ORIGINAL PAPER

Preparation and characterization of electrospun nanofiber-coated membrane separators for lithium-ion batteries

Hun Lee · Mataz Alcoutlabi · Ozan Toprakci · Guanjie Xu · Jill V. Watson · Xiangwu Zhang

Abstract Nanofiber-coated membrane separators were prepared by electrospinning polyvinylidene fluoride-co-chlorotrifluoroethylene (PVDF-co-CTFE) nanofibers onto three different microporous membrane substrates. The nanofibers on the membrane substrates showed uniform morphology with average fiber diameters ranging from 129 to 134 nm. Electrolyte uptakes, ionic conductivities, and interfacial resistances were studied by soaking the nanofiber-coated membrane separators with a liquid electrolyte solution of 1 M lithium hexafluorophosphate in ethylene carbonate/dimethylcarbonate/ethylmethyl carbonate (1:1:1 by volume). Compared with uncoated membranes, nanofiber-coated membranes had greater electrolyte uptakes and lower interfacial resistances to the lithium electrode. It was also found that after soaking in the liquid electrolyte solution, nanofiber-coated membranes exhibited higher ionic conductivities than uncoated membranes. In addition, lithium-ion half cells containing nanofiber-coated membranes were evaluated with a LiFePO₄ cathode for charge–discharge capacities and cycle performance. The cells containing a nanofiber-coated separator membrane showed high discharge specific capacities and good cycling stability at room temperature. Results demonstrated that coating PVDF-co-CTFE nanofibers onto microporous membrane substrates is a promising approach to obtain new and high-performance separators for rechargeable lithium-ion batteries.

H. Lee · M. Alcoutlabi · O. Toprakci · G. Xu · X. Zhang (✉)
Fiber and Polymer Science Program, Department of Textile Engineering, Chemistry and Science, North Carolina State University, Raleigh, NC 27695-8301, USA
e-mail: xiangwu_zhang@ncsu.edu

J. V. Watson
Celgard LLC, 13800 South Lakes Drive, Charlotte, NC 28273, USA

Introduction

Recently, high energy demands have encouraged the development of high-performance lithium-ion batteries for portable electronic devices and electric vehicles [1, 2]. Separators are critical for achieving high performance for lithium-ion batteries. The role of the separators is to prevent the physical contact between the positive and negative electrodes of the battery while allowing the transportation of ions [3, 4]. Polyolefin microporous membranes are the most commonly used separators for lithium-ion batteries because of their excellent mechanical strength and good chemical stability [5, 6]. However, polyolefin microporous membranes can still be improved in aspects such as electrolyte wettability, interfacial resistance, etc., in order to achieve higher performance for lithium-ion batteries.

In recent years, electrospinning has been used to generate nonwoven membranes with controlled structure and morphology [7–9]. Many researchers have used electrospinning to prepare electrospun nanofiber membranes with large porosity and high electrolyte uptake in lithium-ion batteries [10–12]. However, stand-alone electrospun membranes have insufficient mechanical strength and are easily damaged during battery assembly [13–15].

This study reports the preparation and characterization of composite membrane separators prepared by depositing electrospun nanofibers onto polyolefin microporous membranes (Fig. 1). Nanofiber electrospun coatings were prepared on three different Celgard polyolefin microporous membranes using a nozzle-less electrospinning method. Polyvinylidene fluoride-co-chlorotrifluoroethylene (PVDF-co-CTFE) was used for the preparation of

electrospun nanofiber coatings due to its excellent electrochemical stability, good adhesion property, and high temperature resistance [9, 16–19]. The morphology of electrospun nanofiber coatings on the surface of membrane substrates and the electrolyte uptake capacities of nanofiber-coated membranes were investigated. The ionic conductivities were measured by soaking nanofiber-coated membranes with a liquid electrolyte solution. In addition, lithium-ion cells were assembled with nanofiber-coated membranes in order to evaluate electrochemical properties and battery cycling performance. This paper discusses the effect of nanofiber coatings on the performance of membrane separators for lithium-ion batteries by comparing the properties of nanofiber-coated membranes with those of uncoated membranes.

Experimental

Materials

Commercial microporous separators (Celgard® LLC) were used as the base substrate for the deposition of nanofibers. In order to investigate the effect of substrate structure on the properties of electrospun nanofiber coatings, three different microporous membranes were selected. Table 1 lists the polymer type, thickness, porosity, and pore size of these membranes which are labeled as membranes 1, 2, and 3 for the purposes of this study. Membrane 1 is a 25-μm polypropylene (PP) membrane with a pore size of 0.043 μm and a porosity of 41 %. Membrane 2 is 16-μm PE microporous membrane with a pore size of 0.06 μm. Membrane 3 is a 15-μm PP membrane with a larger pore size and lower thickness as compared with the other membranes.

