Preparation of Poly(vinylidene fluoride)/Poly(methyl methacrylate) Membranes by Novel Electrospinning System for Lithium Ion Batteries

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ABSTRACT: Fibrous membranes of poly(vinylidene fluoride)/poly(methyl methacrylate) (PVdF/PMMA) were fabricated by electrospinning method with different concentrations of polymer solution: 14, 16, and 18 wt %. The morphology of the electrospun membranes was observed by scanning electron microscopy. The images revealed that the nanofibers showed uniform diameter and no bead formation was observed with the concentration of 16 wt %. Also, the structure, crystallinity, ionic conduction, and electrochemical stability of the electrospun membranes were characterized. The results suggested that electrolyte uptake, ionic conduction, and electrochemical stability were improved by the addition of PMMA. Furthermore, with the 16 wt % concentration of the polymer solution, the membrane showed a high ionic conductivity of 3.5 mS cm^{-1} at room temperature and electrochemical stability of up to 5.1 V. We predicted that this new method may be very promising for preparing microporous PVdF/PMMA polymer electrolytes. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2616–2620, 2011

Key words: electrospinning; polymer electrolytes; blends; membranes; electrochemistry

INTRODUCTION

Electrospinning is an alternative, novel and efficient way to prepare microporous membranes that are composed of ultrafine fibers with diameters in the range of several micrometers to tens of nanometers.[1,2] Electrospun nanofibers have unique properties such as large surface to volume ratio, high density of pores, and excellent surface adhesion, and thus have attractive application in many areas.[3]

In recent years, electrospinning has been used for the preparation of highly porous membranes that ideally suit for the application as polymer electrolytes (PEs)/separators in lithium batteries.[4,5] Poly(vinylidene fluoride) (PVdF) is a favorable dielectric polymer and has good electrochemical stability and affinity for Li$^+$ ions,[6] so it has been widely used as the polymer matrix of PE in lithium batteries. Jo and co-workers[7] have reported that electrospinning was a valid method to prepare PVdF matrix used as PE. However, high-crystalline PVdF-based PE shows low ionic conductivity. In general, the crystallinity of membranes is one of the major factors that affect the ionic conductivity of PEs. In our work, to further increase ionic conductivity of the PE, low-cost poly(methyl methacrylate) (PMMA) was introduced. PMMA is an amorphous polymer and has excellent compatibility with PVdF.[8,9] Moreover, an amorphous polymer can have a plasticization effect on the polymer, thus resulting in decrease of crystallinity and increase of ionic conductivity.

In this work, highly conductive composite PVdF/PMMA PEs were fabricated via electrospinning method. In general, the concentration of polymer solution is one of the most effective variables to control the morphology and properties of electrospun fiber. The effect of concentration of polymer solution on morphology and properties of membranes were studied.

EXPERIMENTAL

Materials

PVdF (Alfa Aesar) and PMMA (Taiwan) were dried under vacuum at 80°C for 24 h. Liquid electrolyte was made by dissolving 1M LiClO$_4$ in ethylene carbonate/propylene carbonate (1 : 1, v/v). N,N-Dimethylformamide (DMF) and acetone were of analytical purity and used as received without further treatment.

Preparation of polymer electrolyte

The required amounts of PVdF and PMMA (8/2, w/w) were homogeneously dissolved in a mixed solvent of acetone and DMF (6/2, v/v). Electrospun fibrous membranes were prepared by electrospinning. The polymer solution was held in a syringe. The needle (0.5 mm of diameter) of the syringe was connected to a high-voltage power, which supply a high electric voltage of up to 40 kV. A stainless steel plate for collection of electrospun fiber was grounded. The electrospinning was carried out under ambient condition; a high voltage of 27 kV was applied, and tip-to-collector distance was 20 cm, the flow rate was 0.045 mL min^{-1}, and the concentrations of blend polymer solution were 14, 16, and 18 wt %. The membranes were dried under vacuum at 80°C for 12 h before further use.

The gelled PEs were produced by immersing the electrospun membranes in $1M$ LiClO$_4$ in a mixture of ethylene carbonate and propylene carbonate (1 : 1, v/ v) solution for 1 h. The excess electrolyte solution at the surface of the PEs was absorbed with filter paper.

