofibers have been widely studied as promising separators in Li ion batteries. The as-spun membranes presented high affinity for the absorption of liquid electrolytes. In addition, compatibility with the electrodes, excellent thermal and electrochemical features and tunable morphology are of other desirable properties of these nanofibrous separators. Chao and coworkers [43] showed that the electrospun PAN could enhance the porosity and cycle stability up to 76 % and 85 %, respectively. Gopalan et al. [44] reported that electrospun PVDF-PAN nanofibers could reveal 84 % porosity, 300 % electrolyte uptake with a high conductivity of 7.8 mS.cm⁻¹ at room temperature. In addition, electrospun membrane of PVdF-HFP/PMMA has illustrated 377 % electrolyte uptake with ionic conductivity of 2 mS.cm⁻¹ at ambient temperature. Yanilmaz and Zhange [45] also showed the potential of the electrospun PMMA/PAN nanofibers ($\epsilon \sim$ 73 %, EU ~ 370 % and σ ~ 3.2 mS.cm⁻¹) as separator of the Li ion batteries. Moreover, recent evidences suggest that incorporation of nanoparticles into the nanofibers or coating the membranes with the nanoparticles including graphene oxide [46], silica [47-49], Alumina [50,51] and many more, can furtherly improve mechanical and electrochemical characteristics of the separators.

5. Nanofibrous Electrolytes

In general, electrolytes are used in a liquid form in commercial lithium secondary batteries. Liquid electrolytes contain organic solvents and lithium salts. The presence of the flammable and explosive solvents in the structure of the Li ion batteries is a big concern which threatens the safety of these batteries. In addition, a metal cover is essential for sealing of the Li ion batteries leads to the fabrication of inflexible and heavy structures. Solid polymer electrolytes (SPEs) are an ideal choice for the fabrication of lightweight, flexible and safe batteries. However, low ionic conductivity ($\sigma < 10^{-4} m S. cm^{-1}$) of the SPEs limited their practical applications. A schematic illustration of the Li ion battery comprising the SPE is shown in

Figure 2. As it is apparent, the SPE acts as both the electrolyte and the separator. In fact, SPEs simultaneously transfer the Li ions and prevent the physical contact of the two positive and negative electrodes [38].



Figure 2: Schematic illustration of the Li ion battery with the (a) solid polymer electrolyte and (b) nanofibrous polymer electrolyte.

SPEs are commonly synthesized through dispersion of a lithium salt in a polymer matrix by using a hot pressing or a solution casting method. Numerous polymers (e.g. PVDF, PAN, polyvinyl alcohol (PVA), polyethylene oxide (PEO)) have been evaluated as the polymer matrix in the SPEs. Among several polymers, PEO has been examined as the most appropriate matrix due to the ability for the solvation of various salts and additives. In addition, PEO is an abundant and a cost-effective polymer. Lithium tetra fluoroborate (LiBF₄), lithium perchlorate (LiClO₄) and lithium hexafluorophosphate (LiPF₆) are of common lithium salts. In SPEs, lithium ions migrate through local movements of the polymer chains. In polymer structures, the mobility of the polymer chains occur in amorphous regions and above glass transition temperature (Tg). So, the reductions of crystalline regions and Tg of the polymer matrix cause an increment in the ionic conductivity of the SPEs at ambient temperature. Numerous efforts have been devoted to enhance ionic conductivity of the SPEs. Synthesis of single ion conducting and polymer-in-salt electrolytes, preparation of copolymers and addition of various plasticizers and fillers are several attempts have been made for the enhancement of the ion conductivity of the SPEs. As an example, with introduction of plasticizers into the SPEs, plasticizer molecules penetrate between the polymer chains, weaken their interactions, increase movements of the polymer chains and so enhance the ionic conductivity. In addition, incorporation of fillers such as inert and active ceramic fillers (titanium dioxide (TiO₂), aluminum oxide (Al₂O₃), silicon dioxide (SiO₂), etc.) causes formation of more amorphous phases in polymer structures which leads to the increase of the ionic conductivity [52,53].