Electrospun nanofibers were prepared from 15 wt% polymer solution of PVDF-co-CTFE (Solvay® Solef#32008) dissolved in an acetone/N,N dimethylformamide mixture (3:7 by weight).

Preparation of nanofiber-coated separators

Nanofiber coatings were prepared using the nozzle-less electrospinning device (NanoSpider™ NS200, Elmarco) shown in Fig. 2. The electrospinning polymer solution was placed in an open polymer container. An electrode connected with six parallel stainless steel patterned wires was placed in the polymer solution and rotated at a fixed speed of 6 r/min in order to wet the steel wires with the polymer solution. A high voltage was applied to the polymer solution, and multiple polymer jets were ejected (upspinning) from the solution carried on the wire surface. The nanofibers were deposited onto the membrane substrate as it was moved continuously at a fixed speed while

in contact with the grounded collector. The electrospinning parameters used in this work were (1) applied voltage=40 kV, (2) electrode-to-collector distance=15 cm, (3) electrode rotational speed=6 r/min, and (4) membrane movement speed=0.26 m/min.

Structure characterization and property measurements

The morphology of both uncoated and nanofiber-coated membranes was evaluated using a scanning electron microscopy (SEM) (JEOL 6400F field emission SEM at 5 kV). The samples for SEM observation were coated with Au/Pd by a K-550X sputter coater to reduce charging. The diameters of electrospun nanofibers were obtained by measuring 50 fibers randomly selected in SEM images for each sample using Revolution v1.6.0 software.

Liquid electrolyte uptake capacities were measured by soaking preweighed uncoated and nanofiber-coated membrane samples for a fixed time at room temperature in a liquid electrolyte which consisted of 1 M lithium hexafluorophosphate (LiPF$_6$) dissolved in 1:1:1 (by volume) ethylene carbonate (EC)/dimethylcarbonate (DMC)/ethylmethyl carbonate (EMC). Figure 3 shows the schematic of the electrolyte uptake measurement setup. The electrolyte was absorbed both on the surface and in the pores of the membranes. The excess electrolyte solution adhering to the membrane surface was removed by gently wiping with filter paper. The electrolyte uptake capacities of uncoated and nanofiber-coated separator membranes were determined using the following equation:

$$\text{Uptake capacity} \left(\text{mg}\middle/\text{cm}^2\right) = \left(W_t - W_0\right)\middle/ A$$

where W_t is the weight of the electrolyte-immersed membrane, W_0 the weight of a dry membrane, and A the geometrical area of the immersed part of the membrane, as shown schematically in Fig. 3.

For the ionic conductivity measurement, uncoated and nanofiber-coated membranes were completely soaked in the liquid electrolyte of 1 M LiPF$_6$ in EC/DMC/EMC and then sandwiched between two stainless-steel plate electrodes. The ionic conductivities of liquid electrolyte-soaked membranes were measured by electrochemical impedance spectroscopy (EIS) using Potentiostat/Galvanostat/ZRA (GAMRY Reference 600). The measurement was carried out at amplitude of 10 mV over a frequency range of 1 Hz to 1 MHz at a temperature range between 25 and 100 °C. The temperature was controlled in a temperature/humidity chamber
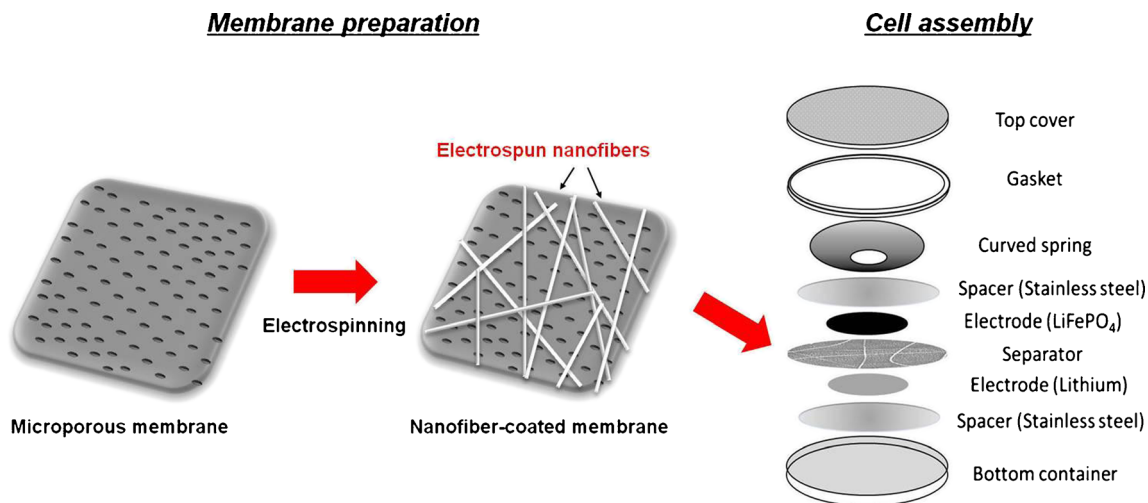
Membrane preparation **Cell assembly**