Measurements

The viscosity of polymer solution was determined by a coaxial cylinder rotational viscometer (Chengdu NXS-11, China) with a Couette geometry (A).

The morphology of the electrospun membranes was observed by scanning electron microscopy (SEM; Hitachi S-3500N, Japan). All samples were sputtered with gold before the analysis.

Fourier transform infrared (FTIR) spectra of the samples were recorded in the range of 450–4000 cm^{-1} on a FTIR: (Perkin-Elmer, USA) 170 (PE Company) spectrometer.

The crystallinity of the electrospun membranes was measured by using a differential scanning calorimeter DSC: (DSC-7, Perkin-Elmer, USA) from 50 to 200°C at a heating rate of 10°C min^{-1} in N$_2$ atmosphere.

The porosity was investigated by immersing the membrane into n-butanol for 1 h and then calculated by using the following relation: $P(\%) = \frac{W_w - W_d}{\rho_b V_p} \times 100$, where W_w and W_d are the mass of the wet and dry membranes, respectively, ρ_b the density of n-butanol, and V_p is the volume of the dry membrane.

The electrolyte uptake was determined by immersing a circular piece of membrane into $1M$ LiClO$_4$ electrolyte solution for 1 h. The electrolyte uptake (ε) was calculated by the equation: $\varepsilon(\%) = \frac{M - M_0}{M_0} \times 100$, where M_0 and M are the weight of electrospun membrane before and after absorbing the electrolyte solution, respectively.

Ionic conductivity was measured with SS/PE/SS blocking cell by AC impedance spectroscopy in the temperature range from 283 to 333 K. The measure-ment was carried out using a CHI 660a electrochemical analyzer (CH Instrument, USA) and over a frequency range of 0.01–10^5 Hz. The ionic conductivity (σ) of the PE was calculated by the equation: $\sigma = l/R_b S$, where l and S are the thickness and area of the membrane, respectively. The bulk resistance (R_b) is obtained from the intercept of the higher frequency side on the Z axis.

The electrochemical stability was evaluated by linear sweep voltammetry (LSV) at a scan rate of 5 mV s^{-1} at room temperature. The electrochemical analyzer was operated over the potential range of 2.5–6.0 V. The electrochemical stability was evaluated using the electrochemical cell that consists of a stainless steel (SS) working electrode, lithium metal as reference electrode as well as counter electrode.

RESULTS AND DISCUSSION

Scanning electron microscopy analysis

Figure 1 presents the images of electrospun PVdF/ PMMA membranes. The fibers of the electrospun membranes were interconnected with a large number of voids and pores. As we all know, the concentration of polymer solution is one of the most effective variables to control the morphology of the electrospun fiber because of the large fluctuation of the solution viscosity caused by the increasing concentration. Under a shear rate of 21.1 s^{-1}, the viscosity was 350.1, 451.4, and 1023.2 Pa s, respectively, when concentrations of the polymer solution were 14, 16, and 18 wt %. As shown in Figure 1, for the lower concentration of polymer solution of 14 wt %, because of the lower viscosity of solution, there were a large number of bead fibers in the picture. However, the nanofibers showed uniform diameter and no bead formation was observed with the concentration of 16 wt %. Moreover, with increase in the concentration of polymer solution to 18 wt %, the viscosity was too high and the fibers became more interconnected and the average diameter of the fibers was increased. Under the condition of our experiment, maybe the optimum concentration of PVdF/PMMA solution for the electrospinning was selected by us.