Vignarooban and coworkers [54] presented that the ionic conductivity of a PEO/LiTF electrolyte can be improved up to 0.049 mS.cm⁻¹ by the addition of 10 wt. % TiO₂. Moreover, the obtained ionic conductivity can be furtherly enhanced to 0.16 mS.cm⁻¹ by introduction of 50 wt. % EC into the as-prepared electrolyte. Johan et al. [55] illustrated that ionic conductivity of a PEO/LiCF₃SO₃/EC electrolyte can be improved from 0.3 mS.cm⁻¹ to 0.8 mS.cm⁻¹ by

the addition of 20 wt. % Al_2O_3 nanoparticles. Embedding 10 wt. % TiO_2 nanoparticles into the PVDF/LiClO₄ polymer membranes yielded ionic conductivity of 0.7 mS.cm⁻¹ at room temperature [56].

Recently, literatures have emerged that offer applying electrospun crystal structures as filler in SPEs. Beside the increment of amorphous phases, electrospun fillers create pathways for transportation of the Li ions which enhance the ionic conductivity. Liu et al. [57] reported a high ionic conductivity of 0.24 mS.cm⁻¹ for the PAN-LiClO₄ electrolyte incorporated with 15 wt. % Li_{0.33}La_{0.557}TiO₃ electrospun nanowires. Tang et al. [58] also presented that ionic conductivity of the PAN-LiClO₄ SPE can be improved to 0.13 mS.cm⁻¹ with the addition of Li7La3Zr2O12 nanowires. An enhancement in the ionic conductivity of the SPEs has also been presented by the addition of well aligned Li_{0.33}La_{0.557}TiO₃ nanowires [59], poly aniline nanofibers [60], Li_{6.4}La₃Zr₂Al_{0.2}O₁₂ nanowires [61] and so on.

It is worth to note that a major problem with the SPEs, synthesized through the solution casting method, is phase separation and formation of crystal phases of lithium salts or crystal regions of lithium salt-PEO. The mentioned unwanted crystalline regions trap Li ions and therefore decrease the fraction of free ions which lead to the reduction of the ionic conductivity. In 2017, Freitag et al. [62] showed that electrospinning technique can also be an efficient method for the fabrication of SPEs. The electrospun PEO/SN/LiBF₄ has shown the highest conductivity of about 0.2 mS.cm⁻¹ at ambient temperature. In addition, the results confirmed the absence of the unwanted crystalline phases including LiBF4 or (PEO)3/LiBF4 in the asspun electrolytes. In another attempt, they showed the potential of the electrospun membranes containing sodium salts as the solvent-free electrolyte in sodium ion batteries [63]. In 2018, Walke et al. [64] evaluated the effect of LiTFSI salt on the electrochemical behavior of the PEO/ SN electrospun electrolytes. The electrospun PEO/SN/LiTFSI electrolyte showed the highest conductivity of 0.28 mS.cm⁻¹ at room temperature, while the SPE with the same chemical composition, fabricated by solution casting method, illustrated ionic conductivity of 0.05 mS.cm⁻¹. In addition, Banitaba et al. [65] examined the concentration effects of the polymer, salt and plasticizer on the characteristics of the PEO/PC/LiClO₄ electrospun electrolytes. The optimum electrospun electrolyte has shown the ionic conductivity of 0.05 mS.cm⁻¹, about 30 times greater than the polymer film electrolyte with similar chemical composition. Moreover, the impact of the TiO₂ nanoparticles on the various properties of the PEO/PC-EC/LiClO₄ has also been investigated [66].

6. Concluding Remarks

In summary, numerous researches have shown the potential of the electrospun nanofibers for being applied as various components including electrodes, separators and electrolytes of the lithium ion batteries. Electrospun nanofibers provide shorter pathways for diffusion of the Li ions in the negative and positive electrodes which cause enhancement of the capacity storage and charge transfer. Applying the electrospinning method for the fabrication of nanofibrous separators improves porosity, electrolyte uptake and ion conductivity which are crucial keys for the development of Li ion batteries. In addition, incorporation of electrospun nanowires instead of nano particles as filler into the SPEs significantly improves their ion conductivity. Moreover, electrospun membranes propose more ionic conductivity compared with the SPEs associated with their unique structures. The outstanding structure of the electrospun nanofibers potentiate the possibility of the fabrication of lightweight and flexible nanofibrous batteries which are applicable in a wide variety of progressive applications.

7. References

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