Fig. 1 Process for the preparation of the cell using electrospun nanofiber-coated membranes

(Ransco RTH-600-S). The conductivity (σ) was calculated by the following equation:

$$\sigma = d \Big/ (R_b \times A_0)$$

where d is the membrane thickness, R_b the bulk resistance of a liquid electrolyte-soaked membrane, and A_0 the cross-sectional area of the membrane.

The interfacial resistance between liquid electrolyte-soaked membranes and the lithium electrode was measured by EIS using the Potentiostat/Galvanostat/ZRA (GAMRY Reference 600). The liquid electrolyte-soaked membranes were symmetrically sandwiched with two lithium electrodes. The measurement was performed over a frequency range of 0.01 Hz to 65 kHz under open circuit conditions.

The electrochemical performance of lithium/lithium iron phosphate (LiFePO$_4$, Hydro-Quebec, carbon content=6 wt%) cells containing liquid electrolyte-soaked membranes was evaluated using an Arbin automatic battery tester. In these cells, the LiFePO$_4$ electrode was prepared by blending LiFePO$_4$ powder (80 wt%), carbon black conductor (10 wt%), and polyvinylidene fluoride binder (10 wt%). The active material loading in the electrode was 2.8 mg/cm^2. The

cells were prepared with the electrolyte-soaked membrane sandwiched between the lithium and LiFePO$_4$ electrodes. Charge and discharge cycles were conducted in the potential window of 2.5–4.2 V at 0.2-C rate.

Results and discussion

SEM images

Figure 4 shows SEM images of uncoated and nanofiber-coated membrane 1, membrane 2, and membrane 3, respectively. Membrane 1 and membrane 3 were made by a dry process using PP, but membrane 2 was made by a wet process using polyethylene. As shown in Fig. 4, three membranes have different pore structures. Membrane 3 has significantly larger pores and higher porosity compared with the other two membranes. The membrane morphology including pore size, porosity, and thickness could affect the electrolyte uptake capability and electrochemical properties of both uncoated and nanofiber-coated membrane separators.

From Fig. 4, it is also found that on nanofiber-coated membranes, electrospun nanofibers were randomly deposited with interconnected network morphology. The loading densities of PVDF-co-CTFE nanofiber coatings are in the range of 0.7–1.0 g/m^2 for the three nanofiber-coated membranes, while the corresponding coating thicknesses are in the range of 3–4 μm.

Figure 5 shows fiber diameter distributions of PVDF-co-CTFE nanofibers on the membrane substrate surfaces. Electrospun PVDF-co-CTFE nanofibers on the three different membrane substrates have comparable average fiber diameters, ranging from 129 to 134 nm.

Table 1 Material type, thickness, porosity, and pore size of membrane separators

	Material	Thickness (μm)	Porosity (%)	Pore size (μm)
Membrane 1	PP	25	41	0.043
Membrane 2	PE	16	40	0.060
Membrane 3	PP	15	74	0.096
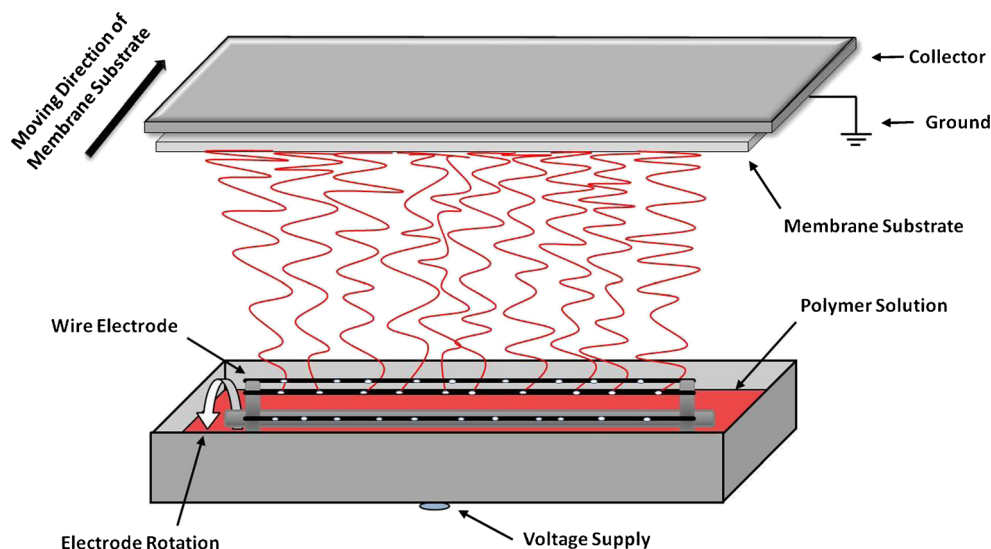
Electrolyte uptake capacity