Fourier transform infrared analysis

FTIR spectra of the electrospun membranes are presented in Figure 2. The —CH$_3$ asymmetric stretching and bending vibration that appeared at 2946 and 1433 cm^{-1}, respectively, for pure PMMA were found to be shifted to 2951 and 1400 cm^{-1} in the PVdF/ PMMA composite membranes. In addition, the stretching vibration of 1723 cm^{-1} for C═O was found to become weak for the composite membranes. The —CF$_2$ wagging and bending vibration that
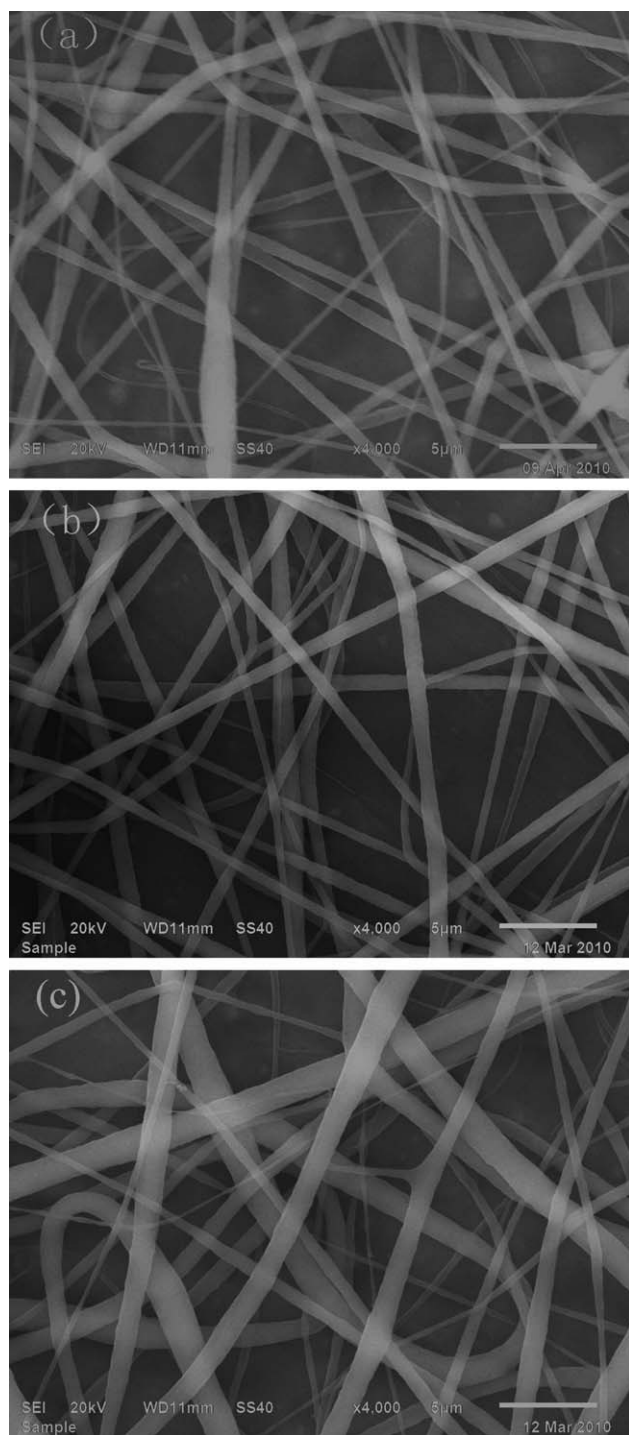
Figure 1 SEM images of the electrospun membranes prepared with different concentrations of polymer solution: (a) 14 wt %; (b) 16 wt %; and (c) 18 wt %.

Figure 2 FTIR spectra of (a) pure PVdF; (b) PVdF/PMMA (14 wt %); (c) PVdF/PMMA (16 wt %); (d) PVdF/PMMA (18 wt %); and (e) pure PMMA.

Differential scanning calorimeteric studies

Figure 3 shows the DSC curves of the electrospun membranes. The crystallinity (χ_c) can be calculated by the following equation: $\chi_c(\%) = \Delta H_f / \Delta H_f^* \phi \times 100$, where ΔH_f^* is the crystalline melting heat of perfectly crystalline PVdF (105 J g^{-1}),[10] ΔH_f is the melting enthalpy of the electrospun membranes, which can be calculated from the integral area of the baseline and each melting curve, and ϕ is the weight fraction of PVdF in sample. As shown in Table I, the crystallinity

Figure 3 DSC thermograms of (a) pure PVdF; (b) PVdF/PMMA (14 wt %); (c) PVdF/PMMA (16 wt %); (d) PVdF/PMMA (18 wt %); and (e) pure PMMA.

