

Nanofiber-Based Membrane Separators for Lithium-ion Batteries

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ABSTRACT

Nanofiber-based membranes were prepared by two different methods for use as separators for Lithium-ion batteries (LIBs). In the first method, Electrospinning was used for the fabrication of Polyvinylidene fluoride PVDF nanofiber coatings on polyolefin microporous membrane separators to improve their electrolyte uptake and electrochemical performance. The nanofiber-coated membrane separators show better electrolyte uptake and ionic conductivity than that for the uncoated membranes. In the second method, Forcespinning® (FS) was used to fabricate fibrous cellulose membranes as separators for LIBs. The cellulose fibrous membranes were made by the Forcespinning® of a cellulose acetate solution precursor followed by a subsequent alkaline hydrolysis treatment. The results show that the fibrous cellulose membrane-based separator exhibits high electrolyte uptake and good electrolyte/electrode wettability and therefore can be a good candidate for high performance and high safety LIB separators.

INTRODUCTION

Polymer nanofibers (NFs) and nanofiber composites have been used in many applications such as biomedical, tissue engineering, electronics and energy storage. In energy storage devices such as lithium-ion batteries (LIBs), the separator plays a key role in separating the positive and negative electrodes to prevent electrical short circuit. Polyolefin microporous membranes such as polyethylene (PE) and polypropylene (PP) are commercially available and have been widely used as separators for LIBs because of their good thermal shut-down ability, electrochemical stability and high mechanical strength. However, these polyolefin-based separators show low porosity, poor electrolyte wettability and high thermal shrinkage at relatively elevated temperatures above 90 °C. Several approaches have been used to overcome these drawbacks including the use of nanoparticle composite additives, coating the membrane separator with a polymer NFs (e.g. PVDF) and/or the use of nonwoven and nanofiber-based separators. The latter approach is very promising and has been widely used due to the fact that NF-based separators exhibit good electrolyte uptake, low interfacial resistance but they show poor mechanical strength which render them difficult to handle during battery-assembly operation.

NFs can be produced by various techniques such as electrospinning, hydrothermal synthesis, template synthesis, phase separation, self-assembly, and other spinning methods (wet, dry and

melt spinning) [1-4]. Electrospinning is so far the method of choice for producing NFs, however it faces several drawbacks such as the need of high electric fields and dielectric solution and safety related issues. Many materials can be electrospun into fibers; however, electrospinning may not be suitable for mass production of certain materials and faces several restrictions regarding safety concern, especially for melt electrospinning where a high current is applied to the melt to stretch the fibers. A wide range of materials can be Forcespun into fibers due to the fact that FS can produce fibers from melt and solutions without the need of applying an electric field during processing. Furthermore, the FS method has proven to be suitable for mass production of nanofibers for biomedical, energy storage, defense and aerospace-related-applications. In the FS method (Figure 1), the electric field used in the electrospinning process is replaced by centrifugal forces to overcome the polymer/material surface tension and therefore stretching the fibers [5].

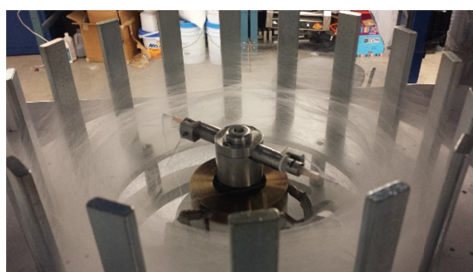


Figure 1a. Photograph of polymer Nanofiber formation by FS process.

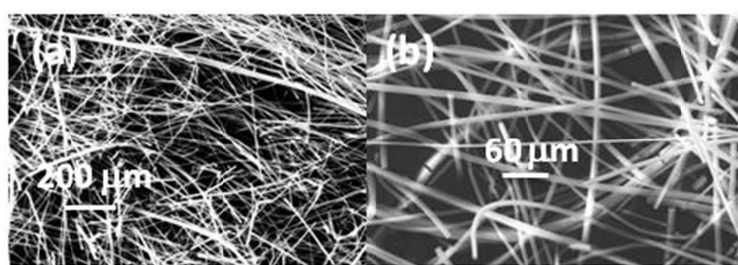


Figure 1b. SEM images of polystyrene/poly(styrene-alt-maleic anhydride) PS/PSMA fibers prepared by the FS method [Alcoutlabi, Lozano et al. unpublished data].

The production of NFs by a FS lab scale system is higher than 60 grams/hr which is much higher than the yield obtained by electrospinning (approximately i.e. 0.1 grams/hour) [6, 7]. Several NF systems and polymer composites have been recently produced by Lozano and coworkers such as polyamide, polyethylene oxide, polylactic acid, polycaprolactone polypropylene, ultra-high molecular weight polyethylene, (2,5-bis(2'-ethyl-hexyl)-1,4-phenylenevinylene), poly(3-hexylthiophene (P3HT), Teflon®AF, cellulose and poly(vinylidene fluoride), indium-tin oxide, PVB/CNTs [Ref 8 and references therein]. In these NF systems, the fibers were produced with average fiber diameters in the nano to submicron range.