Electrolyte uptake capacity indicates the amount of liquid electrolyte solution that can be absorbed per unit area by a separator membrane. For lithium-ion batteries, the separator should easily absorb and retain a large amount of liquid electrolyte solution in order to achieve low internal resistance and good battery performance [2, 5, 6].

Figure 6 shows the electrolyte uptake capacity of electrospun nanofiber-coated membrane 1, membrane 2, and membrane 3. For comparison, the electrolyte uptake capacities of uncoated membranes are also presented. A similar electrolyte uptake capacity is achieved for PP membranes 1 and 3 even though membrane 3 is 40 % thinner. This can be attributed to membrane 3's higher porosity and larger pore size. Membrane 2 has the smallest electrolyte uptake capacity probably because of its low thickness and porosity.

The nanofiber-coated membranes have higher electrolyte uptake capacity than the uncoated membranes due to the presence of electrospun nanofiber coatings. The improvement in electrolyte uptake can be attributed to the capillary effect of the nanofibers and the good affinity of PVDF-co-CTFE to polar electrolyte solution [6, 17].
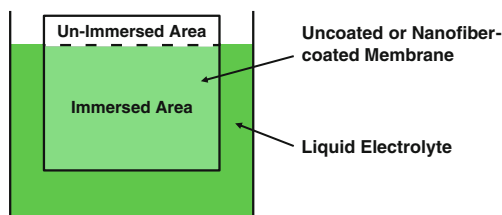

Fig. 3 Schematic of the electrolyte uptake measurement setup

Ionic conductivity

Figure 7 shows the ionic conductivity of liquid electrolyte-soaked uncoated and nanofiber-coated membranes at various temperatures. Ionic conductivity is known to increase with an increase in temperature due to the higher ion mobility occurring with a rise in temperature [20, 21]. After absorbing liquid electrolyte, the ionic conductivity value of a microporous membrane is dependent on its electrolyte uptake, which is affected by many membrane parameters such as porosity and pore size. Uncoated membrane 1, with its relatively small porosity and pore size, has lower ionic conductivity when compared with uncoated membranes 2 and 3. On the other hand, uncoated membrane 3 shows higher ionic conductivity due to its higher porosity and larger pore size (see Table 1).

Results presented in Fig. 7 also show that nanofiber-coated membranes exhibit higher ionic conductivity than uncoated membranes. For example, at 25 °C, the ionic conductivity of liquid electrolyte-soaked nanofiber-coated membrane 1, membrane 2, and membrane 3 is 4.63×10^{-4}, 7.26×10^{-4}, and 7.51×10^{-4} S/cm, respectively. On the other hand, the ionic conductivity of liquid electrolyte-soaked uncoated membranes at the same temperature is 2.31×10^{-4}, 4.02×10^{-4}, and 4.01×10^{-4} S/cm for membrane 1, membrane 2, and membrane 3, respectively. The presence of the nanofiber coating on the membrane substrate surface leads to higher ionic conductivity because the coating provides a 3-D interlaced network of nanoscale fibers that can entrap more liquid electrolyte. In addition, the affinity of the PVDF-co-CTFE polymer for the liquid electrolyte leads to electrolyte-swollen PVDF-co-CTFE nanofibers, which can act as an electrolyte reservoir to help maintain full wetting of the coated membrane and potentially promote better cell performance. Among all membranes studied, nanofiber-coated membrane 3 exhibits the highest ionic conductivity after absorbing the liquid electrolyte.