appeared at 489 and 510 cm^{-1}, respectively, for pure PVdF were found to be shifted to 474 cm^{-1} in the composite membranes. The peak at 1179 cm^{-1} which corresponded to the stretching frequency of —CF$_2$ was shifted to 1182 cm^{-1}. The above observations indicated that there are molecular level interactions between the two polymers in the bicomponent fibers.
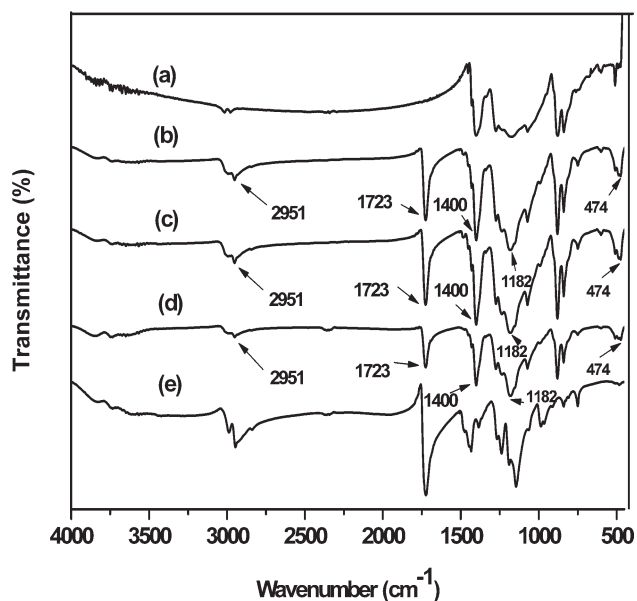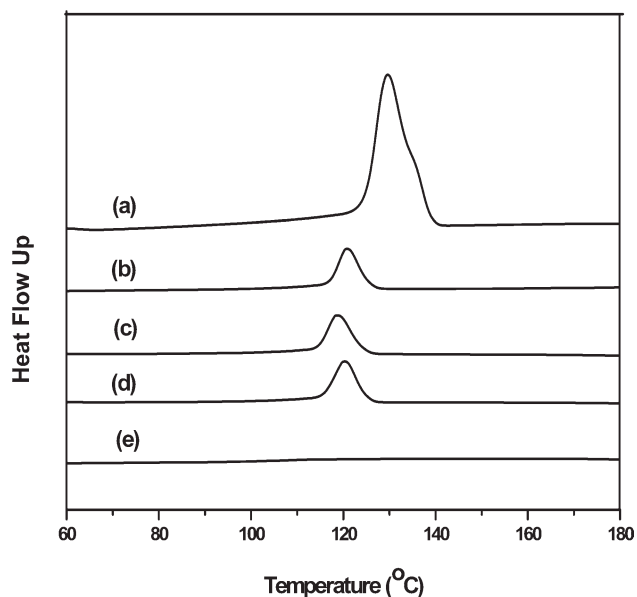
TABLE I
Crystallinity and Porosity of PVdF and
PVdF/PMMA Membranes

Samples	Crystallinity (%)	Porosity (%)
Pure PVdF	38.5	57
PVdF/PMMA (14 wt %)	38.8	65
PVdF/PMMA (16 wt %)	23.5	77
PVdF/PMMA (18 wt %)	32.9	60

of the PVdF/PMMA membranes was 38.8%, 23.5%, and 32.9%, respectively, when concentrations of polymer solution were 14, 16, and 18 wt %. However, the crystallinity of the electrospun PVdF membrane was 38.5%. It is well known that amorphous/crystalline nature affects the ionic conductivity of PEs.[11] Low crystallinity of membrane can supply a beneficial condition for conductivity enhancement. The results suggested that the PVdF/PMMA PEs may have the excellent ionic conductivity.

Porosity measurements and electrolyte uptake

The results of porosity determination by *n*-butanol uptake method are presented in Table I. As shown, the porosity of PVdF membrane was about 57%. However, the porosity of composite electrospun membranes increased from 60% to 77%. Among the composite electrospun membranes, PVdF/PMMA (16 wt %) showed the highest porosity (77%).