Centrifugal spinning coined as the FS method, is gaining popularity and many articles are now being published after Lozano and coworkers first applied for a patent and spun-off a company [6, 7]. Recently, researchers have been producing fibers using the same method with in-house developed systems for biomedical, energy storage, and electronics [9, 10].

We have recently utilized the electrospinning technique to prepare polyvinylidene fluoride (PVDF) nanofiber coatings for microporous separator membranes [10, 11, 12]. Figure 2 shows the approach that we have used to improve the properties and performance of Celgard microporous battery separator membranes by the deposition of PVDF nanofiber coatings on the polyolefin membrane surface. The PVDF nanofiber-coated membranes showed better adhesion to battery electrode and high electrolyte uptake compared to the uncoated membranes. We have also used the Forcespinning method in our laboratory at UTPA to fabricate fibrous cellulose membranes for battery separator applications. We present below results on the use of Electrospinning and Forcespinning® to prepare nanofiber-based membrane separators for LIBs.

The electrolyte uptake and electrochemical performance of these separators are evaluated and the results are discussed.

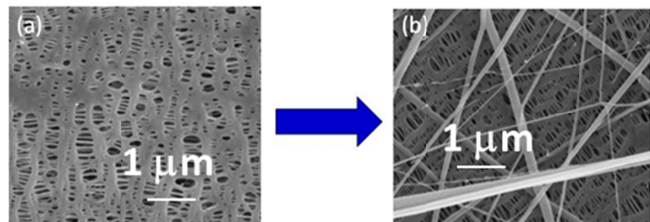


Figure 2: SEM images of separator membranes with (b) and without (a) Electrospun PVDF nanofiber coatings.

EXPERIMENT

Materials and Methods:

a. Electrospinning of PVDF NF coatings:

Celgard[®] microporous battery separator membranes (Celgard[®] LLC) were used as the base substrate for the deposition of nanofibers. Six membrane separators, Monolayer 1, Monolayer 2, Monolayer 3, Trilayer 1, Trilayer 2, and Trilayer 3 were used to investigate the effect of substrate type on the morphology and properties of PVDF copolymer nanofiber coatings, Monolayers 1 through 3 are single-layer of polypropylene (PP) microporous membranes whereas Trilayer microporous membranes consist of a PE monolayer membrane between two outer PP monolayers in a PP/PE/PP configuration. PVDF-co-CTFE (Solvay[®] Solef#32008) dissolved in mixed solution of acetone and N,N-dimethylformamide (3:7 by weight) were used to prepare the electrospun nanofiber coatings. Nanofiber coatings were prepared by using a nozzle-less electrospinning device (NanoSpiderTM NS200, Elmarco).

b. Forcespinning of Fibrous cellulose membranes:

Forcespinning experiments were carried out using a cellulose precursor solution comprised of cellulose acetate (CA, $M_w = 85,000-124,000$, 96% hydrolyzed), dimethyl sulfoxide (DMSO), acetone, ethanol and potassium hydroxide (KOH). Anhydrous potassium bromide (KBr, >99%). The electrolyte uptake of microporous membrane and fibrous cellulose membrane separators was measured by immersing the membrane in an organic liquid electrolyte 1M LiPF₆ in ethylene carbonate, dimethyl carbonate, and diethyl carbonate (EC + DMC +DEC, 1:1:1 in volume) using a method that was described in our previous work [11, 12, 13]. The impedance of liquid electrolyte-soaked membranes was measured by electrochemical impedance spectroscopy (EIS) over a frequency range of 1MHz to 1 Hz under an AC amplitude of 10 mV at room temperature using Reference 600 Potentiostat/Galvanostat/ZRA (Gamry Instruments, Inc.).

RESULTS AND DISCUSSION

The electrolyte uptake capacities (capacity/area) of uncoated membranes, PVDF-co-CTFE nanofiber-coated membranes are shown in Figures 3 (a) and (b), respectively. A comparison between the electrolyte uptake capacity of electrospun nanofiber-coated membranes and uncoated membranes is shown in Figure 3c. The absorption of liquid electrolyte was quick in the first 60 seconds. Monolayer membranes are thicker and have higher porosity and pore size than Trilayer membranes, and hence they can have higher electrolyte capacity than that for Trilayer

membranes [11, 12]. The results in Figure 3c confirm that electrospun nanofiber-coated membranes exhibit higher electrolyte capacity than uncoated membranes. The electrolyte uptake capacity is a measurement indicating the amount of liquid electrolyte solution absorbed by the unit area of a membrane separator. In fact, the electrolyte uptake capacity of a membrane depends on the basic membrane properties such as thickness, porosity, and pore size. For example, a thin sample with high porosity and pore size (less weight) shows higher electrolyte capacity than thicker samples with low porosity and pore size (higher weight) [12, 13]. More experiments will be performed to investigate the effect of porosity, pore size and thickness on the electrolyte capacity of NF-coated membranes with aim to improve the separator performance.