Fig. 4 SEM images of **a** uncoated membrane 1, **b** nanofiber-coated membrane 1, **c** uncoated membrane 2, **d** nanofiber-coated membrane 2, **e** uncoated membrane 3, and **f** nanofiber-coated membrane 3. Magnification: ×10,000
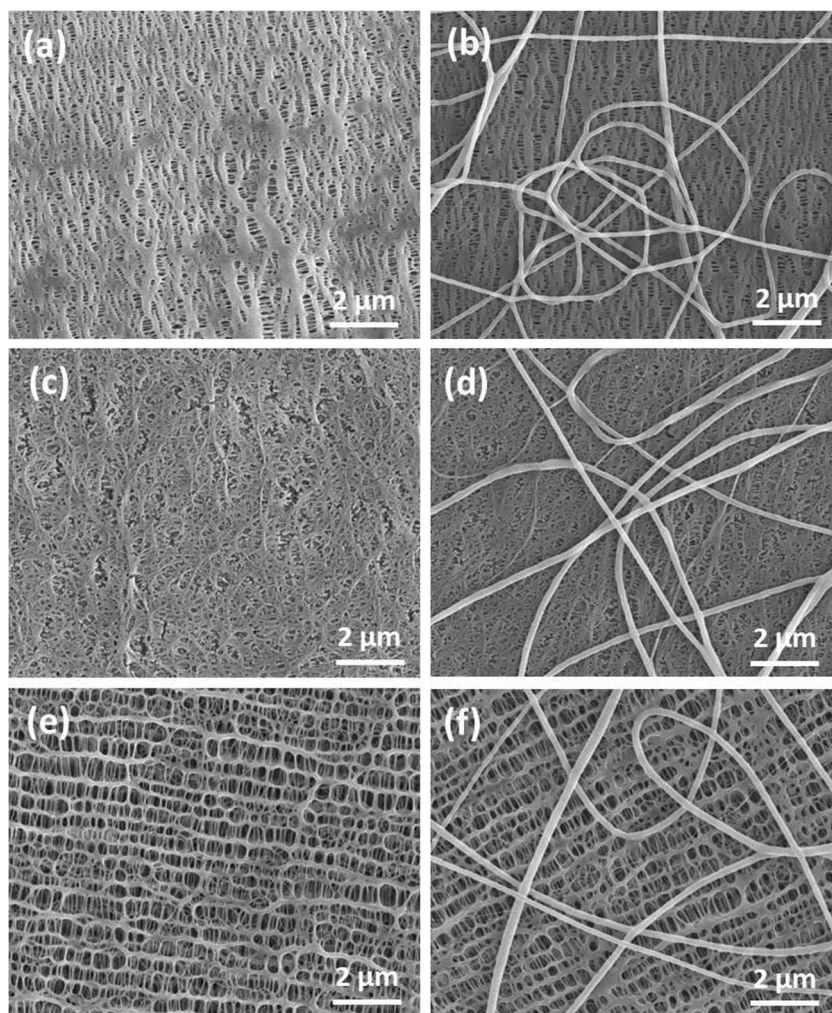
Interfacial impedance

The interfacial resistances between the liquid electrolyte-soaked membranes and the lithium electrode were evaluated using impedance spectra. Figure 8 shows the Nyquist plots for uncoated and nanofiber-coated membranes in the range of 0.01 Hz to 65 kHz. The real axis intercept of the Nyquist plot at high frequency determines the bulk resistance (R_b) of the liquid electrolyte-soaked membrane. The diameter of the semicircle represents the interfacial resistance (R_i) between the liquid electrolyte-soaked membrane and the lithium electrode [22, 23].

As shown in Fig. 8, 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 a 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. As a result, nanofiber-coated membranes exhibit smaller interfacial resistances than uncoated membranes.

Furthermore, nanofiber coatings can improve the adhesion between the membrane and the electrode, which may also help lower interfacial resistance.