The uptake of electrolyte solution of the electrospun membranes is shown in Figure 4. The three-dimensional network structure enables the easy penetration of liquid into the inner cavities through the interconnected pores, and hence the uptake process gets stabilized within short time. The uptake of
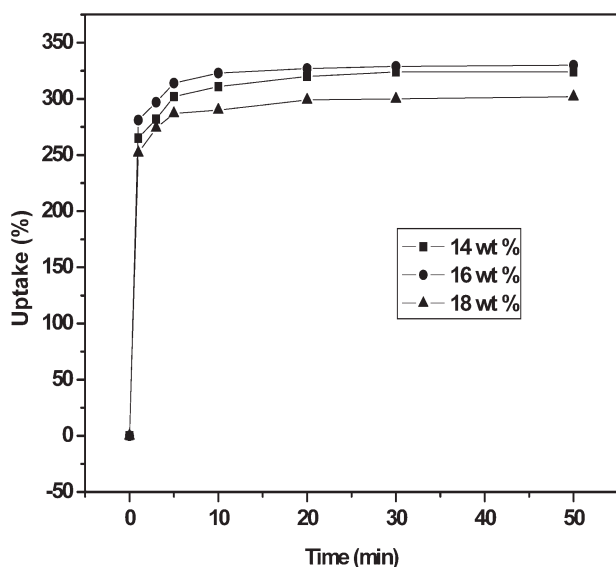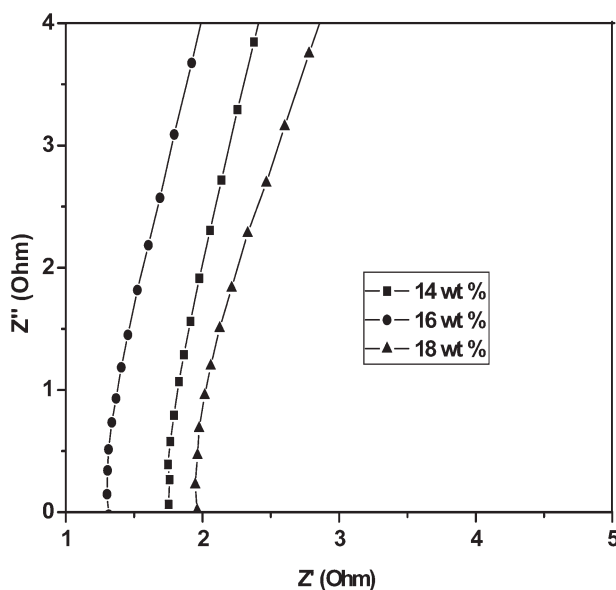
Figure 5 AC impedance spectroscopy of PVdF/PMMA polymer electrolytes (14, 16, and 18 wt %).

PVdF/PMMA membrane was above 300%. A maximum electrolyte uptake of about 260 wt % for electrospun PVdF has been reported.[7] For PVdF/PMMA composite membrane, uptake capability was improved due to the increase of amorphous phase and specific surface area. The uptake of PVdF/PMMA membranes (16 wt %) showed the highest value (330%), because of its uniform fiber diameter and high specific surface area.

Ionic conductivity

Figure 5 shows the AC impedance spectroscopy of the PVdF/PMMA PEs. The disappearance of semicircular
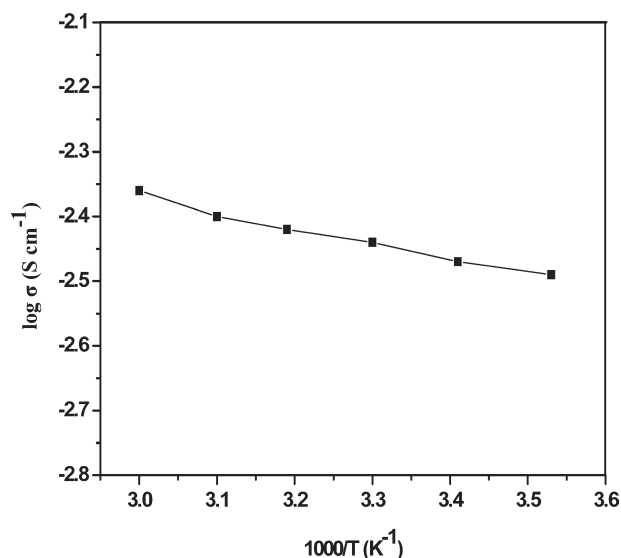
Figure 4 Electrolyte uptake characteristics of PVdF/PMMA membranes (14, 16, and 18 wt %).