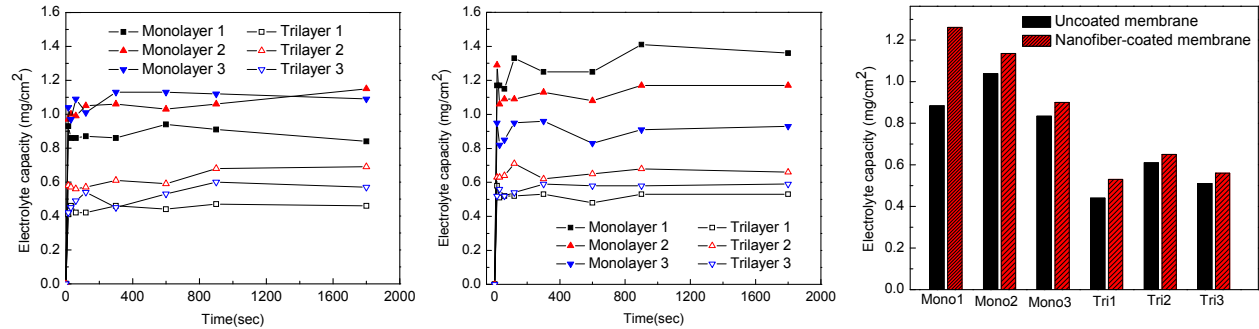


Figure 3: Electrolyte uptake capacities of (a) uncoated and (b) nanofiber-coated membranes. C. is a comparison between the electrolyte capacities of uncoated and nanofiber-coated membranes.

Figure 4 shows the Nyquist plots for uncoated and nanofiber-coated membranes (Monolayers 1, 2 and 3) in the range of 0.01 Hz to 65 kHz. The diameter of the semicircle represents the interfacial resistance (R_i) between the liquid electrolyte-soaked membrane and the lithium electrode.

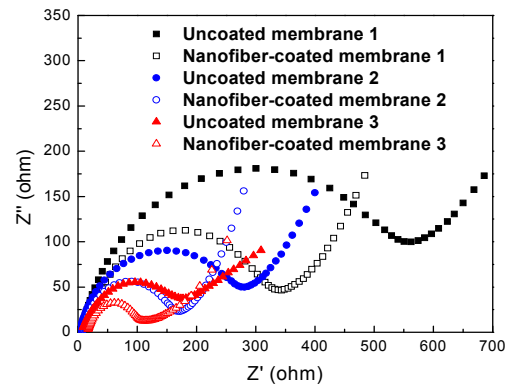


Figure 4: Electrochemical impedance spectra of liquid electrolyte-soaked membranes. Nanofibers were made by Electrospinning.

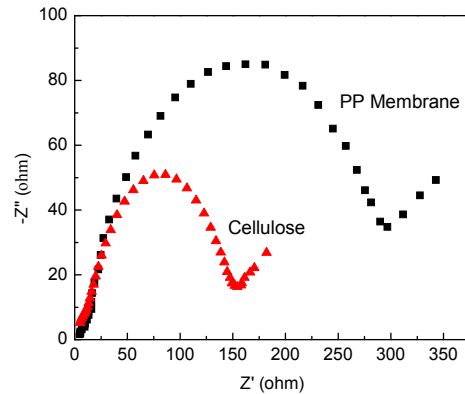


Figure 5: Electrochemical impedance spectra of fibrous cellulose membrane and microporous PP membrane. Nanofibers were Made by Forcespinning.

Fig. 4 shows that the electrode-electrolyte interfacial resistances of nanofiber-coated membranes are smaller than those of uncoated membranes. The PVDF-co-CTFE nanofiber coating on the surface of the membrane substrate can easily absorb liquid electrolyte and swell in electrolyte solution due to the good affinity of PVDF-co-CTFE to polar electrolyte solution. Figure 5 shows the EIS spectra of fibrous cellulose membrane made by Forcespinning compared to that of a

commercial Polypropylene membrane separator. It is seen in Figure 5 that the interfacial resistance of liquid electrolyte-soaked cellulose fibrous membrane is about 200 Ω , while that of PP separator is 400 Ω , which is consistent with our previous results reported on the same membrane separator [11, 12, 13]. Obviously, FS cellulose nonwoven fibrous membranes exhibit a lower interfacial resistance, indicating better interfacial characteristics when used as separators for LIBs. Moreover, we carried out electrolyte uptake experiments on FS nonwoven cellulose membranes and found that their uptake capacity (capacity/mass) was about 370%, which is significantly higher than that for the microporous PP separator (110%), indicating the high electrolyte retention ability of the fibrous cellulose membrane [14].

CONCLUSIONS

Membrane separators were prepared by coating PVDF-co-CTFE nanofibers on the surface of different microporous membrane substrates using electrospinning technique. The nanofiber-coated membranes showed higher electrolyte uptake capacities than the uncoated membranes and also lower interfacial resistance than that for uncoated membranes. Forc spinning[®] technology was also used to prepare fibrous cellulose membrane for LIB separators. The results are promising while the results reported on electrolyte uptake capacity and interfacial resistance of FS fibrous cellulose nonwoven membranes are better than those reported on PP separator. More work is in progress in our laboratory aimed at investigating the structure and morphology of nonwoven separators made by Forc spinning[®] for high electrochemical performance LIBs.

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