Cell performance

The liquid electrolyte-soaked membranes have been evaluated for charge–discharge performance in Li/LiFePO$_4$ cells at room temperature. LiFePO$_4$ has a theoretical capacity of 167 mAh/g and operating potential of 3.4 V. Figure 9 shows the initial charge–discharge curves of the lithium-ion half cells assembled with the uncoated and nanofiber-coated membranes. The C rate used in the charge–discharge tests was 0.2 C. All charge–discharge curves show plateaus between 3.3 and 3.5 V. Based on the LiFePO$_4$ active material for the cathode, the cells exhibit initial discharge capacities of 143, 151, and 147 mAh/g, respectively, when uncoated membrane 1, membrane 2, and membrane 3 are used as the separator. These capacity values are relatively low mainly because the LiFePO$_4$ electrode used in this work has not been optimized.
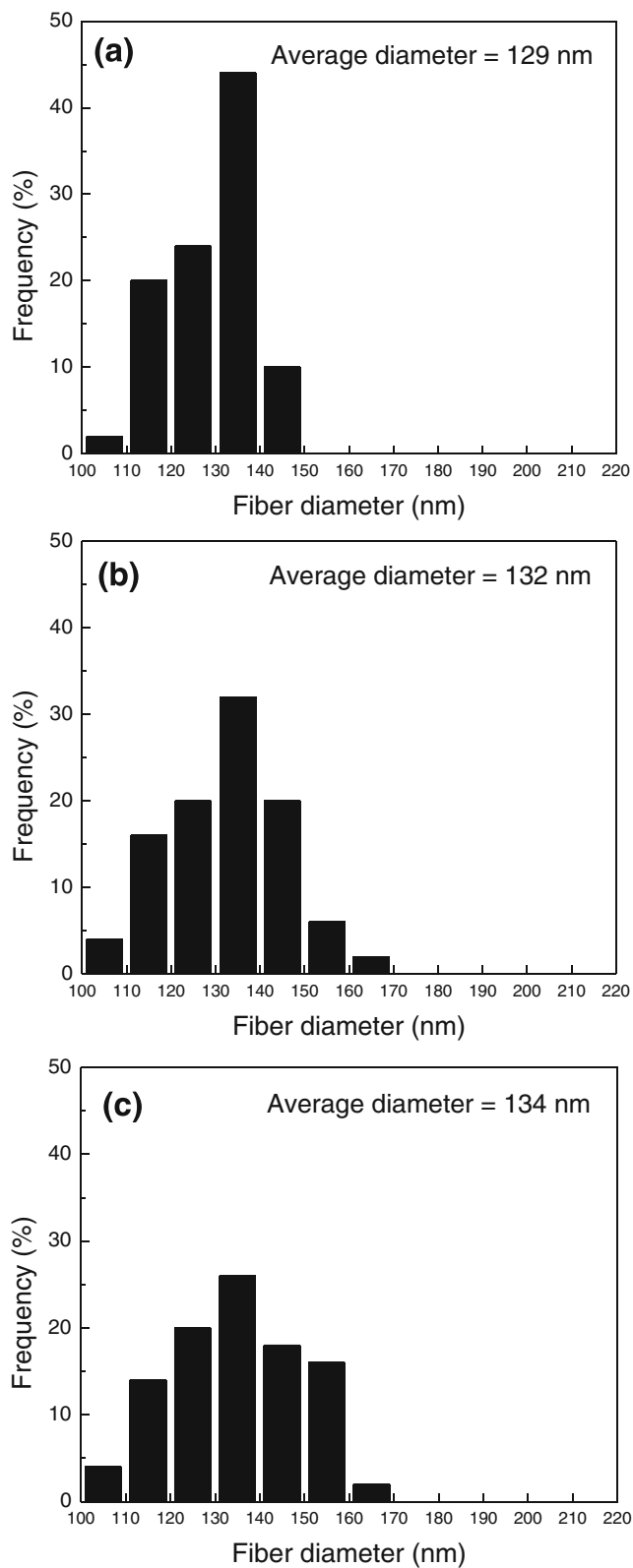
Fig. 5 Diameter distributions of electrospun nanofibers on **a** membrane 1, **b** membrane 2, and **c** membrane 3

However, the results obtained from this LiFePO₄ electrode can still provide important information on the effect of
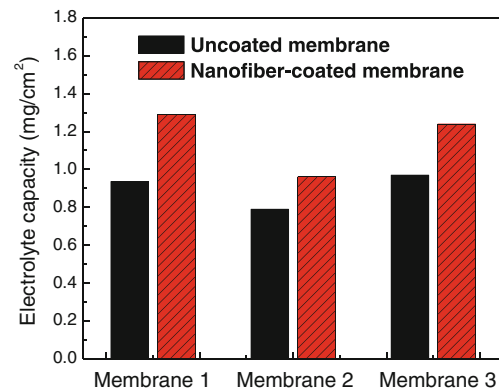

Fig. 6 Electrolyte uptake capacities of uncoated and nanofiber-coated membranes

different separators on the cell performance. The initial discharge capacities of the cells assembled with nanofiber-coated membrane 1, membrane 2, and membrane 3 are 157, 160, and 159 mAh/g, respectively. The cells using nanofiber-coated membranes have higher discharge capacities than those using uncoated membranes probably because of their higher ionic conductivity and lower interfacial resistance.

Figure 10 presents the discharge capacities of cells that were assembled with uncoated and nanofiber-coated membranes. The discharge capacities of the cells made using uncoated membrane 1, membrane 2, and membrane 3 are 142, 149, and 140 mAh/g, respectively, at the 50th cycle. For nanofiber-coated membrane 1, membrane 2, and membrane 3, the discharge capacities of the cells at the 50th cycle are 149, 154, and 155 mAh/g, respectively. Nanofiber-coated membrane 3 with the highest discharge capacity of 155 mAh/g at the 50th cycle has 92 % of the theoretical capacity of LiFePO₄ (167 mAh/g). All three coated membranes have stable discharge capacities during cycling. The introduction of PVDF-co-CTFE nanofiber coating onto the microporous membrane surfaces does not have any detrimental effect on the cycling stability of the cells in 50 cycles. The rate performance of the cells
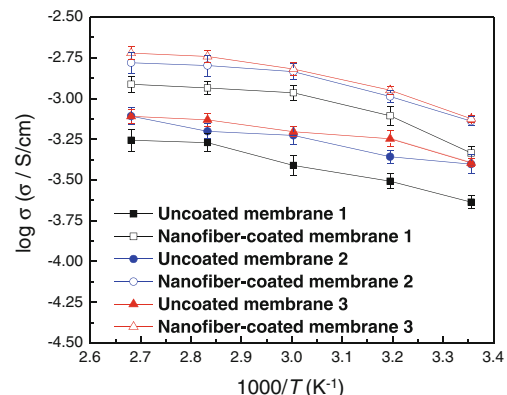