Figure 6 Temperature dependence of the ionic conductivity for PVdF/PMMA polymer electrolyte (16 wt %).
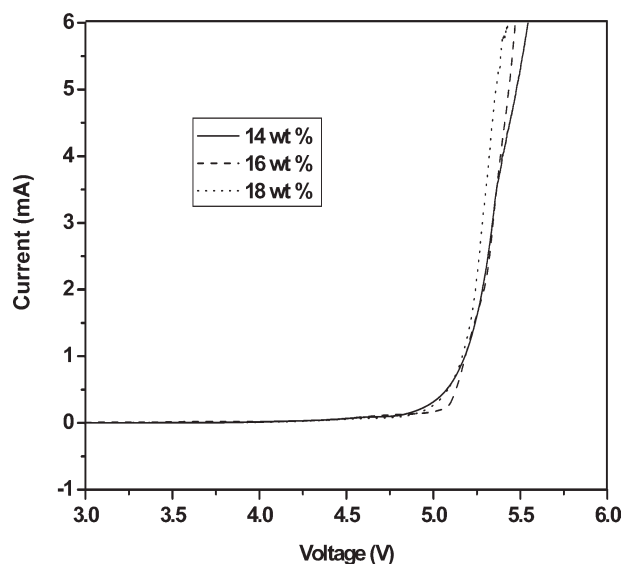
Figure 7 Linear sweep voltammogram curves of PVdF/PMMA polymer electrolyte (14, 16, and 18 wt %).

in high frequency region in the complex impedance plot leads to a conclusion that the current carriers are lithium-ions and the total conductivity is mainly the result of ion conduction.[12] The room temperature ionic conductivity was 2.4, 3.5, and 1.2 mS cm^{-1}, respectively, when the concentrations of polymer solution were 14, 16, and 18 wt %. The ionic conductivity of PVdF/PMMA (16 wt %) was up to 3.5 mS cm^{-1} at room temperature, which is much higher than PVdF-based electrolytes reported in literature.[7] The high ionic conductivity showed by the electrospun PVdF/PMMA PEs resulted from the high surface area, three-dimensional network structure, and the easy penetration of liquid into the inner cavities through the interconnected pores. Another critical reason may be result of the existence of PMMA. For PVdF/PMMA PEs that were made from different concentrations of polymer solution, the crystallinity, porosity, and electrolyte uptake were three of the major important factors that affect the ionic conductivity of PEs. Due to its highest porosity and electrolyte uptake, the ionic conductivity of PVdF/PMMA (16 wt %) was the highest.

Figure 6 shows the temperature dependence of the ionic conductivity of PVdF/PMMA PE (16 wt %). The linear plot of PE suggested an Arrhenius-type thermally activated process. To further discuss the ionic conductivity behavior in the PE, the activation energy for transportation of ions was estimated by using the Arrhenius equation: $\sigma = \sigma_0 \exp(-E_a/RT)$,[13] where σ is the conductivity, σ_0 the pre-exponential index, E_a the activation energy, R the gas constant, and T is the testing absolute temperature. Therefore, the activation energy can be calculated from the slope of the imitated straight line according to Arrhenius equation, namely 4.2 kJ mol^{-1}.

Electrochemical stability

The electrochemical stability of the PVdF/PMMA PEs was evaluated by linear sweep voltammetry measurements. As shown in Figure 7, the PVdF/PMMA (16 wt %) exhibited an anodic stability of up to 5.1 V. PVdF/PMMA (14 wt %) and PVdF/PMMA (18 wt %) both showed stability of 4.9 V. An anodic stability of about 4.5 V has earlier been reported for the PVdF PE.[7] The increase in electrochemical stability for PVdF/PMMA PEs than that of PVdF may be due to the combined presence of PVdF and PMMA in the composite membranes. These results suggested that the prepared PEs are expected to be very suitable for applications in lithium ion batteries.

CONCLUSIONS

Microporous PVdF/PMMA fibrous membranes were prepared using the electrospinning technique. The fibers of the electrospun membranes were interconnected with a large number of voids and pores, and the membranes showed the uniform fiber diameter when the concentration of the polymer solution was 16 wt %. The PVdF/PMMA membranes showed excellent electrochemical properties due to the interconnected porous structure and the addition of PMMA. Among the PVdF/PMMA membranes studied, PVdF/PMMA membrane (16 wt %) exhibited the highest electrolyte uptake, ionic conductivity, and electrochemical stability. The PVdF/PMMA PE (16 wt %) showed a high ionic conductivity of 3.5 mS cm^{-1} at room temperature and a good electrochemical stability of 5.1 V. These results suggested that this novel electrospinning method may be potential and promising for preparing membranes of lithium ion batteries.

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