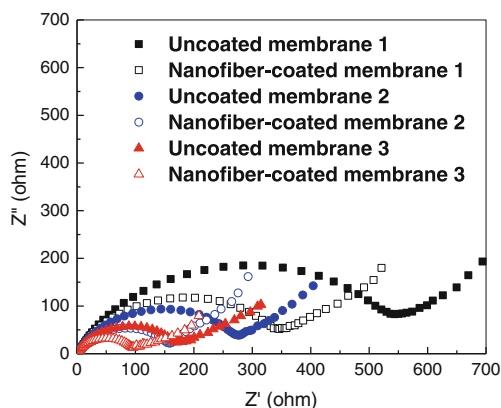Fig. 7 Ionic conductivity of liquid electrolyte-soaked membranes at various temperatures

Fig. 8 Electrochemical impedance spectra of liquid electrolyte-soaked membranes

is shown in Fig. 11. It is seen that the discharge capacities of all six cells decrease with an increase in C rate. At a high rate of 8 C, the discharge capacities of the cells made using uncoated membrane 1, membrane 2, and membrane 3 decrease to 76, 77, and 80 mAh/g, respectively. On the other hand, cells using nanofiber-coated membrane 1, membrane 2, and membrane 3 showed higher discharge capacities of 84, 86, and 89 mAh/g, respectively. The improved rate performance in these cells is probably due to the increased ionic conductivity of nanofiber-coated membranes after soaking with liquid electrolyte. The results demonstrate that coating polyolefin microporous membranes with PVDF-co-CTFE electrospun nanofibers
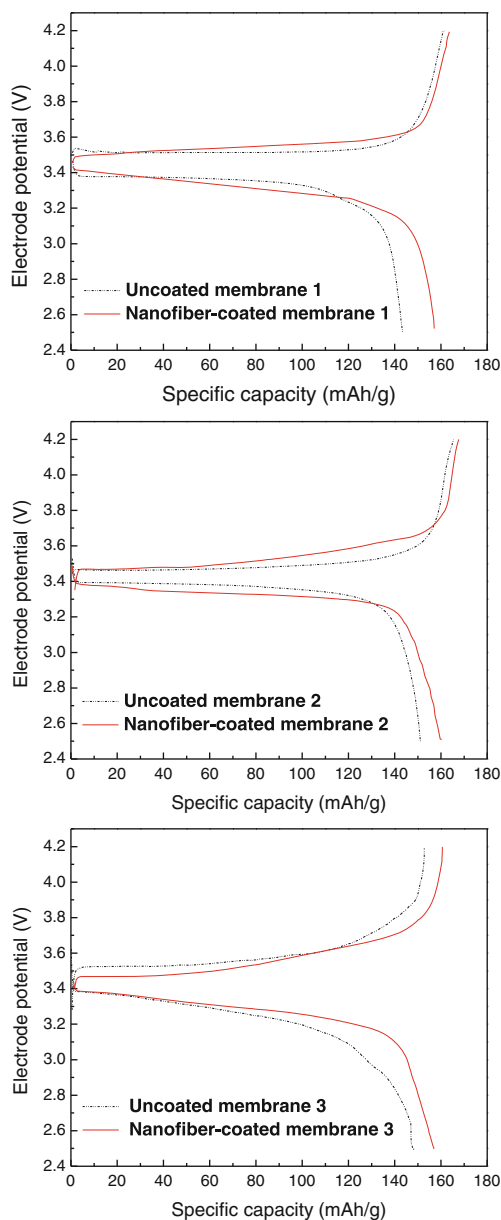

Fig. 9 Initial charge and discharge curves of Li/LiFePO$_4$ cells containing liquid electrolyte-soaked membranes at 0.2-C rate
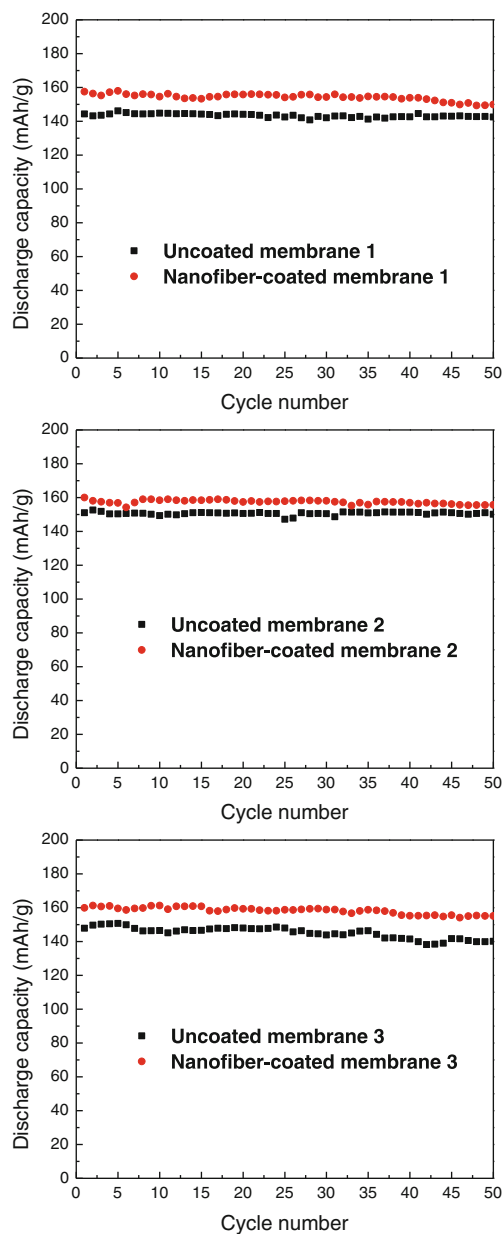

Fig. 10 Cycle performance of Li/LiFePO$_4$ cells containing liquid electrolyte-soaked membranes at 0.2 C-rate
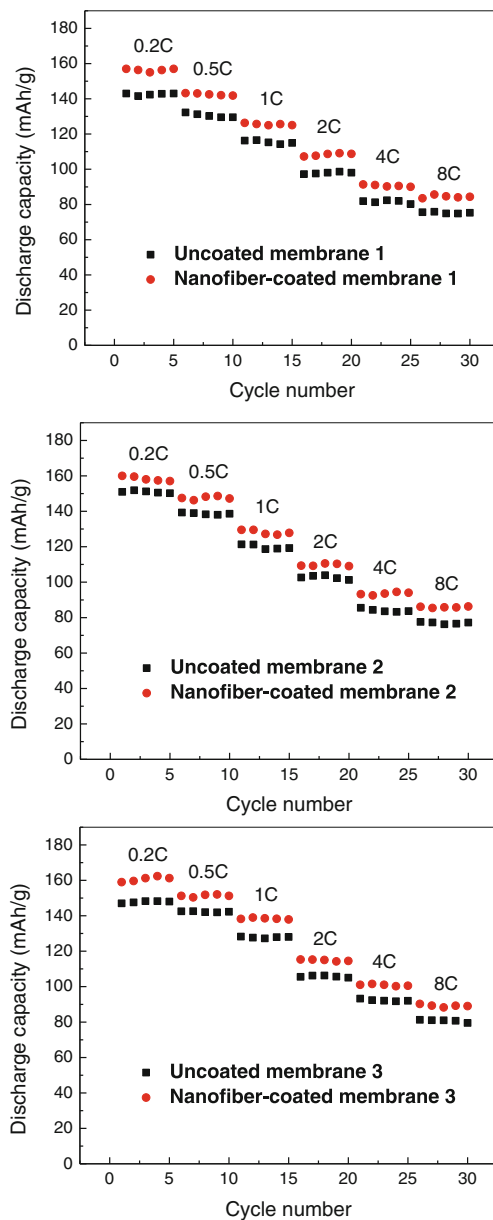
Fig. 11 Rate performance of Li/LiFePO₄ cells containing liquid electrolyte-soaked membranes

is a promising approach to obtain high-performance separators for advanced lithium-ion batteries.

Conclusion

Composite membrane separators were prepared by coating PVDF-co-CTFE nanofibers on the surface of three different microporous membrane substrates using the electrospinning technique. The nanofiber coatings on the substrates formed an interconnected fibrous structure with average fiber diameters in the range of 129–134 nm. The nanofiber-coated membranes showed higher electrolyte uptake capacities than uncoated

membranes. The ionic conductivity of liquid electrolyte-soaked membranes was also improved by the coating of nanofibers on the membrane substrates. In addition, the cells assembled with nanofiber-coated membranes exhibited lower interfacial resistance than those with uncoated membranes. Li/LiFePO₄ cells using nanofiber-coated membranes also showed improved discharge capacities compared with those using uncoated membranes. Therefore, coating PVDF-co-CTFE nanofibers onto microporous membrane substrates is a promising approach to obtain new and high-performance separators for rechargeable lithium-ion batteries.

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